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Polarons in crystalline and non-crystalline materials*

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Abstract

The current state of polaron theory as applicable to transition metal oxides is reviewed, including problems such as impurity conduction where disorder plays a role. An estimate is given of the **conditions under which polaron formation leads to an enhancement of the mass but no hopping energy. The binding energy of a polaron to a donor or acceptor in narrow-band semiconductors is discussed. The experimental evidence about the conductivity of TiO_2 and NiO is reviewed.** Impurity conduction in NiO and conduction in glasses containing transition metal ions is discussed and it is emphasized that the activation energy for hopping nearly all vanishes at low temperatures. Pollak's theory of a.c. impurity conductivity is reviewed and applied to the problem of dielectric loss in these materials.

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Principal symbols used

W_D	activation energy for hopping due to disorder,
W_H	polaron hopping energy,
W_p	polaron binding energy,
ΔW	resonance energy between two centres,
J	$\frac{1}{2}$ band width for a rigid one-dimensional lattice,
J_p	$\frac{1}{2}$ polaron band width for a one-dimensional lattice,
m^*	rigid-lattice effective mass,
m_p	polaron effective mass,
m	electron mass,
E	total activation energy in the conductivity,
E_c	binding energy at an impurity centre,
ω_0	optical phonon frequency.

1. Introduction

In recent years theoretical work by various authors (for a summary see Appel 1968) has provided a basis for understanding conduction in oxides of transition metals and other materials where **interaction between electrons and optical phonons is strong**. In particular it is predicted that, if the interaction is strong enough, a 'small polaron' will be formed and at sufficiently high temperatures this will move by a hopping process with mobility of the form $\mu_0 \exp(-W_H/kT)$. Bogomolov *et al.* (1968) have recently discussed conduction in TiO_2 and given evidence for small polaron behaviour with $W_H \sim 0.13 \text{ eV}$.

A quite different kind of hopping motion has also been described in the literature. In this, an electron moves by thermally activated hopping from one localized state to another, an activation energy being required for each hop because the localized states have quantized energies extending over a certain range. The localization is *not* a consequence of interaction with phonons, but would occur in a rigid solid and is caused by random electron fields or by a disordered arrangement of atoms: the hopping, however, is due to an exchange of energy with phonons. The best known example of this process is impurity conduction in doped and compensated germanium, where the localization is due to the random fields set up by charged minority centres. **Anderson** (1958) was the first to give a clear description of the conditions for this kind of **localization** to occur and Miller and Abrahams (1960) gave a theoretical description of the mechanisms of conductivity in silicon and germanium. **If two centres have quantized energy levels differing by W_D** , the chance per unit time that an electron jumps from the lower to the higher is proportional to

$\exp(-W_D/kT)$. In impurity conduction in oxide semiconductors, both W_D and W_H will affect the conductivity.

The main purpose of this paper is to examine conduction processes in which **both these activation energies** play a role. These processes include impurity conduction in oxides, particularly transition metal oxides, and conduction in oxide glasses containing transition metal ions. Both d.c. and a.c. conduction will be discussed. We shall also describe what is known about other mechanisms of conduction in transition metal oxides, and in particular **the nature of the energy binding a carrier to a donor or acceptor.**

2. Polaron motion in a molecular lattice

In this section we shall use **a model similar to that of Holstein (1959)** to establish certain points about **an electron moving in an array of molecules in which both the terms W_H and W_D may play a role.** We consider two identical molecules, 1, 2, and introduce configurational coordinates q_1, q_2 to describe (say) the inter-nuclear distance in each molecule. Let the energy of either molecule be Aq_1^2, Aq_2^2 (figure 1), *without* the addition of an electron. Let the energy of an extra electron placed in molecule 1 for a given value of q_1 be $-Bq_1$ relative to some arbitrary zero. Then the energy of molecule 1 with an electron in it is:

$$Aq_1^2 - Bq_1, \quad (1)$$

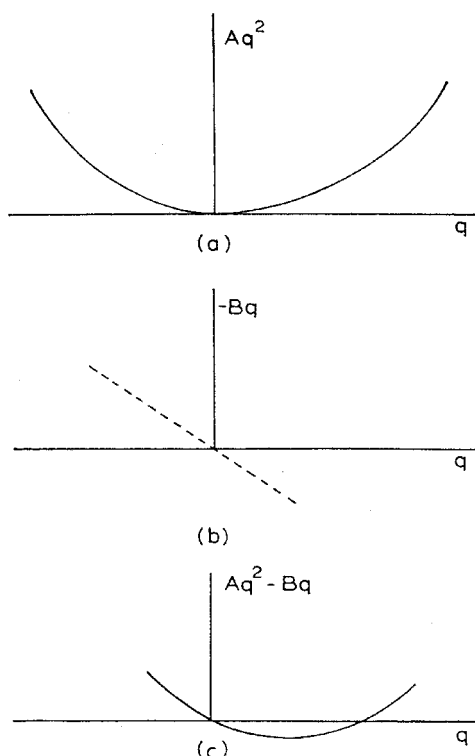


Figure 1. Energy of a molecule as a function of a configurational parameter q , as described in the text.

which is a minimum when $q_1 = q_0$, where

$$q_0 = B/2A.$$

The energy (1) (the polaron energy) can then be written $-W_p$, where

$$W_p = Aq_0^2. \quad (2)$$

The formulae are illustrated in figure 1.

If an electron is to jump from one molecule to another, the configurational parameters q_1, q_2 must be such that the electron's energy is the same in either molecule: thus

$$Bq_1 = Bq_2, \quad (3)$$

so that $q_1 = q_2$. The energies required to distort molecules 1 and 2 to configurations in which $q_1 = q_2 = q$ are

$$A(q_0 - q)^2 \quad \text{and} \quad Aq^2,$$

which add up to a total energy W_H given by

$$W_H = A(q_0^2 - 2q_0q + 2q^2). \quad (4)$$

This is a minimum when

$$q = \frac{1}{2}q_0$$

and (4) then has the value

$$W_H = \frac{1}{2}Aq_0^2 = \frac{1}{2}W_p. \quad (5)$$

This is the **activation energy for hopping**, the chance per unit time that an electron jumps from one molecule to another being proportional to $\exp(-W_H/kT)$. We note that W_H is half the polaron energy W_p . Corrections to this simple theory to be discussed below, however, show that W_H is often less than $\frac{1}{2}W_p$.

The energy $\hbar\omega$ required to transfer an electron optically from one molecule to another, without moving the ions (i.e. according to the Franck-Condon principle) is

$$\hbar\omega = Bq_0 = 2W_p. \quad (6)$$

This is perhaps most easily seen pictorially by introducing **a single configurational coordinate x** , where

$$q_1 = \frac{1}{2}q_0 - x, \quad q_2 = \frac{1}{2}q_0 + x.$$

Then we can draw as in **figure 2 curves I, II showing the energy of either molecule with the electron on it**: clearly $\hbar\omega = 4W_H$. This process has been referred to as 'photon-assisted hopping'. Various calculations of the temperature dependence of this absorption line have been made (see section 10).

In figure 2 the dotted line shows that, in the excited state, the resonance energy of the electron jumping backwards and forwards will lower the activation energy by an amount J , where $2J$ is the one-dimensional band width to be discussed later in this section. In considering the transfer of an electron from one molecule to the next we have to consider two cases:

- (a) The **adiabatic case** where the electron goes backward and forward several times during each excitation of the lattice. In this case Emin and Holstein (1969) find that

$$W_H = \frac{1}{2}W_p - J.$$

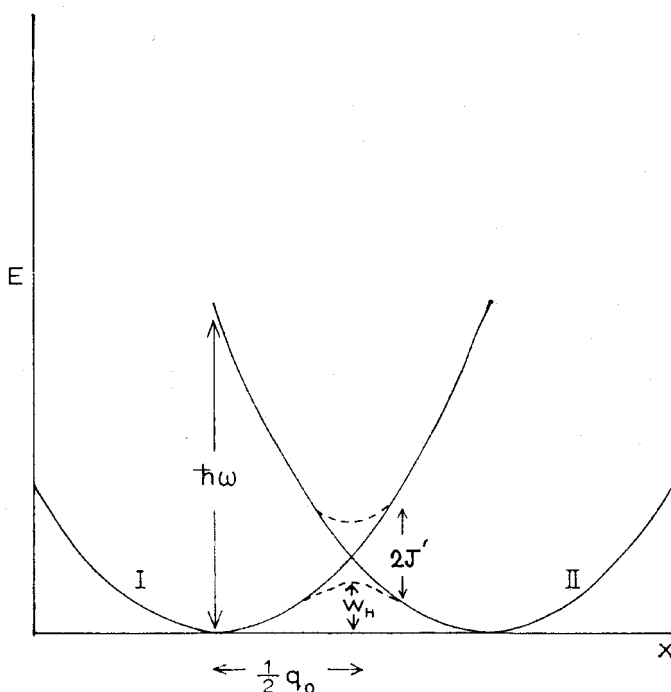


Figure 2. Energy of an electron in a pair of molecules, as a function of a configurational parameter x . $\hbar\omega$ is the energy of an absorbed photon. W_H is the hopping energy if $J = 0$. J' is the distance between the two dotted lines.

- (b) The **non-adiabatic case** when the electron has a low chance of making the transfer during each excitation, and **J can be neglected**.

The use of J in this way assumes, however, that the band width is the same for the two distorted molecules as for the molecules in their undistorted state, and we shall see (section 3) that this may not be so in a polar lattice. For this reason we introduce a quantity J' ($J' < J$) for the band width for an electron resonating between the two excited molecules, and write

$$W_H = \frac{1}{2} W_p - J'. \quad (7)$$

We turn now to the case when some random field in the solid separates the energies of an electron on the two centres by W_D (as in impurity conduction). Instead of (3), the condition for a jump to take place is

$$B(q_1 - q_2) = W_D.$$

If the electron is initially on molecule 2, the energy required to produce such a state is:

$$A(q_2 + W_D/B)^2 + A(q_0 - q_2)^2. \quad (8)$$

This is a minimum when

$$q_2 = q_0/2 - W_D/2B \quad (9)$$

and substituting in (8) we find that the activation energy W for hopping is

$$W = W_H + \frac{1}{2}W_D + W_D^2/16W_H. \quad (10)$$

In practical cases $W_H > W_D$ and the last term is probably negligible.

The activation energies for jumping upwards and downwards are thus $W_H \pm \frac{1}{2}W_D$, and the application of the principle of detailed balancing gives for the relative populations of the two states $\exp(-W_D/kT)$, as we should expect.[†]

It is clear from (8) and (9) that for our simple model the total activation energy is divided equally between the two sites even in the presence of the disorder term W_D . In more realistic models this may not be true because of (a) a nonlinear electron-phonon interaction, (b) anharmonic terms in the lattice vibrations and (c) a change in the vibrational frequency or force constant in going from the neutral to the ion-molecule. An unequal division of the hopping energy may also occur in some transition metal oxides and ferrites, where an internal spin rearrangement is necessary at one site before a hopping transition can occur (section 16). A mechanism of this type has been postulated for hopping between high and low spin states in CoO (Bosman and Crevecoeur 1968).

A simple extension of the above model to allow for (c) shows that if we write $A_2/A_1 = \theta$, then the fraction (β) of the total hopping energy expended at the site containing the electron (site 2) is given by $(1 + \theta)^{-1}$. We return to this point in section 8 and show that the deviation of θ from unity is usually small but may be sufficient to give observable terms in the thermopower.

We turn now to the factor outside the exponential in the hopping probability. We introduce the usual notation of polaron theory. Thus $2J$ is the band width for the rigid one-dimensional lattice: in the tight binding treatment the energy of an electron is $-2J \cos ka$ where k is the wave number and a the lattice parameter. For a pair of centres, with $W_D = 0$, there are two wave functions as in figure 3 and the energy separation is $2J$. If the centres are far apart at a distance R from each other, then J depends on R as

$$J \sim I \exp(-\alpha R),$$

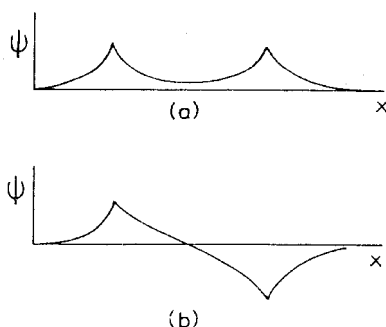


Figure 3. Wave functions ψ of even and odd parity for an electron on two centres.

[†] In Mott (1967, section 7.11) the activation energy is given as $W_H \pm W_D$, which is not correct.

where I is of the order of the ionization energy of the atoms: α is defined so that the wave function of each centre falls off as $\exp(-\alpha r)$. We write ω_0 for the frequency of the optical phonon assuming no dispersion, and denote by γ

$$\gamma = W_p/\hbar\omega_0.$$

Values of γ of order 5 are common.

Then as already stated we may distinguish two different cases.

- (a) The **adiabatic case** ($J' \sim \frac{1}{2}W_p$). Here **the molecules are near enough together for the electron to tunnel from one to the other and back several times during one excited state of the phonon system at $x = 0$ (figure 2).** The polaron is thermally activated over the potential barrier along the lower adiabatic and the jump probability is (Emin and Holstein 1969, Lang and Firsov 1968)

$$p \exp(-W_H/kT)$$

and W_H is given by (7) and p in this case is equal to ω_0 . The mobility is thus of the form

$$\mu = \mu_0 \exp(-W_H/kT), \quad (11)$$

where

$$\mu = ea^2\omega_0/kT \sim 0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

In real cases W_H may be smaller than (7), as shown in section 3.

- (b) The **non-adiabatic case** ($J' < \frac{1}{2}W_p$). Here, although the motion of the polaron in its well is adiabatic, the chance of the electron tunnelling from one molecule to the other during an excited state of the whole system is small. In this case we can write as a good approximation $W_H = \frac{1}{2}W_p$. The theory has been investigated by Holstein (1959), Klinger (1965, 1968a), Lang and Firsov (1968), Friedman (1964b) and for $W_D \neq 0$ by Schnakenberg (1968). For high temperature ($T > \frac{1}{2}\Theta$),

$$p = \frac{1}{2}\pi^{1/2}J^2/\hbar(W_HkT)^{1/2}. \quad (12)$$

Clearly this will be valid only if p is less than ω_0 : if in addition we take T such that $kT \sim \hbar\omega_0$, then hopping will be non-adiabatic if $J < \hbar\omega_0$. In the non-adiabatic case, p contains the factor $\exp(-2\alpha R)$, as in the usual (Miller–Abrahams 1960) theory of impurity conduction. Note that the mobility $ea^2p/kT \exp(-W_H/kT)$ contains $T^{-3/2}$ outside the exponential; this factor makes uncertain experimental attempts to identify an activation energy if W_H is small.†

We turn now to the behaviour at low temperatures. One of the most striking and important results of polaron theory for a crystalline lattice (Holstein 1959, Lang and Firsov 1964, Klinger 1965, Friedman 1964b) is that at low temperatures zero-point energy enables the polaron to move from molecule to molecule without thermal

† All the results come from the theory of multiphonon processes, in which interaction between the phonons (the process responsible for heat conduction) is neglected. If this were sufficiently large, it would presumably be correct to replace p by kT/\hbar , the factor used in chemical rate theory. The pre-exponential term in the mobility would then be independent of T . We feel that the connection between chemical rate theory and polaron theory needs further investigation, but shall not discuss the matter further here.

activation, carrying its polarization with it. It then behaves like a heavy particle moving by the usual band mechanism. The transition from hopping to band behaviour occurs at a temperature (T_i) where $\hbar\tau^{-1} \sim J_p$. Here τ is the hopping time and $2J_p$ the polaron band width. T_i is predicted to be of the order $\frac{1}{2}\Theta$ but is sensitive to the parameters and for a very small value of J can be less. Plots of the transition temperature following calculations by Holstein and by Firsov are given by Appel (1968).

At the absolute zero of temperature, two polarons on adjacent sites with the same energy will be described by two wave functions of odd and even parity (if $W_D = 0$). These are shown in figure 3. The splitting ΔW between the energies of the two states, neglecting unimportant terms, is given by (Holstein 1959, p. 371)

$$\left. \begin{aligned} \Delta W &= 2\hbar\omega_0 \exp(-\gamma) && \text{adiabatic case,} \\ \Delta W &= 2J \exp(-\gamma) && \text{non-adiabatic case.} \end{aligned} \right\} \quad (13)$$

A polaron moving at the absolute zero with wave number k will thus have energy above the bottom of the band

$$2J_p(1 - \cos ka), \quad (13.1)$$

where

$$J_p = \hbar\omega_0 \exp(-\gamma) \quad \text{or} \quad J \exp(-\gamma),$$

whichever is the smaller. $2J_p$ is the polaron band width. We can define the polaron mass m_p by equating (13.1) to $\hbar^2 k^2 / 2m_p$ for small values of k . Thus

$$\left. \begin{aligned} m_p &= (\hbar^2 / 2Ja^2) \exp(\gamma) \\ &= m^* \exp(\gamma) \end{aligned} \right\} \quad (\text{non-adiabatic}), \quad (14.1)$$

where m^* is the rigid lattice effective mass; and

$$m_p = (\hbar / 2\omega_0 a^2) \exp(\gamma) \quad (\text{adiabatic}). \quad (14.2)$$

The factor $\hbar / 2\omega_0 a^2$ is equal to $2m-4m$ for typical values of $\hbar\omega_0$ (0.1–0.05 eV); $(m_p/m) \exp(-\gamma)$ is thus not large, in spite of the occurrence of the square root of the ionic mass M in $1/\omega_0$.

In (14), the quantity γ depends on the vibrational energy of the ions and is constant only for the temperature range $T \lesssim \frac{1}{4}\Theta$, when the zero-point motion of the ions is dominant. At higher temperatures it tends to

$$\gamma(1 + 4kT/\hbar\omega_0),$$

giving an exponential increase in m_p with temperature, and a rapid decrease in the mobility (Holstein 1959). For the adiabatic case there are no clear theoretical predictions of the variation in band width with temperature (Eagles 1966), but we anticipate a less rapid decrease in the mobility.

We now discuss **mobilities at temperatures for which there is no hopping**. For conduction in a wide band the drift mobility is given by $\mu_D = e\tau/m^*$. But if the band width is less than kT , then all the states are equally populated and the mobility is (Fröhlich and Sewell 1959, Friedman 1964a, Lang and Firsov 1964)

$$\begin{aligned} \mu_D &= (e/kT) \langle v^2 \tau \rangle \\ &\simeq (ea^2/\hbar)(J_p/kT)(\tau/\hbar). \end{aligned} \quad (15)$$

Here $\langle v^2\tau \rangle$ is averaged through the band, and $2J_p$ is the polaron band width. Since τ cannot be less than $\hbar J_p$, and $ea^2/\hbar \sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $a = 3 \text{ \AA}$, the lower limit for a band (i.e. non-hopping) mobility is about

$$J_p/kT \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

We next consider **mobilities in a crystal at intermediate temperatures**. As the temperature is lowered the multiphonon processes are frozen out and ultimately a temperature is reached where the main contribution is from jumps in which a single optical phonon is absorbed and emitted (Holstein 1959), and $W_H \rightarrow \hbar\omega_0$. For intermediate temperatures the formula given by several authors for non-adiabatic processes is

$$\mu_D = 2(ea^2/kT)(J/\hbar)^2\pi^{1/2}\tau \exp(-W/kT),$$

where

$$\tau = \frac{1}{4}\hbar(W_H kT)^{-1/2} [\sinh(\frac{1}{2}\hbar\omega_0/\beta) / \frac{1}{2}\hbar\omega_0\beta]^{1/2}$$

and

$$W = W_H \tanh(\frac{1}{4}\hbar\omega_0\beta) / \frac{1}{4}\hbar\omega_0\beta \quad (15.1)$$

and $\beta = 1/kT$. This formula is only valid for $T \gtrsim \frac{1}{4}\Theta$, and shows an appreciable reduction in W at the lowest temperature.

In the two-centre problem when the energies of the states are different ($W_D \neq 0$), the high temperature hopping activation energy is expected to drop continuously from $W_H + \frac{1}{2}W_D$ to $\frac{1}{2}W_D$ as the temperature is lowered. A detailed theory has been given by Schnakenberg (1968); see also Klinger (1968a). The multiphonon processes and then the processes involving a single optical phonon freeze out and the activation energy $\frac{1}{2}W_D$ is provided by acoustic phonons. We apply this mechanism to impurity conduction and other processes involving thermally activated hopping between one state and another in section 13. The fact that W drops from the polaron value W_H (~ 0.2 – 0.4 eV) to the much lower value W_D as T drops below $\frac{1}{2}\Theta$ will be important for our considerations.

Whether localized states due to disorder and hence a term W_D occur depends on Anderson's (1958) condition for localization. This involves the ratio of the spread of energies (V_0) to the total band width, $2zJ_p$, where z is the number of neighbours with which the d function overlaps (probably 4 in NiO^\dagger). $2J_p$ is the polaron band width. The Anderson condition is:

$$V_0 > 6(2zJ_p).$$

The relation between V_0 and W_D depends in Miller and Abrahams' theory on the degree of compensation; a rough estimate would be $W_D \sim \frac{1}{3}V_0$. Thus Anderson localization should occur if

$$W_D > 4J \exp(-\gamma).$$

The condition for the occurrence of a term W_D depends then on a comparison between J_p (the polaron band width) and the random field in a disordered solid.

[†] Allowing for the anisotropy of the d functions—see section 4.

3. Polarons in an ionic lattice

Polaron theory has been applied to molecular lattices, notably sulphur, by Spear and his co-workers (Adams and Spear 1964, Gibbons and Spear 1966) and to transition metal oxides. This article is about the oxides, and we must therefore review the applications of polaron theory to ionic lattices.

The possibility that an electron in an ionic crystal can be trapped by the polarization cloud which it forms round it was first predicted by Landau (1933) and is discussed by Mott and Gurney (1940, p. 86). The argument is as follows. At a large distance from the electron the potential energy of another electron in a crystal is $e^2/\kappa r$, whereas if the ions could not move it would be $e^2/\kappa_\infty r$, where κ, κ_∞ are the static and high-frequency dielectric constants. Thus the potential energy $V_p(r)$ in the potential well due to the displacement of the ions is given by

$$V_p(r) = -e^2/\kappa_p r,$$

and

$$1/\kappa_p = 1/\kappa_\infty - 1/\kappa. \quad (16)$$

The potential (16) can be taken as the self-trapping potential of the electron itself; the electron ‘digs its own potential well’.

As a rough approximation we suppose that (16) is valid up to a radius r_p ; the electron moves in the potential well (cf. figure 4)

$$\left. \begin{aligned} V_p(r) &= -e^2/\kappa_p r, & r > r_p \\ &= -e^2/\kappa_p r_p, & r < r_p. \end{aligned} \right\} \quad (17)$$

We have to determine r_p . There are two limiting approximations.

(i) The effective mass m^* of the electron is so high that the kinetic energy $\hbar^2\pi^2/m^*r_p^2$ due to its localization in the well is negligible. Then r_p must be somewhat less than the inter-ionic distance. It can be calculated if the phonon spectrum is known, or estimated if all the optical phonons are assumed to have the same

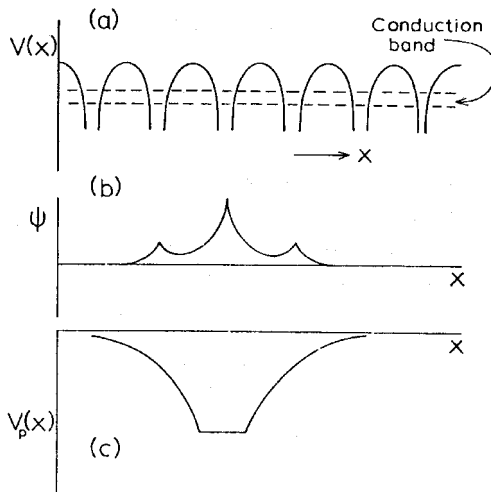


Figure 4. (a) is the field of the electron in the undistorted lattice; (b) is the wave function of the electron in the polaron in the intermediate case; (c) is $V_p(r)$ given by (17).

frequency. The polaron in this case is called a ‘small polaron’. The energy is made up of the following terms

- (a) The energy required to polarize the medium, $\frac{1}{2}e^2/\kappa_p r_p$.
- (b) The lowering of the potential energy of the electron, $-e^2/\kappa_p r_p$.

Thus the polaron energy $-W_p$ is given by

$$-W_p = -\frac{1}{2}e^2/\kappa_p r_p. \quad (18)$$

The formula treats the medium as a continuum. A more exact method is to treat the interaction of the electron with the whole spectrum of optical phonons. One then finds (Holstein 1959, Klinger 1965, Appel 1968)

$$W_p = (2N)^{-1} \sum_q |\gamma_q|^2 \hbar \omega_q, \quad (19)$$

where N is the number of centres per unit volume, and ω_q is the frequency of an optical phonon of wave number q . $|\gamma_q|^2$ is the electron–phonon coupling constant and using the continuum polarization model (Fröhlich 1954, Eagles 1964) can be approximated by

$$(e^2/\hbar \omega_q a) 4\pi/a^2 q^2 \kappa_p.$$

To evaluate (19) one needs to know the phonon spectrum. If dispersion is neglected and summation over q replaced by integration over a sphere equal in volume to the first Brillouin zone, then W_p is given by (18) with

$$r_p = \frac{1}{2}(\pi/6)^{1/3} \bar{a}. \quad (20)$$

Here \bar{a}^{-3} is the number of centres per unit volume. This probably underestimates W_p since the continuum approximation breaks down near the centre.

(ii) The other extreme is the ‘large polaron’, which occurs when m^* is not large. Here we have to add the kinetic energy $\hbar^2 \pi^2 / 2m^* r_p^2$ of an electron shut up in a box of radius r_p ; thus the total energy is

$$-W_p = -\frac{1}{2}e^2/\kappa_p r_p + \hbar^2 \pi^2 / 2m^* r_p^2. \quad (21)$$

This is a minimum when

$$r_p = 2\pi^2 \hbar^2 \kappa_p / m^* e^2,$$

giving an energy

$$W_p = 1 \frac{1}{4} e^2 / \kappa_p r_p = e^4 m^* / 8\pi^2 \kappa_p^2 \hbar^2.$$

We reproduce these crude formulae in order to illustrate the principles involved.

The well-known treatment of Fröhlich (1954) and of Allcock (1956) is in essentials the same as this, but makes a self-consistent calculation of the potential. They first introduce the coupling constant

and find

$$\alpha^2 = (e^2/\kappa_p)^2 m^*/2\hbar^3 \omega_0$$

and an effective mass

$$m_p = 0.02 m^* \alpha^4.$$

$$\left. \begin{aligned} W_p &= 0.1 \alpha^2 \hbar \omega_0 = m^* e^4 / 20 \kappa_p^2 \hbar^2 \end{aligned} \right\} \quad (22)$$

We note that the effective mass contains ω_0^2 and thus is proportional to M . This is because ions outside the polaron radius move adiabatically, with a velocity proportional to the polaron's velocity. Inside this radius the ions cannot follow the electron: 'dynamic' terms occur obtained by applying perturbation theory to the interaction: these are of lower order in α and have been investigated in many papers. They are not of importance for the problems treated here.

Figure 4 shows schematically the potential energy $V_p(r)$ and the wave function of a polaron in the intermediate case. A number of papers have treated the intermediate case between large and small polarons (e.g. Langreth 1967, Eagles 1966, and Appel 1968). We shall not review them here, because as we shall see in the next section m^* is extremely anisotropic for transition metal oxides, and we doubt if present calculations are reliable, apart from the very recent one of Kahn (1968). However the following consideration gives some indication of how large r_p must be for hopping to disappear.

As regards the motion of the small polaron, all the considerations of section 2 apply except that W_H is not necessarily equal to $\frac{1}{2} W_p$. This can be seen as follows. The potential well (17) is illustrated in figure 5. Thermal fluctuations may produce a well $-\xi e^2/\kappa_p r$ on one atom and $(1 - \xi) e^2/\kappa_p r$ on the adjacent atom. The wells are the same depth, so that an electron can jump from one atom to the next, when $\xi - \frac{1}{2}$ (figure 5 (b)). If the atoms are so far apart that the charge clouds do not overlap appreciably, then the energy to produce configuration (b) is made up of the following terms.

- (a) The energy required to raise the electron from the configuration of figure 5 (a) to that of figure 5 (b). This is equal to W_p .
- (b) The energy released in relaxing the displacement of the ions which causes the potential well on atom (1), which is $-\frac{3}{4} W_p$.
- (c) The energy required to form the well on atom (2) which is $\frac{1}{4} W_p$. These add up to $W_H = \frac{1}{2} W_p$. If however the two wells are near enough to each other for the

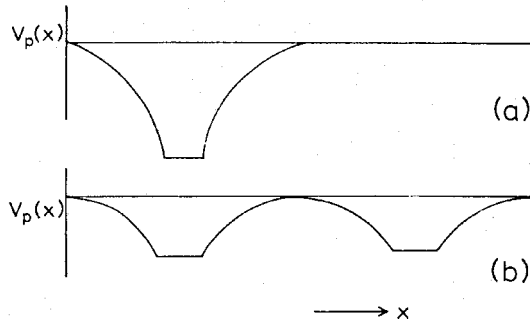


Figure 5. Potential well $V_p(x)$ on two atoms. (a) For electron in equilibrium in one atom; (b) in the configuration in which the electron can jump.

two polarization clouds to overlap, W_H is decreased and elementary electrostatics (Mott 1968c) shows that now

$$W_H = \frac{1}{4} \frac{e^2}{\kappa_p} \left(\frac{1}{r_p} - \frac{1}{R} \right), \quad (23)$$

where R is the distance between the centres. For a small polaron in NiO, r_p may be about 1 \AA and $R \sim 3 \text{ \AA}$, so that a reduction by *circa* 30% is likely. Using a different formalism, Killias (1966) was the first to point out that W_H might be less than $\frac{1}{2} W_p$ in a paper discussing conduction in glasses containing transition metal ions. Formula (23) is doubtless not valid when r_p approaches R , but it shows that for polarons in the intermediate range, for which r_p is larger than the small polaron value (20), the hopping energy drops to practically zero while the polaron energy is still a considerable fraction of the small polaron value. In this range the mobility is given by (15) and should be of order $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Although no formal proof has been given, it is probable that when $W_H \neq \frac{1}{2}$, we should write for the effective mass instead of (14):

$$m_p/m = (\hbar/2\omega_0 a^2) \exp(\gamma'), \quad (24)$$

where

$$\gamma' = W_H / \frac{1}{2} \hbar \omega_0.$$

We referred also in section 2 to the reduction of W_H and hence γ' due to resonance in the case of adiabatic transfer as discussed by Emin and Holstein (1969) and Lang and Firsov (1968). Figure 5(b) shows clearly that for an ionic lattice the resonance term in equation (7) J' must be less than J , because the electron in the polarization wells will decay more rapidly outside each well. Its magnitude however, has not been estimated.

In formula (24) the factor outside the exponential is in the range 2–4. The polaron mass under conditions when the hopping energy has become negligible ($\sim \hbar \omega_0$) is thus of order 10. If we compare this formula with the small polaron formulae (22), we see that hopping starts when

$$m^* \alpha^4 \sim 500m.$$

Putting in numerical values with $\kappa_p = 7$ and $\hbar \omega = 0.05 \text{ eV}$, this gives

$$\alpha^2 \sim 40$$

and $W_p \sim 4\hbar\omega_0$. Little reliance can be placed on numerical values which depend sensitively on the value chosen for κ_p , but it can be emphasized that as m^* increases a hopping energy comes into existence and W_H/W_p increases steadily towards $\frac{1}{2}$.

4. Rigid band structure of transition metal oxides

By 'rigid band' is meant the band when the ions of the lattice are held rigidly in place, so that no polaron can be formed.

In TiO_2 , V_2O_5 and the titanates the d band is empty in the pure stoichiometric crystal, and electrons can be introduced by reduction which produces donors. For SrTiO_3 tight-binding calculations have been carried out by Kahn and Leyendecker (1964). They find that the energy surfaces near the bottom of the band form a

number of ellipsoids with $m^*/m \sim 20$ along the major axis of each ellipsoid and $m^*/m \sim 1$ in the two perpendicular directions. Doubtless the difficulty of estimating the charge on each atom is too great for numerical results to be significant; but since d wave functions of types $xyf(r)$ or $(x^2 - y^2)f(r)$ are large in four coplanar directions and small in a third, we conjecture that energy surfaces of this type may be normal in cubic transition metal oxides. If so, the density of states near the bottom of the band will be proportional to $\sqrt{(m_1 m_2 m_3)}$ where m_1 etc. are the three masses and is thus large; but in the greater part of the band it will not be large. The conjectured constant energy surfaces and density of states are shown in figure 6. The smallest of the effective masses will determine the kinetic energy term \hbar^2/mr_0^2 in (21), and this decides whether a small polaron is formed or not. It is therefore possible that observations may give large values of m_{eff} , which for theory would predict small polaron formation if m^* were isotropic, without this in fact being the case.

In many transition metal oxides one expects the overlap between the d functions to be through the oxygen ions. For the rock salt structure, the lowest bonding states will be $e_g(x^2 - y^2, \text{etc.})$, which are filled by the O^{2-} electrons; there will then be a narrow t_{2g} band ($xy, \text{etc.}$) with six states per atom and then the broader antibonding e_g states. For the CsCl structure t_{2g} and e_g are reversed.

In TiO_2 and other materials with no d electrons in the stoichiometric state, electrons provided by donors will move in the band which has weak interaction with O^{2-} and is therefore narrow. Small polaron formation, as observed for TiO_2 , is therefore more likely.

For these and other antiferromagnetic oxides there are electrons in the d band and they would be metals if the d band were not split in some way. A splitting due to

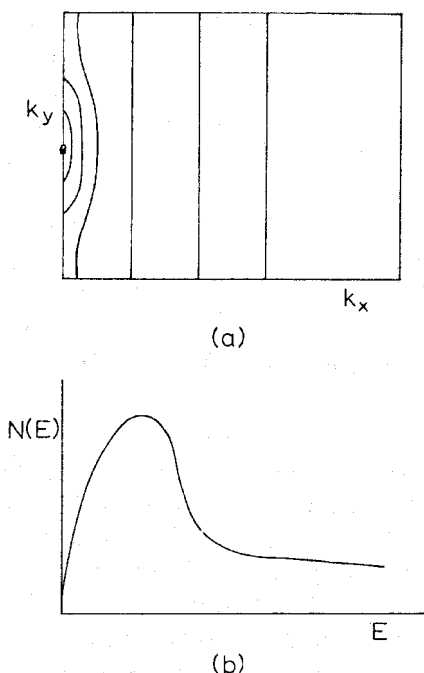


Figure 6. (a) Surfaces of constant energy in k space in a d band; (b) density of states in a d band (schematic).

the crystal structure has been postulated for some oxides (e.g. Ti_2O_3 , see Mott 1969b), but in NiO the splitting must be due to the correlation term e^2/r_{12} (Hubbard 1964, Mott 1968b, Adler 1968). A calculation such as that of Yamashita (1963) cannot give a reliable result since this splitting is neglected, as Yamashita himself states. We need hardly emphasize that the splitting is *not* due to the *long-range* antiferromagnetic order and remains above the Néel point, it is simply the energy required to form Ni^+ and Ni^{3+} ions, which is large.

The motion of a carrier (e.g. a Ni^{3+} ion) can be described as follows: if $\Psi_n(q_1 \dots q_N)$ is the Slater determinant for all the electrons in a crystal of NiO, with an electron missing from atom n then the wave function for the moving carrier will be

$$\sum \exp(ika_n) \Psi_n. \quad (25)$$

There will be a band $E(k)$ of energy levels for the carrier, and we conjecture that as for the single particle case the energy surfaces will be ellipsoids with one heavy and two comparatively light masses.

For the Ni^{2+} ion the arrangement of electrons is as in figure 7; if a hole is adjacent to it, in the low spin state and with the same spin direction, the electron can jump from one e_g state to another. The integral J that gives the band width ($2J$) for the motion of a hole as described by (25) is the same as that which determines the antiferromagnetism, and is estimated by Appel (1966) to be 0.35 eV. If the hole is in the high spin state, then as pointed out by Appel the motion is from one t_{2g} state to another (transition from e_g to t_{2g} being prevented by symmetry). Figure 8, from Appel (1966), shows the kind of overlap envisaged. The band width will be considerably smaller.

However the spin on a hole is not parallel to that on the neighbouring Ni^{2+} ions. The arrangement of spins is shown in figure 9. Austin *et al.* (1967) have measured the directional dependence of the conductivity in single magnetic domains of antiferromagnetic NiO, and find no anisotropy; this shows directly that electrons move through the oxygen ions and not between nearest neighbours: the antiferromagnetic coupling is also through the oxygen ions. We have to ask how the electron moves through the metal ion with anti-parallel spin. If the carrier B is in the low spin state† there is no transition of an up spin electron from A to B in figure 9 which is allowed by symmetry. If B is in the high spin state, this is possible, but such a transition

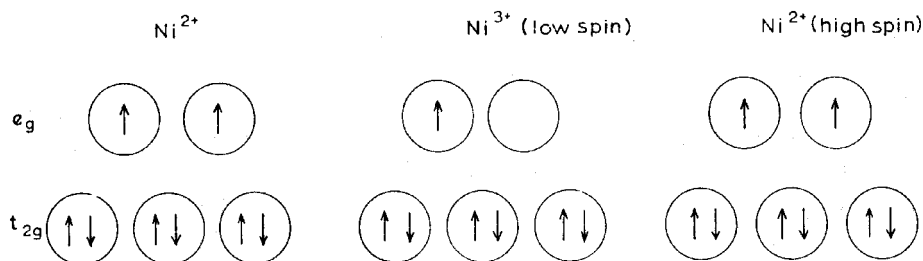


Figure 7. Spin arrangements in NiO on Ni^{2+} ions and on a carrier (Ni^{3+}).

† Electron spin resonance data by Höchli *et al.* (1965) show that Ni^{3+} ions in MgO form a low-spin state. They are probably analogous to bound holes in NiO.

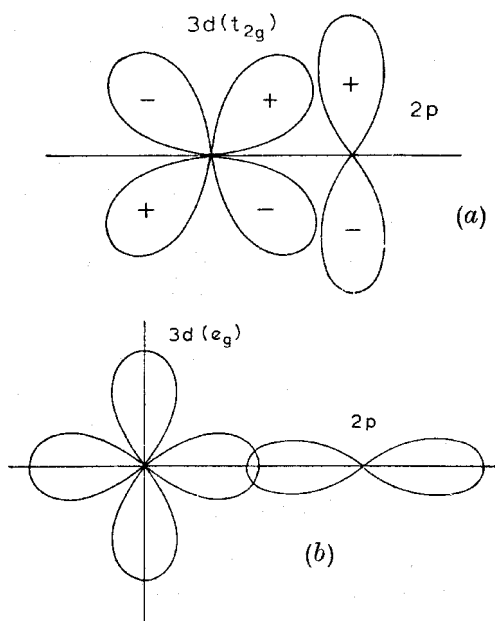


Figure 8. Overlap between Ni and oxygen wave functions. (a) e_g ; (b) t_{2g} .

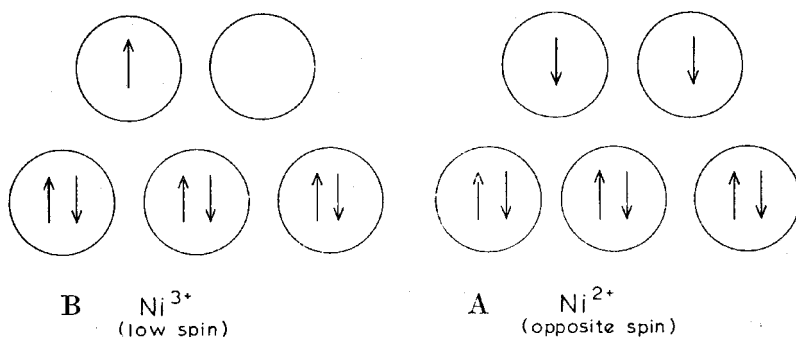


Figure 9. Spin arrangements for movement of a hole in antiferromagnetic NiO.

leaves A in an excited state with *circa* 1–2 eV energy. The antiferromagnetism should therefore split the band $E(k)$ into two very much narrower bands. If this in fact occurred it would certainly lead to small polaron formation and a heavy mass $> 100m$ as in TiO_2 .

It seems to us that two mechanisms are possible, both of which are mentioned by Appel (1968, p. 329).

- (a) If small polarons are formed, the carrier can only move if thermal agitation reverses the spin on a neighbouring atom. Appel concludes that at room temperature this would cut down the mobility by a factor 10. The mobility would tend to zero as $T \rightarrow 0$, instead of infinity as we expect for TiO_2 (apart from Conwell–Weisskopf scattering).
- (b) According to de Gennes (1960) in a magnetic semiconductor the spins near the carrier are 'canted'; adjacent to the carrier the spins may be swung round

so as to be nearly parallel with it. In our case for the rigid band, we see that the energy of the carrier is lowered by some multiple of J if this occurs, which will be much greater than the energy needed to change the spins (a multiple of kT_n). At low temperatures, then, the carrier carries with it a 'spin polaron' which has the same relationship to spin waves as a polaron has to phonons. If the spin polaron is large, the effective mass of the carrier should not be greatly affected.† Appel (1968, p. 329) mentions this possibility but says that J_p is too small to give appreciable canting. This is not so for the rigid lattice band, but may be so for the polaron band of width J_p . We think, however, that since the rigid band is anisotropic, the polaron may be 'small' in the direction in which m_p is large, but may allow the carrier wave function to overlap its neighbours in the other directions. If so, canting will occur. The mobility should then tend to infinity as T tends to zero. We shall see (section 12) that there is no firm information about the d.c. mobility at low temperatures; but the a.c. mobility (section 14) does *not* show any activation energy at low temperatures. We think therefore that for NiO the carriers may move by the second mechanism.

Feinlieb and Adler (1968) have suggested that the carriers in NiO are holes in the oxygen $2p$ band and not Ni^{3+} moving in a way described by an equation of type (25). They argue that, since the optical spectrum shows the lines of localized Ni^{2+} ions split as predicted by crystal field theory (Newman and Chrenko 1959), the overlap between ions cannot be great enough to allow conductivity by the mechanism of formula (25) with the observed mobility ($\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). We think this conclusion is unlikely to be correct; the overlap is known from the Néel temperature. The reason why the crystal field lines are comparatively sharp is because they are essentially exciton lines, and so should not be broadened by the kinetic energy term which determines J .

5. Energy required to remove an electron from a donor

In an element or other material in which $\kappa = \kappa_\infty$ the energy E required to remove a carrier from its impurity centre is given by

$$E = m^* e^4 / 2 \hbar^2 \kappa^2 \quad (26)$$

and the radius of the orbit is

$$r_H = \hbar^2 \kappa / m^* e^2.$$

In an ionic lattice this may be modified in various ways. For a broad-band semiconductor (large polarons), the force attracting the carrier to the centre is:

$$\begin{aligned} e^2 / \kappa_\infty r^2, & \quad r < r_p, \\ e^2 / \kappa r^2, & \quad r > r_p \end{aligned}$$

and a formula of type (26) should be valid with some average value κ_{av} of κ , for instance that obtained by Simpson (1949), namely

$$\frac{1}{\kappa_{av}} = \frac{1}{\kappa} + \frac{5}{16} \left(\frac{1}{\kappa_\infty} - \frac{1}{\kappa} \right).$$

† We are grateful to M. de Gennes for discussions on this point.

The high frequency dielectric constant κ_∞ will, however, play no role if r_p , the polaron radius, is much smaller than the distance d between the metal ion and the charged acceptor or donor. Then the attraction between the polaron and centre is always $e^2/\kappa r^2$, where κ is the static dielectric constant. In this connection it is worth emphasizing that r_p for a bound polaron is likely to be smaller than for a free polaron. This is because the rigid lattice band width $2zJ$ is smaller; for a bound polaron z should be the number of nearest neighbour metal sites with the same energy, and thus half the number for a free polaron. Thus a bound polaron may be ‘small’, while the free polaron is comparatively large.

The binding energy E_c of a polaron to a charged centre will normally be given by

$$E_c = e^2/\kappa d, \tag{27}$$

where d is the distance from the positively charged trapping centre ($\sim 3\text{--}4\text{ \AA}$). This is the reason, according to Bogomolov *et al.* (1968b), why all centres in TiO_2 are ionized at about 100 K; a small polaron is formed and $\kappa \sim 100$, so $E_c \sim 0.03\text{ eV}$. The formula (27) should be valid for lithium-doped NiO and in general for narrow-band oxide semiconductors. However if the Bohr radius $\kappa\hbar^2/m_p e^2$ is greater than d , as it may be for materials with very high dielectric constant, the binding energy will be given by the Bohr formula

$$E_c = m_p e^4/2\hbar^2 \kappa^2.$$

According to Mott (1969b) this is so for the titanates, where $\kappa \sim 1000$ and $m_p \sim 6m$.

6. Application of considerations of section 5 to NiO

A striking feature of NiO is that the activation energy E_c in the conductivity drops with lithium concentration. A drop with increasing doping is of course usual in semiconductors which are elements; here two effects can be separated.

- (a) A drop in E_c which occurs because the dielectric constant occurring in (26) increases due to the presence of occupied donors (Castellan and Seitz 1951, Mott and Davis 1968).
- (b) A drop and eventual disappearance of E_c due to overlap between orbitals. This is the metal-insulator transition and should occur when $n^{1/3}a_H \sim 0.25$ (Mott 1968b). For nickel oxide the ‘radius’ a_H is d as defined in the last section and the activation energy does not tend to zero. We think that the explanation is of type (a).

Austin *et al.* (1967) give the following values of E from resistivity data:

Lithium content (at.%)	E (eV)
—	0.6
0.029	0.37
0.144	0.33
0.211	0.274
0.537	0.200

We surmise that $e^2/\kappa d$ ($= 0.4$ eV) is a good approximation to E_c (these specimens are compensated and we should take E , not $\frac{1}{2}E$ in $\exp(-E/kT)$). Probably in the absence of lithium the acceptors are Ni vacancies; these should hold *two* positive holes (e.g. two Ni^{3+}) and E_c should be

$$E_c = (e^2/\kappa d)(2 - \frac{1}{2}).$$

With $\kappa \sim 12$ and $d \sim 3 \text{ \AA}$ this approximates to 0.6 eV, so we estimate the activation energy for a single Li ion to be 0.4 eV.

We suggest that the energy drops for increasing lithium content because Ni^{3+} bound to Li^+ is a *dipole*. As we shall see in section 14 the bound polaron has twelve states in which it resonates between the twelve Ni ions adjacent to the Li^+ . The separation between these states is of order 0.01 eV, and if kT is greater than this we can treat the dipoles as producing a dielectric constant

$$1 + 4\pi N(2ae)^2/kT,$$

where N is the number of lithium ions per unit volume.† For concentrations of lithium greater than 0.3×10^{-2} per Ni atom this is already large compared with unity; thus the mean energy released by these dipoles in the field of the ionized centres is

$$e^2/2\kappa R,$$

where $(4\pi/3)NR^3 \sim 1$. An equal amount of energy will be released round the free carrier. Thus the activation energy to release a carrier may be written very approximately as

$$\frac{e^2}{\kappa} \left\{ \frac{1}{d} - \left(\frac{4\pi}{3} \right)^{1/3} N^{1/3} \right\}. \quad (28)$$

The drop in E_c predicted is of the right order, being 30% for 1% lithium.

7. Number of carriers in a conduction band

In this section we quote some well-known formulae which will be used in our analysis. Materials like NiO containing Li_2O are compensated extrinsic semiconductors. If there are N donors per unit volume and KN acceptors ($K < 1$), and the energy to ionize a donor is E , then, if $J_p \gg kT$, the number n of electrons per unit volume in a parabolic conduction band is, if $n \ll N$ (Mott and Gurney 1940, p. 159),

$$n = PK \exp(-E/kT), \quad (29)$$

where

$$P = (2\pi m_p kT/h^2)^{3/2}.$$

m_p is here the density of states effective mass, as modified by polaron formation. If the rigid band mass depends on direction, then if m_1, m_2, m_3 are the three components, we must write

$$m^{3/2} = (m_1 m_2 m_3)^{1/2} \times n^{2/3},$$

† This may also happen at very low temperatures if the ground state for the hole resonating between twelve nearest Ni ions is degenerate as suggested for centres of similar types by Sussman (1962).

where n is the number of equivalent band maxima in the many-valley situation, or the degree of degeneracy at the bottom of the band.

If $J_p < kT$, or if the carriers are small polarons in the hopping range of energy, then

$$P = 2(N_0 - n)K, \quad (30)$$

where N_0 is the number of sites per unit volume on which an electron can sit (e.g. the number of Ti ions in TiO_2).

If $a \sim 4 \text{ \AA}$, J_p is of order kT when $m_p (= \hbar^2/2Ja^2) \sim 12m$. For this value of m_p , the factor

$$(2\pi m_p kT/\hbar^2)^{3/2} \sim 10^{21} \text{ cm}^{-3},$$

which is about $0.1N_0$. Thus for effective masses of this order (30) gives a rather larger value than (29), but not very much larger.

8. Thermoelectric effects

In a wide-band semiconductor the thermoelectric power is given by

$$S = (k/e)\{\ln(n/P) + \alpha'\}, \quad (31)$$

where n, P are defined in the last section and $\alpha'kT$ is the kinetic energy of a carrier ($\alpha' = 2$).[†] We expect a similar formula to apply to narrow-band semiconductors. If J_p is the band width, then if $J_p \ll kT$ the kinetic energy must be small compared with kT and α' should tend to zero. A formal proof that this is so has been given by Sewell (1963) and Klinger (1965).

In impurity conduction or in glasses containing transition metal ions, then if

- (a) a localized (hopping) polaron is formed on each site, and
- (b) all sites have the same energy (so that $W_D = 0$), then (31) gives the Heikes (1961) formula

$$S = (k/e)[\ln\{c/(1-c)\} + \alpha']. \quad (32)$$

Here $c, (1-c)$ are the concentrations of each type of ion. For such polarons, the polaron is in an activated state at the instant of hopping; whether a contribution to the thermopower comes from W_H is not immediately obvious. Several authors (Sewell 1963, Schotte 1967, Èfros 1967, Klinger 1968a) have, however, shown that it does not, for models in which $W_D = 0$ and nonlinear effects in the phonon coupling and lattice vibrations are neglected. On the other hand, according to Heikes (1961), a term α' in (32) does arise of the form

$$\alpha' = \Delta S'/k,$$

where $\Delta S'$ is the change in the entropy of an ion due to the presence of an electron.

We can estimate $\Delta S'$ as follows. The entropy of a simple harmonic oscillator is $k \ln(\hbar\omega_0/kT)$. We consider all the ions which are neighbours to the electron. Then

$$\Delta S'/k = \sum \Delta\omega_0/\omega_0,$$

where $\Delta\omega_0$ is the change in frequency. Suppose each ion is held in position by a potential energy

[†] This assumes a mean free path independent of energy.

$$V(x) = \frac{1}{2}px^2\{1 + \frac{1}{2}\lambda(x/a)^2 + \dots\}.$$

Then, if polaron formation changes x by Δx ,

$$W_p = \frac{1}{2}p \sum (\Delta x)^2.$$

The change in frequency is given by $V''(x)$ and is

$$\Delta\omega_0/\omega_0 = 3\lambda(\Delta x/a)^2,$$

which can be written

$$\Delta\omega_0/\omega_0 = 3\lambda W_p / \frac{1}{2}pa^2.$$

$\frac{1}{2}pa^2$ is the energy required to displace an atom through a distance a , and will be 10–20 eV; W_p is perhaps $\frac{1}{2}$ eV, λ is probably about unity. We think that $\Delta S'/k$ might be from 0.1 to 0.2.

If the activation energy is not divided equally between the two sites, because of anharmonic and other effects mentioned in section 2, a term in (32) may arise from W_H . This has been discussed by Heikes *et al.* (1961, 1963). The following argument shows that such a term is probably a general feature of such models.

Electrons are assumed to be localized on sites a distance a apart, with $W_D = 0$. In the presence of an electric field (no temperature gradient), (8) shows that the chance that an electron hops in the direction of the field F is

$$C \exp \left\{ - (W_H - \frac{1}{2}eaF)/kT \right\}$$

and in the opposite direction

$$C \exp \left\{ - (W_H + \frac{1}{2}eaF)/kT \right\}.$$

The net jump probability is then

$$2C \exp(-W_H/kT) \sinh(eaF/kT), \quad (33)$$

which for small fields gives a net current of

$$(eaF/kT)neC \exp(-W_H/kT).$$

Next we consider the effect of temperature on the intermolecular hopping probability. We use the model of section 2. We assume that the total activation energy is not divided equally between the two sites, supposing that the site initially containing the electron requires a fraction β of the total energy. The jump probability is proportional to the chance of finding both molecules in the excited states q_1 and q_2 at the *same time* where $B(q_1 - q_2) = \frac{1}{2}eaF$. The chance that an electron hops in the direction of the field is then

$$C \exp \left\{ -\beta W/k(T + \frac{1}{2}\delta T) \right\} \exp \left\{ -(1 - \beta)W/k(T - \frac{1}{2}\delta T) \right\},$$

which reduces to

$$C \exp \left[- (W/kT) \{ 1 - (1 - 2\beta) \delta T / 2T \} \right], \quad (34)$$

where $W = W_H - \frac{1}{2}eaF$. For the reverse direction the hopping probability is

$$C \exp \left[- \{ (W_H + \frac{1}{2}eaF)/kT \} \{ 1 + (1 - 2\beta) \delta T / T \} \right] \quad (35)$$

and the net current, assuming small fields and temperature gradients is

$$ne a C \left\{ \frac{e a F}{k T} + (1 - 2\beta) \frac{W_H}{k T} \frac{a}{T} \frac{dT}{dx} \right\} \exp(-W_H/kT). \quad (36)$$

The diffusion current is $eD \cdot dn/dx$ where

$$D = a^2 C \exp(-W_H/kT)$$

and

$$dn/dx = n \partial(E_F/kT) / \partial x.$$

Equating (36) to the diffusion current we obtain

$$eF = \{E_F/T - (1 - 2\beta)W_H/T\} dT/dx \quad (37)$$

and

$$S = (k/e) \{E_F/kT - (1 - 2\beta)W_H/kT\}. \quad (38)$$

Thus if $\beta = \frac{1}{2}$ and the hopping energy is equally divided, then $\alpha' = 0$ in (32) and there is no extra contribution to the thermopower. We note that E_F in (38) is the Fermi energy measured from the *bottom* of the polaron well.

For the case where the force constants at the two sites are different and (in the notation of section 2) $A_2/A_1 = \theta$, then $\beta = (1 + \theta)^{-1}$. The second term in the bracket of (38) is then

$$\alpha' = (W_H/kT)(1 - \theta)/(1 + \theta),$$

which is similar to the expression obtained by Heikes *et al.* (1963) using a different method. We now estimate its magnitude as follows.

In molecules the force constant usually decreases as the internuclear separation (x) is increased and empirical optical data (Herzberg 1950) show that

$$Ax^4 = \text{constant}.$$

Thus

$$\delta A/A = -4\delta x/x = -4q_0/x_0,$$

where x_0 is the interatomic spacing. Typically we expect $q_0 \sim 0.1 \text{ \AA}$, $x_0 \sim 5 \text{ \AA}$, giving $\delta A/A \sim 0.1$. This gives

$$\theta = (1 - 4q_0/x_0) \simeq 0.9$$

so that

$$\alpha' = (1/20)(W_H/kT).$$

Thus for molecular solids α' is probably negligible in the hopping (high temperature) range.

We turn now to the situation when the energies of a polaron on the metal ions, as in impurity conduction, are distributed over a range of energies. In this case a term W_D occurs in the hopping energy. For the thermopower we may use (Mott 1967, Cutler and Mott 1969) the 'metallic' formula:

$$S = \frac{\pi^2 k^2 T}{3e} \left\{ \frac{d \ln \sigma(E)}{dE} \right\}_{E=E_F}. \quad (39)$$

If polarons are formed, we think that this formula should remain valid with the addition of a small constant term α' as discussed above. $\sigma(E)$ may be written:

$$\sigma(E) = \sigma_0(E) \exp \{-W_D(E)/kT\},$$

and the Hall effect is n type (i.e. positive) for both electron and hole conduction. For motion in a square four-site network $\mu_H \sim \mu_D$ and the sign for hole motion is the opposite of that for electrons.

These conclusions apply to local states based on s type wave functions. Calculations (Friedman 1964a) for electrons in anthracene, where the symmetry is essentially trigonal, show that $\mu_H/\mu_D \sim -20$, in reasonable agreement with experiment.

(c) Non-adiabatic hopping by small polarons. A number of authors have discussed this problem with divergent conclusions. In an early paper Friedman and Holstein (1963) used an intuitive approach to calculate the modification of the two-site jump rate in a magnetic field. Later authors (Klinger 1965, Kurosawa 1963, Firsov 1964, Schnakenberg 1968) applied the Kubo formalism to the same model but each obtained a different result. Recently Holstein and Friedman (1968) have given a Kubo treatment which confirms their original findings (see also Firsov 1968). The essential features of their earlier treatment may be summarized as follows.

In a tight binding model, the effect of a magnetic field is to multiply the matrix element between sites \bar{R}_m and \bar{R}_n by a phase factor (Peierls 1933):

$$\exp(ie/2\hbar c)\bar{B} \cdot (\bar{R}_m - \bar{R}_n).$$

This does not alter the direct jump rate between two sites, but if indirect jumps through neighbouring sites are also considered an effect can arise. Of particular importance is the equilateral three-site configuration since this gives rise to the largest effect. The effect of \bar{B} on the ions is neglected.

In a magnetic field there is an interference between the probability amplitude for direct jumps and for two-stage jumps involving virtual occupation of the third site. This gives rise to a change in the jump rate which is *linear* in B only for jumps in which the energies of all three sites are momentarily the same. This theory, therefore, does not ascribe the effect to a Lorentz force: the Hall current is a quantum interference effect. The transverse jump rate (w_t) or Hall current is proportional to:

$$JB \exp(-E'/kT),$$

where E' is the minimum activation for a triple-site coincidence, and the Hall mobility is given by:

$$\mu_H \propto w_t/Bw_d \simeq \frac{ea^2}{\hbar} \frac{J}{(kTW_H)^{1/2}} \exp\left\{-\frac{E' - W_H}{kT}\right\}, \quad (42)$$

where w_d is the jump probability for direct jumps. To obtain E' we note that the energy for a triple-site coincidence in the notation of section 2 is

$$A(q_1 - q_0)^2 + Aq_2^2 + Aq_3^2,$$

where $q_1 = q_2 = q_3$. Differentiating to obtain a minimum gives:

$$q_1 = q_0/3$$

and a total energy of $\frac{2}{3}A^2$ or $\frac{4}{3}W_H$ where W_H is the activation energy for a two-site coincidence. Thus μ_H varies as $\exp(-W_H/3kT)$ and has a smaller activation energy than the drift mobility. Also for the Hall coefficient R :

$$R = (\mu_H/\mu_D)/nec = (1/nec)(kT/J) \exp(\frac{2}{3}W/kT). \quad (43)$$

Thus for both hopping and narrow-band conduction in structures where interaction between three sites is dominant $\mu_H \gg \mu_D$. Holstein (private communication) has recently shown that the Hall effect is also positive (i.e. *n*-type) for electrons and holes in the hopping region. In this geometry each site has two nearest neighbours, as for example in the f.c.c. lattice.

On the other hand for hopping in a square four-site array (e.g. a b.c.c. lattice) the Hall and drift mobilities are found to be comparable and the signs for electron and hole motion are different. We note that, for a given configuration, the sign of the Hall effect is always the same in the hopping and narrow-band temperature ranges.

(d) *Adiabatic hopping.* In the adiabatic case a Hall effect can arise through the influence of the magnetic field on the motion of the ions (Herring 1960). A detailed theory has been given recently by Emin and Holstein (1969)[†] for a three-site molecular model. The wave function of the electron follows the nuclei and the polaron energy depends on the instantaneous position and velocity coordinates (*v*) of the ions. In a magnetic field extra terms arise in the vibrational energy, proportional to Bv , and these are equivalent to a Lorentz-like force on the nuclei. The jump probability, which depends on an energy coincidence in configuration space, is modified, but the effect is only significant for jumps involving a triple-site energy coincidence.

Emin and Holstein (1969) have shown that for high temperatures ($T \geq \frac{1}{2}\Theta$):

$$\left. \begin{aligned} \mu_H &= \frac{1}{2}ea^2(\omega_0/2\pi kT)f(T)\exp\left\{-\left(\frac{1}{3}W_H - J\right)/kT\right\}, \\ \mu_D &= \frac{3}{2}ea^2(\omega_0/2\pi kT)\exp\left\{-(W_H - J)/kT\right\}, \end{aligned} \right\} \quad (44)$$

where $f(T) = 1$ for $J \ll kT$, and $f(T) = kT/J$ for $J > kT$.

An important feature is that when $J \sim W_H/3$ the activation energy in the Hall mobility is very small (but never negative), and much lower than the activation energy in the drift mobility. Also, at high temperatures μ_H may *decrease* with temperatures, and μ_D may be comparable with or larger than μ_H in contrast with the non-adiabatic case.

All these treatments of the Hall effect for hopping motion assume *s* type wave functions and the energy of the carrier's spin in the magnetic field is neglected. This implies that the spin state of the carrier is unchanged in the hopping transition.

(e) *Hopping in disordered systems.* To extend the theory to the case where disorder is present it is necessary to calculate the Hall current for jumps between aggregates of three or more nearest neighbour sites. We do not know of any treatment of this problem for small polarons, but Holstein (1961) has used a similar approach to calculate the high-frequency Hall mobility for impurity conduction ($K \ll 1$) in non-polar semiconductors. Here, as in the Miller–Abrahams theory, the mobility is determined by considering least resistance chains, and the d.c. mobility is determined by hops over distances which are greater than average. At high frequencies, jumps between aggregates are less important, and the main contribution to μ_H is from three-site configurations, in which the sites are roughly equilateral with an average spacing somewhat smaller than the average site separation.

An important conclusion by Holstein is that, since the three-site configuration plays a dominant role, the sign of the Hall effect in impurity conduction is positive

[†] We are indebted to Dr Holstein for a preprint of this paper.

for both electrons and holes. This applies to non-polar materials, and polar materials where the hopping is non-adiabatic. We do not know of any treatment for the adiabatic case; since the mechanism is different it is not clear what sign to expect.

Amitay and Pollak (1966) observed no Hall effect for impurity conduction in Si and concluded that Holstein's statistical assumptions were not valid for their case. However, for non-polar but non-crystalline materials where conduction is either by thermally activated hopping or band conduction with a very short mean free path, an n -type Hall coefficient has been found even when the thermopower indicated p -type conduction. Examples are amorphous germanium (Clark 1967), chalcogenide glasses (Male 1967) and liquid Te-Tl alloys (Cutler and Field 1968, Enderby and Simmons 1969).† We think that in such cases the sign of the Hall coefficient is not directly related to the p or n -type nature of the conductor.

10. Optical properties of polarons

10.1. Free polarons (near infra-red)

Optical properties of bound and free polarons have been discussed by several authors. We first discuss the near infra-red using the Franck-Condon principle. First we use the molecular model of section 2. We have already seen that the energy $\hbar\omega$ required to make an electron transfer from one molecule to another (photon-assisted hopping) is $2W_p$ or $4W_H$. An absorption line at this frequency is to be expected whether the polaron is in the hopping range of temperature or not. Also any lines due to ejection of the electron into higher bands will have their frequency increased by $2W_p/\hbar$ (Eagles 1963, Kudinov and Firsov 1965).

If we use the continuum model of section 3 appropriate to a polar crystal, $2W_p$ is the depth of the potential well of figure 4 and $\hbar\omega$ ($=2W_p$) is the energy required to eject the electron into the rigid lattice band. Since the electron is acted on by a Coulomb field due to the polarization, in principle we should expect a series of exciton lines leading up to a series limit. These however will be broadened by temperature and zero-point motion.

Bogomolov *et al.* (1968b), Klinger (1965, 1968a) and Reik and Heese (1967; see also Appel 1968) have discussed the temperature broadening of this line for small polarons. Bogomolov *et al.* give, for the conductivity at frequency ω ,

$$\sigma(\omega) = zne^2a^2\left(\frac{J}{\hbar}\right)^2\frac{1}{\hbar\omega}\left(\frac{\pi\hbar^2}{8W_pkT}\right)^{1/2}\exp\left\{-\frac{(\hbar\omega-2W_p)^2}{8W_pkT}\right\}, \quad (45)$$

where z is the number of nearest neighbours. This formula is based on the assumption that the rigid band width (J) is much less than W_p . If this is not so the final states into which the electron is ejected are spread over the interval J and this gives an additional temperature independent broadening of the absorption line (Firsov 1968a). For a large polaron the absorption increases continuously with frequency and may show structure due to thermal excitation of the electron within the polarization well (Feynman *et al.* 1962). Excitation into the rigid lattice band should lead to weak photoconductivity, but as far as we know this has not been observed.

† A review of such materials has been given by Mott (1969a).

10.2. Bound polarons (near infra-red)

For small polarons bound to impurity centres we expect similar behaviour, but photon assisted hopping may occur to sites *away* from the impurity. For transitions in which the electron moves from the centre the energy required in an optical transition will be different as the following argument shows. Initially the energy of the system is

$$E_1 = A'q_0^2 - B'q_0 - \Delta_1,$$

where Δ_1 is the potential at site 1 due to the impurity. After the optical transition the energy of the system is

$$E_2 = A'q_0^2 - \Delta_2,$$

so that

$$\begin{aligned}\hbar\omega = E_2 - E_1 &= 2A'q_0^2 + \Delta_1 - \Delta_2 \\ &= 2E_p' + \Delta.\end{aligned}$$

Here A' and B' imply modified constants for a polaron near a centre. For TiO_2 Bogomolov *et al.* (1968a) estimate $E_p' = 0.7 \text{ eV}$ for bound polarons compared with $E_p = 0.4 \text{ eV}$ for free polarons, but the observed shift depends on the nature of the donor.

10.3. Bound polarons (far infra-red)

At temperatures such that $T \lesssim \frac{1}{4}\Theta$, the motion of the electron between equivalent sites is not thermally activated. For two equivalent sites, we have already seen (equation (11)) that two states are formed of odd and even parity like the wave functions of H_2^+ , with an energy separation (ΔW) of order $\hbar^2/m_p a^2$. In principle an optical transition should occur at $\hbar\omega = \Delta W$. The process is analogous to nuclear tunnelling or inversion in molecules. Electric dipole transitions of this type have been observed in the far infra-red for polarons bound to rare earth centres in CdF_2 (Eisenberger *et al.* 1968). They should be present in NiO , TiO_2 but have not been observed.

Debye-type dielectric loss in which interaction with phonons plays a part is discussed in section 14.

10.4. Narrow-band behaviour (far infra-red)

For polarons moving according to the band mechanism, we expect, for the conductivity $\sigma(\omega)$ with angular frequency ω ,

$$\sigma(\omega) = (ne^2/m_p)\tau/(1 + \omega^2\tau^2), \quad (46)$$

where n is the number of carriers per unit volume and m_p the polaron mass $\sigma(\omega)$ is a measure of the free carrier absorption. The absorption due to polarons in a narrow band is thus expected to start decreasing when $\omega\tau \sim 1$ and die out at higher frequencies. Since $J_p > \hbar/\tau$, where J_p is the band width, measurements of this frequency give an upper limit for τ and give a lower limit for J_p .

11. Effective mass and mobility in TiO_2

We have seen that a polaron, in a given range of temperature, can behave either like a heavy particle with the relationship between energy and wave number which is

familiar in band theory, or as a particle that moves by thermally activated hopping from site to site. It has however proved difficult to distinguish experimentally between these two mechanisms of charge transport in low-mobility semiconductors, and to prove that hopping exists. The clearest evidence in the literature for polaron hopping in crystals is perhaps that of Gibbons and Spear (1966) on electrons injected into sulphur. In semiconductors, even if the drift mobility μ_D has been obtained through an analysis of the thermopower and conductivity or in other ways, d.c. transport measurements do not discriminate easily between hopping with small activation energy W and narrow-band conduction, with or without polaron enhancement of mass. This is because the **mobility μ_D predicted by non-adiabatic theory varies as $T^{-3/2} \exp(-W/kT)$ and for adiabatic theory as $T^{-1} \exp(-W/kT)$** and the former term masks the second. Any activation energy in the Hall mobility is much weaker and for adiabatic hopping μ_H may even decrease with rising temperature.†

Recently Bogomolov *et al.* (1968b) and others of the Leningrad school have carried out a series of electrical, optical and E.S.R. measurements on **TiO₂** from which they obtain strong evidence for the existence of **small polarons, with a mass of about 150 m , and a hopping energy of 0.13 eV.** This will now be reviewed. We give first some relevant parameters for TiO₂, perpendicular and parallel to the axis of the rutile structure,

$$\begin{aligned} \kappa^a &= 89, & \kappa_\infty^a &= 6.8, & \kappa_p^a &= 9.6, & a &= 4.6 \text{ \AA}, \\ \kappa^c &= 173, & \kappa_\infty^c &= 9, & \kappa_p^c &= 7.4, & c &= 3 \text{ \AA}. \end{aligned}$$

The Ti⁴⁺ ions form a body-centred tetragonal lattice. From (18) the polaron energy W_p is ~ 0.6 eV, since $\bar{a}^3 = \frac{1}{2}a^2c$. The polaron radius estimated from (20) is $\frac{1}{2}\bar{a}(\pi/6)^{1/3}$, or ~ 1.1 Å. The model probably underestimates W_p ; on the other hand, if J is comparable with W_p , then W_p will be reduced by the kinetic energy of the electrons which favours delocalization (cf. section 3 and Eagles 1966). The experimental evidence by Bogomolov *et al.* for the polaron mass and binding energy in TiO₂ is summarized below.

11.1. Thermopower

The analysis of measurements of thermopower in the temperature range 100–300 K using (31) shows that $N_d \exp(-\alpha')$ is very close to N , the number of Ti⁴⁺ ions per cm³; the carrier concentration was determined by an indirect method using chemical analysis. From the arguments in section 8 we conclude that $\alpha' \lesssim 2$ for band or hopping conduction, so that $N_d > 0.1N$. This implies a band width less than kT at 100 K, or $m_p \gtrsim 50m$.

11.2. Optical and ESR measurements

Semiconducting samples of TiO₂ show an absorption peak at 0.8 eV which correlates in intensity with the magnitude of the conductivity and is independent of the nature of the donor centres (Bogomolov *et al.* 1968a,c). At temperatures above

† Polarons give rise to optical effects (section 10) but it must be emphasized that these do not depend on the polaron being in the hopping range of T and they depend on W_p rather than W_H . Also the absorption closely resembles that of some lattice defects so that care is needed in the interpretation of such data.

~ 50 K a single peak is observed at **0.8 eV** and this is attributed to **free polarons**. Below 10 K a single peak is observed at $\hbar\omega \sim$ **1 eV**, the exact position depending on the nature of the donor centre, and this is attributed to **bound polarons**. From the analysis of their optical data, using (45) they estimate $J \sim 0.1$ eV, $W_p = 0.4$ eV giving $\gamma (= W_p/\hbar\omega_0)$ equal to 4. A comparable value for J was also estimated from band structure calculations. This gives for the rigid-band mass $m^* (= \hbar^2/2Ja^2) \sim 3m$. Using non-adiabatic theory the polaron mass is

$$m_p = m^* \exp(\gamma) \simeq 150m$$

and†

$$J_p = J \exp(-\gamma) \simeq 2 \times 10^{-3} \text{ eV}.$$

Using adiabatic theory,

$$m_p = \hbar/2a^2\omega_0 \simeq 100m.$$

They remark that the appropriate treatment may lie between adiabatic and non-adiabatic; a value of m_p/m between 100–150 seems likely.

Klinger (1968b) has remarked that the free carrier peak at 0.8 eV could arise from an internal ($d-d$) transition of the Ti^{3+} ion. A broad absorption peak is observed in Ti_2O_3 at ~ 0.8 eV but the oscillator strength observed in TiO_2 by Bogomolov and Mirlin (1968c) is at least 50 times larger.

Bogomolov *et al.* (1968d) have also studied the electron spin resonance of defect centres in TiO_2 as a function of carrier concentration in the temperature range 77–280 K. They infer that the line width is primarily due to exchange interaction with the free carriers and estimate a value of $m_p \sim 100m$ from their data.

11.3. Hopping at high temperatures

We turn now to the evidence for hopping at high temperatures and here the situation is less clear cut. We expect a gradual transition to hopping above ~ 400 K in TiO_2 . Figure 11 shows the mobility characteristics for lightly reduced rutile above ~ 100 K. For conduction perpendicular to the c axis the drift mobility (which is directly proportional to the conductivity above ~ 30 K) shows an increase above ~ 300 K with an activation energy of 0.13 eV. For conduction along the c axis the activation energy is 0.07 eV. However, the Hall mobility decreases with temperature and $\mu_H > \mu_D$ above 300 K in contrast with the predictions of non-adiabatic theory. The discussion in section 9(d) shows that the high temperature behaviour of μ_H is not inconsistent with Holstein's adiabatic theory of hopping since $W_H/3$ is probably comparable with J .

Equation (33) shows that the drift mobility for hopping *increases* with electric field for high fields ($eaF > kT$). Band models usually lead to a decrease in mobility with field since the relaxation time decreases with carrier velocity. Preliminary studies on TiO_2 (Bogomolov, private communication) show an increase in μ_D with field but the interpretation is complicated by other effects.

† In the crystals used by these workers $N_D \sim 10^{18} \text{ cm}^{-3}$. All the donors are ionized above 20 K giving a Miller–Abrahams disorder energy $W_D \sim 0.5e^2 \kappa^{-1} R_D^{-1}$ of order 10^{-3} eV; according to Anderson's criterion the narrow-band behaviour proposed by Bogomolov *et al.* at $T \sim 400$ K is compatible with this value of W_D .

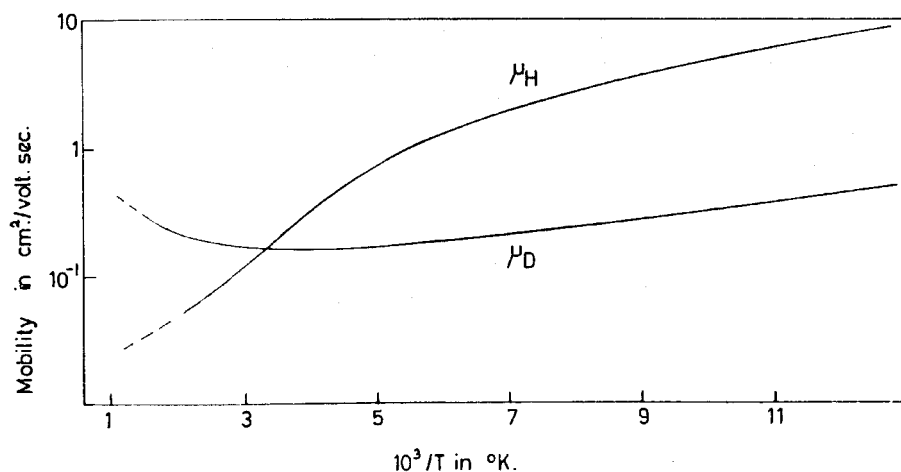


Figure 11. Hall and drift mobilities μ_H and μ_D in TiO_2 as a function of $1/T$ (Bogomolov *et al.* 1968b).

11.4. Low temperatures

We turn now to the behaviour at low temperatures. A striking feature in TiO_2 , and also in materials like SrTiO_3 where the effective mass is in the range 5–10, is that the Hall mobility is very small ($\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) above *circa* 300 K but rises to large values at temperatures below about 50 K. In TiO_2 , μ_H is about $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 30 K and μ_D , estimated from the conductivity, is 10 – $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Much larger Hall mobilities ($\sim 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are observed in SrTiO_3 in the helium region. It is of interest to see if these high mobilities are compatible with a polaron of large mass.

We have seen that at temperatures below $\sim \frac{1}{2}\Phi$ the polaron behaves like a heavy particle in a band, and the relaxation time is determined by phonon and impurity scattering. For Conwell–Weisskopf scattering by charged centres the relaxation time is proportional to $e^4/m_p^2 v^4 \kappa^2$ or $e^4/(kT)^2 \kappa^2$. Thus the scattering does not depend on m_p and we expect it to be small in TiO_2 because κ is large.

Since the band width J_p is less than kT , single-phonon scattering (optical or acoustical) is prohibited by the need to conserve energy and wave vector (Fröhlich and Sewell 1959). The main contribution is from two-phonon processes which are weak at low temperatures. For acoustic processes Fröhlich and Sewell find $\mu_D \propto (\Theta/T)^4$ and for optical scattering Lang and Firsov (1964) give $\mu_D \propto \exp(\hbar\omega_0/kT)$. Thus a large increase in mobility is predicted at low temperatures, if the impurity scattering is not too strong. However, a puzzling feature is that $\mu_H \gg \mu_D$ at $\sim 30 \text{ K}$ in TiO_2 . Since the estimated polaron band width ($J_p \sim 0.002 \text{ eV}$) is about kT at this temperature, we would expect μ_H and μ_D to be comparable.

At temperatures below $\sim 20 \text{ K}$ the carriers are trapped in donor-defect sites and there is evidence of impurity conduction (Hasiguti *et al.* 1961). Dielectric loss measurements in this region by Dominik and MacCrone (1967), which show that the carriers are polarons, will be discussed in section 14.

Becker and Hosler (1965) have shown that the Hall coefficient, though isotropic at low temperatures, becomes very anisotropic above 200 K. We conjecture that the polaron mass, though doubtless dependent on direction, does not lead to any great

anisotropy in the Hall current; but in the high temperature region, due to the term $1/R$ in formula (23), the hopping activation energy, as we have seen, depends on direction. Theory does not at present allow us to predict the anisotropy which may well be considerable.

12. Mobility and effective mass of carriers in NiO

We have already seen that NiO becomes a p -type semiconductor when doped with lithium or partially reduced, and we have discussed the nature of the carriers. In this section the experimental evidence relevant to polaron formation is described.

Some relevant quantities are: $\kappa = 12$, $\kappa_\infty = 5.4$, $\kappa_p = 10$, $a = 4.18 \text{ \AA}$, $\hbar\omega_0 = 0.08 \text{ eV}$. The polaron radius r_p calculated from the small polaron formula (20) is 1 \AA , which gives $W_p (= e^2/\kappa_p r_p)$ equal to 0.7 eV . We shall see that r_p is probably greater and W_p smaller, the polaron being intermediate between large and small. J is estimated at 0.3 eV contrasted with 0.1 for TiO_2 .

Early work on this material showed a difference between the activation energies deduced from the thermopower and the resistivity. This difference, as much as 0.1 eV or more, was assumed to be the activation energy W_H for hopping. Later workers (Ksendsov *et al.* 1963, Bosman and Crevecoeur 1966, Austin *et al.* 1967) have shown that, when grain-boundary resistance is eliminated, these quantities agree. They conclude that hopping, i.e. a mobility of the form $\exp(-W_H/kT)$, is ruled out. It should be emphasized, however, that $\frac{1}{2}\Theta$ is about 400 K and therefore that no hopping is expected below this temperature (unless brought about by spin interactions, see below). We shall see that at high temperatures hopping may occur.

12.1. Drift mobility

Bosman and Crevecoeur (1966) have made measurements on the resistivity and thermopower. When $T > 1000 \text{ K}$ all the carriers are free and the drift mobility μ_D can be deduced directly from the conductivity. The value is found to be $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Equation (15) shows that, for conduction in a narrow band,

$$2(J_p/kT) < \mu_D \quad (\text{in cm}^2 \text{ V}^{-1} \text{ s}^{-1}).$$

Thus, if conduction is by the band mechanism, J is less than 0.015 eV , and $m_p (= \hbar^2/2J_p a^2) > 20m$.

Also at high temperatures these authors find from the thermopower that $P \exp(\alpha')$ is close to $3N$, where N is the number of Ni atoms per cm^3 . Again, this suggests either small polaron formation or $J_p < kT$.

Austin *et al.* (1967) deduce the quantity $m_p(\mu_D/\mu_H)^{2/3}$ from the measured thermopower and Hall coefficient. They find that it is close to $150m$. Arguments given below suggest that μ_D/μ_H lies between 1 and 10. Again we have evidence that m_p is large.

When $T < 1000 \text{ K}$ and the centres are not all ionized, μ_D can be deduced from the measured resistivity and thermopower, assuming either

- (a) P is constant, or
- (b) $P \propto T^{3/2}$.

The results are shown in figure 12 and also the measured Hall mobility. At temperatures above 200 K , μ_H and μ_D are independent of the Li concentration (up to $\sim 0.3 \text{ at. \%}$), and impurity conduction is negligible. At high temperatures, μ_H is

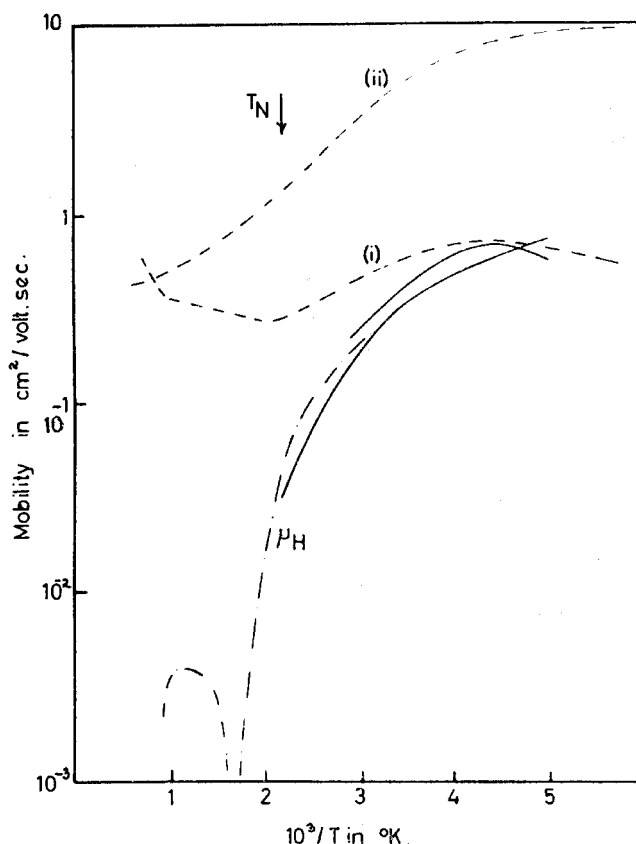


Figure 12. Hall and drift mobility in NiO (Bosman *et al.* 1966, Austin *et al.* 1967). (i) Drift mobility assuming P , the density of states, is constant; (ii) drift mobility calculated assuming P_d proportional to $T^{3/2}$.

strongly influenced by the disappearance of the antiferromagnetism and changes sign; this behaviour will be discussed later. For curve (ii), μ_D is much larger than μ_H at 200–300 K, but assumption (b) is only valid if $J_p > kT$. We think assumption (a), curve (i) is preferable for the reasons above. This leads to the values of μ_D/μ_H that we have quoted above and $\mu_D \sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $\sim 300 \text{ K}$; thus $J_p < 0.012 \text{ eV}$ or $m_p > 30m$ for a band conduction mechanism.

With such small values of the polaron band width J_p , Anderson localization (i.e. a small term W_D) might well occur due to the random fields of the ionized lithium centres. We shall show in section 13 that W_D is cut down by the dipoles on unionized centres; but when $T > 1000 \text{ K}$ some weak Anderson localization ought to occur (cf. table), particularly for high concentrations of lithium. For this reason, as well as others to be discussed below, we think hopping is likely at high temperatures.

12.2. Hall mobility

In NiO, μ_H shows a very anomalous behaviour near the Néel point and the Hall constant changes sign, as in n -type Fe_2O_3 . CoO on the other hand shows no such change at T_N , and μ_H is almost constant ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) above 200 K apart from a weak minimum at $\sim 1000 \text{ K}$ (van Daal and Bosman 1967). In CoO, μ_H and μ_D are

comparable, and the behaviour of μ_H at high temperatures is consistent with Holstein's adiabatic theory of hopping, with $W_H \sim 0.1\text{--}0.2\text{ eV}$.

We recall that Holstein's non-adiabatic theory for μ_H predicts no sign reversal at the transition from band to hopping conduction, for s -states with spin neglected. The situation for the adiabatic case is not clear. However, in NiO and Fe_2O_3 , it seems certain that the sign reversal is associated with the onset of magnetic disorder and the change in internal magnetic field. The effect of this on a hopping model is not known, but Maranzana (1967) has shown that a reversal can occur for a wide-band model when carriers with spin-orbit coupling are scattered by spin-disorder. Van Daal and Bosman (1967) have shown qualitatively that his theory accounts for the behaviour in NiO and Fe_2O_3 , but does not explain its absence in CoO. But this does not *prove* that the carriers move in a band, and the validity of this theory in a situation where $J_p < 0.2kT$ is not established.

12.3. Optical properties

We have seen that small polarons give rise to optical absorption in the near infra-red (section 10), which has been observed in TiO_2 . Similar studies have been made on Li doped NiO by Austin *et al.* (1968), but in this material they are complicated by the strong crystal-field absorptions between 1 and 5 eV. Also, a high temperature is needed to ionize the Li centres and free carrier absorption was only observed in the far infra-red. The latter measurements showed that at temperatures above $\sim 500\text{ K}$, the conductivity $\sigma(\omega)$ at frequency ω is identical with the d.c. conductivity up to frequencies of at least $2 \times 10^{12}\text{ Hz}$. This is consistent with polarons hopping in a lattice or moving in a narrow band (cf. section 10.4). But if the latter is true, this evidence implies that $\tau < 10^{-13}\text{ sec}$ and therefore the band width must be at least 0.01 eV; it follows that $m_p < 40m$.

In the near infra-red, Austin *et al.* (1968) observed an absorption peak at ~ 1 micron which they ascribe to bound polarons. This would imply that $W_p \sim 0.5\text{ eV}$ for bound polarons.

12.4. Mechanisms for the mobility

Suppose first that the carrier moves by the band mechanism at low temperatures carrying its spin polarization as described in section 4(b). Then the evidence in section 12.1 suggests that m_p is greater than or equal to $30m$. If the rigid band mass were isotropic, so large a value for m_p would certainly suggest small polaron formation and hopping at high temperatures. Since J is greater than or equal to $\hbar\omega_0$ the adiabatic formula should be used, giving

$$m_p \sim 2m \exp(\gamma),$$

so that we deduce γ greater than or equal to 3. The lower value is considerably less than $W_p/\hbar\omega_0$, since $\hbar\omega_0 = 0.08\text{ eV}$, whether we take the small polaron theoretical value for W_p (0.7 eV) or that observed for optical absorption for bound polarons (0.5 eV). We think that we have to do with a polaron of intermediate size between 'large' and 'small'. For such polarons we set (cf. formula (24)) $m_p = 2m \exp(\gamma')$,

$$\gamma' = W_H/\frac{1}{2}\hbar\omega_0$$

and deduce that $W_H \sim 0.12\text{ eV}$. As we have seen, a situation in which $W_H < \frac{1}{2}W_p$ is to be expected in such cases. Above the transition temperature of order 400 K a small hopping energy should be observable in the mobility, particularly if account were

taken of the factor $1/T$ outside the exponential in the adiabatic formula (11). The slight rise in μ_D above ~ 500 K for curve (i) in figure 12 supports this view and corresponds to $W_H \sim 0.1$ eV.

There remains however the possibility that below $\frac{1}{2}\Theta$ the carrier can only move as a consequence of a thermally activated spin reversal on one of its neighbours, as proposed by Appel (1966, 1968) and discussed in section 4(a). If so, this cuts down the mobility by a factor of order 10 at ~ 300 K and $\mu_D \rightarrow 0$ as $T \rightarrow 0$. Since the a.c. mobility and the impurity conduction do not show an activation energy at low temperatures, we doubt if this mechanism applies to nickel oxide, though it doubtless would for smaller values of J .

13. Impurity conduction

In a doped and compensated semiconductor, impurity conduction gives the major contribution to the conductivity at low temperatures. In elements such as silicon and germanium the process is well understood. The energy levels are spread over a range of energies of order $e^2/\kappa R$, where R is the distance between the majority centres, and in the theory of Miller and Abrahams (1960) the jump frequency from one site to another can be written:

$$\nu \exp(-2\alpha R) \exp(-W_D/kT), \quad (47)$$

where

$$W_D = f(K)e^2/\kappa R \quad (48)$$

and f is a function of the compensation K which is tabulated in their paper, and ~ 0.3 for $K = \frac{1}{2}$ and ν depends on the phonon spectrum. In a recent paper (Mott 1969a) one of us has pointed out that at very low temperatures the observed value of W_D should tend to zero because the most probable jump will not be to nearest neighbours but to a more distant site for which the energy difference is smaller. Minimizing the factor (47) leads to a conductivity of the form

$$C \exp[-A\{W_D(\alpha R)^3/kT\}^{1/4}], \quad A \sim 1, \quad (49)$$

where R is the mean distance between centres.

The purpose of this section is to extend these considerations to the polar materials discussed in this article. For such materials the arguments of sections 2 and 3 show that the jump probability will have an activation energy

$$W = W_H + \frac{1}{2}W_D,$$

where W_H is the polaron activation energy of (18). At low temperatures between $\frac{1}{2}\Theta$ and $\frac{1}{4}\Theta$ the polaron energy should die away as in (15.1) and W will tend to (48). In contrast, however, to the case of a crystalline lattice, where the hopping energy disappears completely below $\sim \frac{1}{2}\Theta$, in impurity conduction the term W_H dies away gradually.

At very low temperatures W_D should tend to zero according to (49), but rough estimates suggest that this should occur only at helium temperatures and below.

Similar considerations apply to glasses containing transition metal ions of mixed valencies; these will be considered in section 15.

Impurity conduction has been observed in Li doped NiO by Bosman and Crevecoeur (1966) and Springthorpe *et al.* (1965). Some conductivity measurements

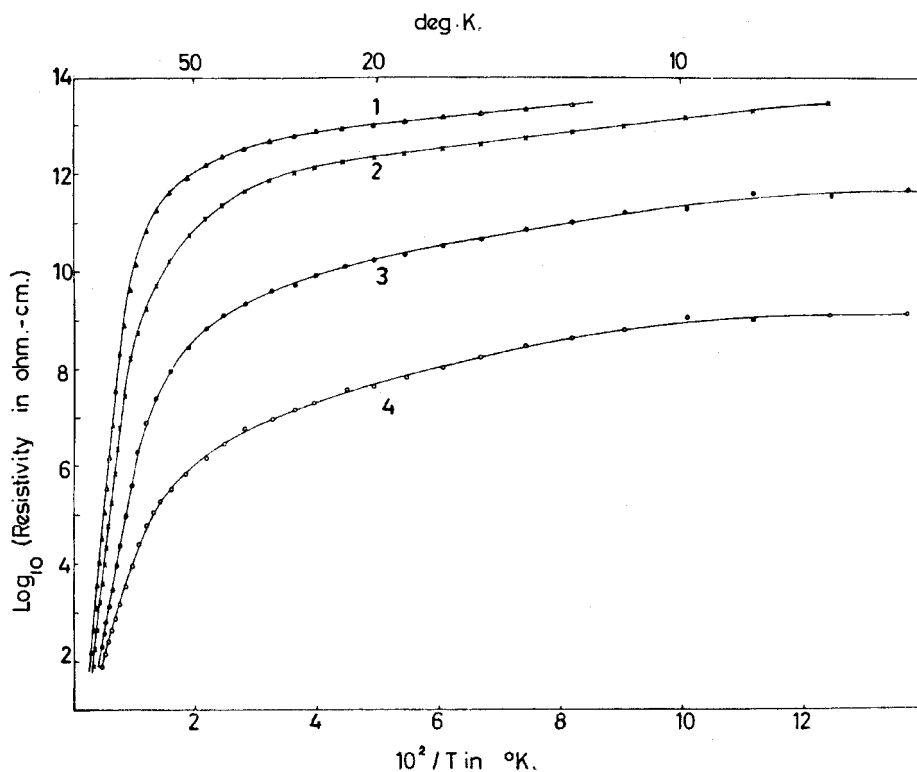


Figure 13. Impurity conduction in NiO; $\log \rho$ is plotted against $1/T$. The curves 1, 2, 3, 4 are for the crystals listed in the table.

which have been extended† down to 7 K, are shown in figure 13. The onset of impurity conduction is marked by the following.

- (a) A drop in the activation energy E for conduction at temperatures between 50 and 100 K, from 0.2–0.4 eV at high temperatures to 0.004 eV or less at 10 K. At temperatures below the transition to impurity conduction E drops slowly from ~ 0.05 eV to the final value, whereas in crystalline germanium it is constant.
- (b) A maximum in the Seebeck coefficient and in the Hall mobility at 150–200 K.

These authors attribute the impurity conduction to the presence of compensating donor centres (probably oxygen vacancies), and assume that some of the $\text{Li}^+\text{Ni}^{3+}$ acceptors receive an electron from these donors which hops from one centre to another.

Few other measurements on polar materials have been reported but similar behaviour has been observed in CoO , Fe_2O_3 , V_2O_3 and other $3d$ oxides (Austin and Turner, unpublished). Some of the samples show no evidence of an activation energy at low temperatures, a point which will be considered below.

† We are indebted to Mr C. E. Turner for these measurements.

Sample	$N_A \times 10^{-19}(\text{cm}^{-3})$	$R \text{ (\AA)}$	$W_D \text{ (eV)}$	$E \text{ (eV)}$	αR
1	5.4	25	0.03	0.003	7
2	6.5	23	0.03	0.003	10
3	16	18	0.04	0.0035	13
4	24	15	0.05	0.004	15

E is the observed activation energy at 15 K.
 W_D is the Miller–Abrahams term $0.5e^2\kappa^{-1}R^{-1}$.

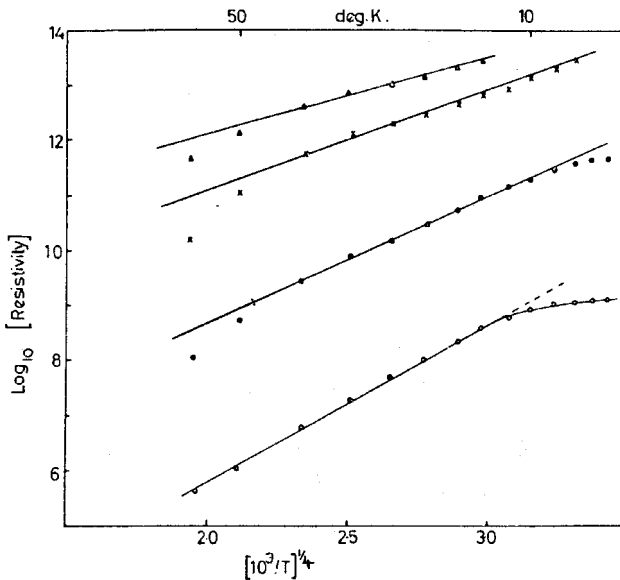


Figure 14. Impurity conduction in NiO; $\log \rho$ is plotted against $1/T^{1/4}$.

Here we consider briefly the data on NiO in figure 13. The average spacing between the acceptors ($R = N_A^{-1/3}$) and the Miller–Abrahams energy ($W_D = 0.5e^2/\kappa R$) are given in the table. All the samples are lightly compensated (Austin *et al.* 1967) and $K \sim 0.1$, except perhaps for sample 4 where $K \sim 0.5$.

We see that the Miller–Abrahams term W_D is almost an order of magnitude larger than the observed activation energies E at low temperatures. If the electron hops preferentially a distance greater than the nearest neighbour distance then we expect the conductivity to be given by (49). Figure 14 shows a plot of $\log \rho$ versus $T^{-1/4}$ for temperatures below ~ 60 K. In contrast with figure 13 the curve is linear over much of the range. On the other hand, if one deduces from the observations the optimum jump distance pR , using the relation (Mott 1968c)

$$p^4 \sim (3W_D/2kT)/\alpha R,$$

one finds a value only about 30% greater than R . We are doubtful therefore whether (49) is the correct explanation of the low activation energies. We note too that in samples 3 and 4, E appears to vanish at the lowest temperatures. This effect is marked also in Fe_2O_3 and in glasses (section 15).

Our argument so far has neglected the dipole nature of the acceptor levels. We have suggested in section 6 that these may have a major effect on the activation

energy E in the conductivity. We now propose that the quantity κ in the Miller–Abrahams formula (48) should be replaced by

$$\kappa_{\text{eff}} = \kappa + 4\pi Ne^2 a^2 / \kappa kT,$$

where N is the number of (uncompensated) lithium centres per unit volume. The second term gives the contribution from the dipoles; it is valid only if $kT > \Delta W$ where ΔW is the resonance splitting of the states formed by the bound polaron (see section 14). We have no evidence about the magnitude of this in NiO but in TiO₂ the quantity $\Delta W/k$ is in the helium range of temperatures (cf. section 14). The hopping probability will therefore vary with T as

$$\exp \{-0.5(e^2/R)/(\kappa kT + 4\pi Ne^2 a^2 / \kappa)\} \quad (50)$$

and will tend to a value independent of T at low temperatures.

This explanation can only be valid if the resonance energy ΔW is lower than kT at the lowest temperatures ($\sim 7\text{ K}$) of the experiment.

14. Hopping conduction for alternating currents

Three kinds of problem arise: (a) hopping in regular lattice with $W_D = 0$, (b) hopping around an impurity centre and (c) impurity conduction. For (a) the conductivity $\sigma(\omega)$ varies with frequency only if ω^{-1} is comparable with the time (τ_H) spent in the act of hopping between two sites, and this is much less than the ‘staying’ time at one site. Klinger (1965) and Reik and Heese (1967) have shown that, for small polarons,

$$\sigma(\omega) = \sigma(0) \exp(-\omega^2 \tau_H^2) \sinh(\hbar\omega/2kT) / (\hbar\omega/2kt), \quad (51)$$

where

$$\tau_H^2 \sim \hbar^2 / W_H kT.$$

Equation (51) predicts a peak in the near infra-red at $\hbar\omega \sim 4W_H$ and in this frequency range the formula is equivalent to (45). Free carrier absorption of this type has been discussed for TiO₂ in section 11.2 and for SrTiO₃, LaCoO₃ and other oxides by Reik and co-workers (Reik 1967).

Here, we consider problems of type (b) and (c) in which the conductivity $\sigma(\omega)$ is due to polarization currents. These are present at *low* frequencies ($\omega < \omega_0$). In the first we calculate the conductivity $\sigma(\omega)$ at frequency ω due to pairs of centres at a well-defined distance from each other. The analysis is applicable to situations such as on Ni³⁺ ion bound to a Li⁺ ion in NiO and able to move round it in the way illustrated in figure 15. Loss of energy due to such centres has been observed by

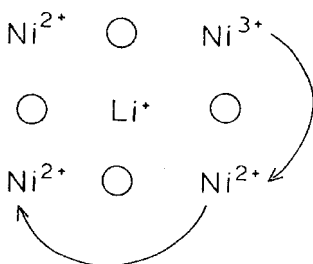


Figure 15. A bound hole (Ni^{3+}) in NiO doped with Li_2O .

Snowden and Saltzburg (1966), Austin *et al.* (1968) and by Kabashima and Kawakubo (1968), and at low temperatures in TiO_2 a loss probably due to a similar process has been observed by Dominik and MacCrone (1967). The treatment we shall give derives from various authors. It is only meaningful if polarons of high effective mass are formed, since otherwise the states of odd and even parity (figure 3, equation (13)) will be separated by resonance energies ΔW large compared with kT .

The other problem is that of impurity conduction, in which $\sigma(\omega)$ is determined by averaging over all pairs of centres. The problem has been investigated in detail, notably by Pollak and Geballe (1961), Pollak (1964) and by Tanaka and Fan (1963) for non-polar semiconductors, the main contributions being from distant pairs so that ΔW is small. We shall summarize with a view to its application to polar materials, such as vanadate glasses.

14.1. Hopping between pairs of centres

The simplest case arises when there are pairs of centres at a distance R from each other with energy levels differing by W_D and when W_D is greater than the resonance energy ΔW . If $W_D/kT \gg 1$, then the population of the upper level is $\exp(-W_D/kT)$. In the presence of a field F the population is increased by the factor $\pm eRF/kT$. A dipole is produced by this transfer of charge and the energy of the induced dipole in the field is

$$(e^2 R^2 F^2 / kT) \exp(-W_D/kT).$$

The static dielectric constant κ , averaging over all directions of R , is given by

$$\kappa - \kappa_\infty = \frac{4\pi N e^2 R^2}{3 kT} \exp\left(-\frac{W_D}{kT}\right),$$

where N is the number of pairs per unit volume. It follows that the conductivity $\sigma(\omega)$ at frequency ω is given by

$$\sigma(\omega) = \frac{4\pi N e^2 R^2}{3 kT} \exp\left(-\frac{W_D}{kT}\right) \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2}, \quad (52)$$

where $1/\tau_0$ is the probability per unit time for a jump *downwards*. In the approximation of Miller and Abrahams (1960) (single phonon transition), $1/\tau_0$ is independent of T and contains the tunnelling factor $\exp(-2\alpha R)$. When polarons are formed τ_0 could be deduced from Schnakenberg's (1968) paper, the interaction being with acoustic phonons.

Suppose now that the difference in energy between the two levels, W_D , is less than ΔW , the resonance energy. An extreme case is $W_D = 0$. If ψ_a, ψ_b are atomic wave functions on the two sites, then the eigenstates of the system are (unnormalized) as in figure 3:

$$\psi_1 = \psi_a + \psi_b, \quad \psi_2 = \psi_a - \psi_b \quad (53)$$

and

$$\Delta W \sim W \exp(-\alpha R),$$

where W is the ionization energy of one of the centres. Neither of these states has a dipole. If $W_D \neq 0$, the dipole is easily seen to be

$$\sim (W_D/\Delta W)eR.$$

Thus (52) becomes

$$\sigma(\omega) = \frac{4\pi Ne^2 R^2}{3 kT} \exp\left(-\frac{\Delta W}{kT}\right) \left(\frac{W_D}{\Delta W}\right)^2 \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2}. \quad (54)$$

This formula is used by Pollak in his discussion of a.c. impurity conduction at very low temperatures, and we shall return to it below.

Formula (54) predicts that when $W_D = 0$ there would be no dielectric loss. There is of course a resonance absorption given by $\hbar\omega = \Delta W$, and as we stated in section 10 this has been observed in CdF_2 . This line is broadened by temperature (cf. Fröhlich 1949, p. 102). There can be no Debye loss unless the temperature is so high that $1/\tau_0$, the phonon-assisted jump probability between the two levels, is *greater* than $\Delta W/\hbar$ (Sewell 1963). However, if more than two sites are involved (twelve Ni sites are adjacent to Li^+ in NiO), the first excited state of the carrier is degenerate. Professor Fröhlich (see also Fröhlich *et al.* 1963) has pointed out to us that a dipole can then be formed by the electrons in the degenerate state and the conductivity is then of the form

$$\frac{4\pi Ne^2 R^2}{3 kT} \exp\left(-\frac{\Delta W}{kT}\right) \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2}, \quad (55)$$

where τ_0 as before is the time constant for a downward jump.†

Formula (55), we believe, should be used to describe the results of Dominik and MacCrone (1967) who observe a temperature-dependent loss angle in rutile at helium temperature as illustrated in figure 16. From the variation of the maximum ($\omega\tau \sim 1$) with temperature they deduce that $\Delta W \sim 10^{-4}$ eV. This would correspond to a polaron mass of $\sim 10^3 m$; this is bigger by 5 than that deduced by Bogomolov *et al.* (section 11), but we have seen that the mass of a bound polaron can be bigger than that of a free one. $1/\tau_0$ is about 10^5 s^{-1} , which is of the order of the factor outside the exponential in the impurity conductivity in germanium and seems not improbable in this case.

MacCrone (1969) has also estimated the resonance energy ΔW from the dielectric loss in a magnetic field. At a critical field B_c spin reversal transitions are induced between the states ψ_1 and ψ_2 by the a.c. magnetic field associated with the applied electric field. A sharp increase in the polarizability is observed at $B_c = \Delta W/\mu$, where μ is the magnetic moment of the electron, giving

$$\Delta W = 0.93 \times 10^{-4} \text{ eV}.$$

Kabashima and Kawakubo (1968) have measured $\sigma(\omega)$ in lithium-doped nickel oxide for microwave frequencies, and Austin *et al.* (1968) have made measurements in the far infra-red. The loss is proportional to lithium content, which (see below) rules out impurity conduction and suggests that the process is that illustrated in figure 15, namely the motion of a hole round a Li^+ ion. For low values of ω , the conductivity was found to be proportional to ω^2 , but for higher values of ω it behaved like $\omega^2/(1 + \omega^2\tau^2)$ with $\tau \sim 2 \times 10^{-10} \text{ s}^{-1}$. Both σ and τ were independent of T between 200 K and 100 K. It seems reasonable to assume that this is the process described by (55). The time τ , the 'staying time' on each site, is not $\hbar/\Delta W$, but in the

† Sussman (1962) has pointed out that the ground state for an electron centred on a number (> 3) of atoms equidistant from a trapping centre may be degenerate. If this is so in our case, no term in ΔW should occur in (55).

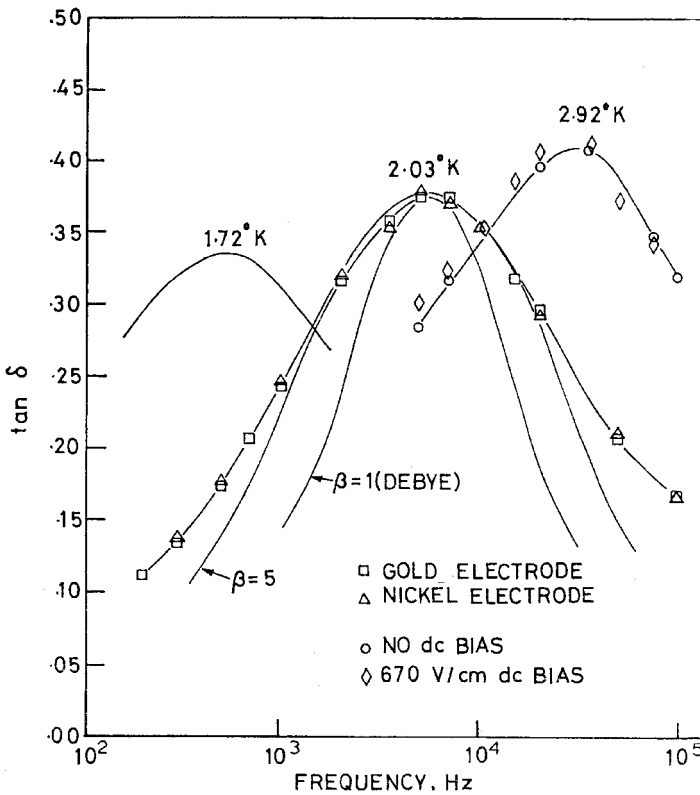


Figure 16. Loss angle $\tan \delta$ as a function of frequency in TiO_2 at helium temperature (Dominik and MacCrone 1967).

non-hopping region is a 'non-diagonal' process involving interaction with one or more phonons; an analysis of its value has not been given. In the hopping range of temperatures, τ will be the hopping time.

Above 200 K Kabashima and Kawakubo find that $\sigma(\omega)$ rises with an activation energy of 0.08 eV, and Austin *et al.* (1968) find in the far infra-red activation energies of 0.1–0.14 eV (and 0.2–0.3 eV for CoO). Some results are shown in figure 17. At high temperatures formula (55) becomes

$$\sigma = (Ne^2 R^2 / kT) / \tau_0, \quad (56)$$

and $1/\tau_0$ will contain the hopping activation energy and be of the form

$$1/\tau_0 \simeq \nu \exp(-W_H/kT).$$

We have seen in section 12 that values of W_H of this order are to be expected for NiO; it is noteworthy that hopping apparently sets in at a lower temperature for a bound than for a free polaron, probably because of the narrower band width. The theory assumes that τ_0 is independent of ω . For higher frequencies ($\omega > \omega_0$) we conjecture that the hopping probability in (56) will vary as in (51) giving a peak in the near infra-red for bound polarons.†

† For a recent theory, see Klinger and Blakher (1969).

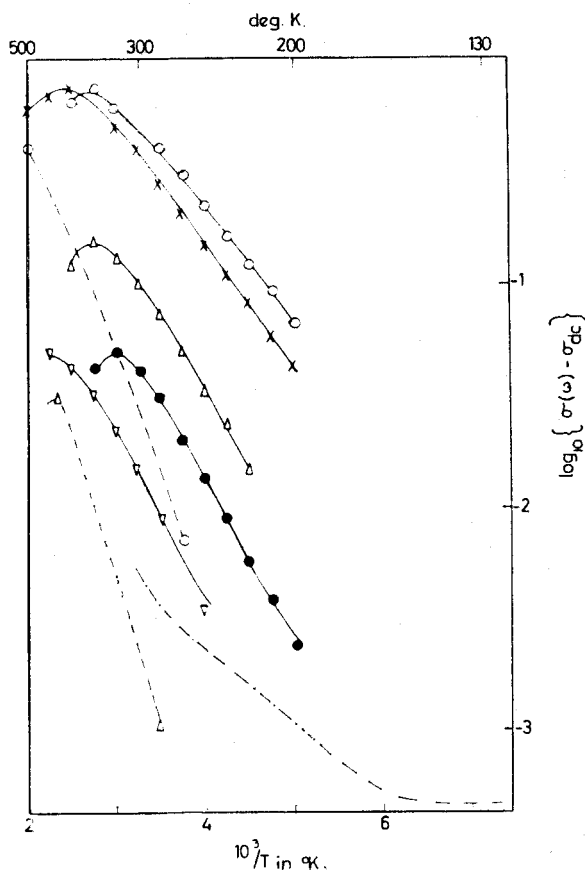


Figure 17. Polarization conductivity (σ_{pol}) in the far infra-red for various crystals of NiO (full curves) and CoO (broken curves), after Austin *et al.* (1968). Also shown (chain curve) is σ_{pol} from microwave data by Kabashima and Kawakubo (1968) on a NiO crystal with 0.014 at.% Li.

14.2. Impurity conduction

To obtain $\sigma(\omega)$ for impurity conduction, one has to average over all R and all W_D for all pairs of occupied and empty centres. The analysis of Pollak (1964) gives for non-polar materials over a range of T that $\sigma(\omega)$ is independent of T and proportional to $\omega^{0.8}$, and this behaviour has been observed by Pollak and Geballe (1961) in doped silicon and Owen (1967) in chalcogenide glasses. The description given here is meant to be applicable to impurity conduction when neither K for $1 - K$ is small and also to the glasses described in the next section. We first outline the situation when, if polarons are formed, they are in the non-hopping range of T . Under these conditions, the d.c. impurity conduction is of the form (Mott 1969a)

$$\sigma = N(E_F)kT(e^2 R^2/kT) \exp(-W_D/kT)/\tau_0. \quad (57)$$

The first two terms arise because only electrons with energies differing by $\sim kT$ from the Fermi energy have a high probability of hopping. Pollak's analysis is for $K \ll 1$, so the gas is non-degenerate and one can substitute N for $N(E_F)kT$ in (55).

Adapted to our case, Pollak's analysis is as follows. If there are N_A acceptors per unit volume, to which an electron can jump, then if W_D were the same for all possible hops, we should have

$$\sigma(\omega) \sim N(E_F)kTN_A(e^2/kT) \int R^2 \exp(-W_D/kT) \frac{\omega^2}{1 + \omega^2\tau^2} 4\pi R^2 dR.$$

To obtain the conductivity we have to average over all W_D : so $\exp(-W_D/kT)$ has to be replaced by kT/W_{av} , where W_{av} is the range of energies over which the quantities W_D are distributed. In the integral, the main contribution comes from values of R for which τ , which contains the factor $\exp(-2\alpha R)$, is such that

$$\omega\tau \sim 1.$$

Thus

$$\sigma(\omega) \sim 4\pi N(E_F)N_AkT\omega R^4\Delta R/W_{av},$$

where ΔR is the range of values of R for which $\omega\Delta\tau \sim 1$. If we write $\tau_0 = \tau_\infty \exp(2\alpha R)$ and $\omega\tau_0 \sim 1$, then

$$2\alpha R = \ln(1/\omega\tau_\infty)$$

and

$$2\alpha\Delta R = 1.$$

Thus

$$\sigma(\omega) \sim \pi\{N(E_F)/W_{av}\}N_AkT(e^2/\alpha^5)\omega\{\ln(1/\omega\tau_0)\}^4. \quad (58)$$

Equation (58) gives a value of $\sigma(\omega)$ which is proportional to a power of ω rather less than linear (in practice $\omega^{0.8}$) and proportional to T . In Pollak's case (non-degenerate gas due to small compensation), $N(E)kT$ has to be replaced by N_D and $\sigma(\omega)$ is independent of T as observed by Pollak and Geballe (1961).

If hopping polarons are formed, $1/\tau_0$ is of the form $\nu \exp(-W_H/kT)$ and the last term in (58) must be replaced by

$$\{\ln(\nu/\omega) - W/kT\}^4 \quad (59)$$

and a complicated variation with temperature is expected.

Pollak also considers the behaviour at very low temperatures, when for the value of R , the distance between centres, for which $\omega\tau \sim 1$, the resonance energy $\Delta W \gg kT$. A drop of $\sigma(\omega)$ to zero as some power of T is then expected.

15. Glasses containing transition metal ions

Many glasses containing transition metal ions, for instance vanadium or iron, are semiconductors. It is generally recognized that the conductivity in such glasses is due to the presence of ions of more than one valency, for instance V^{4+} and V^{5+} or Fe^{2+} and Fe^{3+} ; an electron can then pass from one ion to another and the mechanism is similar to impurity conduction in ionic crystals such as NiO as described in section 13. In the vanadium glasses at any rate there is evidence that the energies of an electron on all vanadium sites are spread over a small range at most comparable with kT at room temperature; the ligand fields surrounding a V^{4+} and a V^{5+} ion must be identical. Schmid (1968) has suggested that at the temperature at which the glass solidifies the electron is moving rapidly from ion to ion so that the average field acting on the surrounding atoms during solidification is the same for all vanadium

sites. This is not necessarily so for all glasses; some glasses containing Cu^+ and Cu^{2+} investigated by Drake and Scanlan (1969) show a big activation energy (~ 1 eV) in the conductivity, suggesting that the sites are not identical, so that to move an electron from Cu^+ on to a Cu^{2+} site takes energy. Glasses containing iron may be intermediate (Mott 1968c).

Mott (1967) proposed the following formula for the conductivity:

$$\sigma = c(1 - c)(e^2/RkT) \exp(-2\alpha R) \exp(-W/kT). \quad (60)$$

R is here the mean distance between the ions, c the ratio V^{4+}/V , α is, as in other sections, the rate of decay of a wave function and W the hopping activation energy:

$$W = W_H + \frac{1}{2}W_D,$$

where W_H is the polaron hopping energy, W_D is the average change in energy in going from site to site. The activation energy in σ is wholly a hopping energy. Apart from the small term W_D , all the electrons are in equivalent sites. W , therefore, according to the considerations of section 8, should not occur in the thermopower. The Seebeck coefficient S should be given by the Heikes formula (32) if $W_D < kT$, or by formula (39) otherwise.

One of the most striking facts about vanadate glasses is that if c or $1 - c$ are not too small, S satisfies the Heikes formula, being independent of T and proportional to $\ln\{c/(1 - c)\}$. Figure 18 from Kennedy and Mackenzie (1967) shows this. This suggests strongly that $W_D < kT$. For iron-containing glasses the formula is not

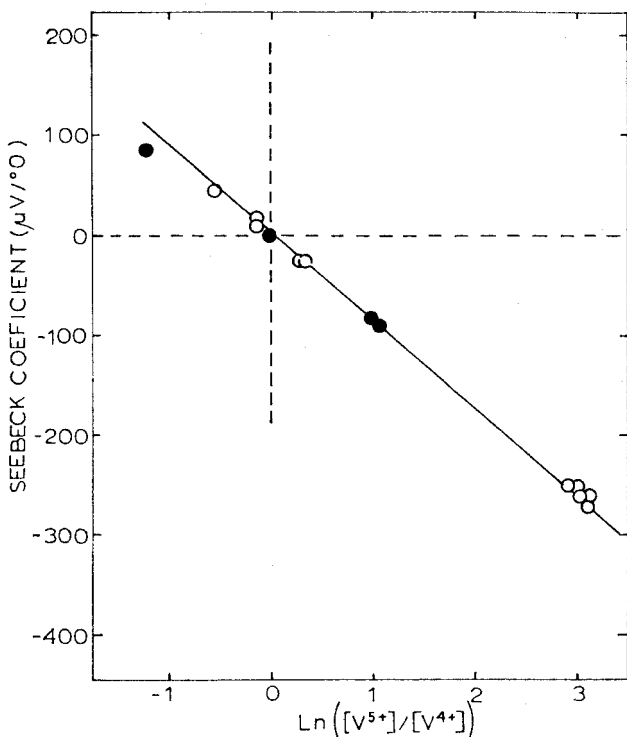


Figure 18. Seebeck coefficient of vanadate glasses as a function of V^{5+}/V^{4+} (Kennedy and Mackenzie 1967). The coefficient does not vary with T .

satisfied and Mott (1968c) has suggested that W_D is much larger and that formula (39) ought to be used.

Except at low temperatures, then, W_D may be negligible in vanadate glasses. We next ask whether the observed values of W correspond to the theoretical values of W_H . In glasses, as the ions are further separated than in crystals, the approximation $W_H = \frac{1}{2} W_p$ should be a good one, so we expect:

$$W_H = e^2/4\kappa_p r_p$$

and r_p should have the limiting small polaron value (20). The activation energies have been investigated by a number of authors (Denton *et al.* 1954, Baynton *et al.* 1956, 1957, Munakata 1960, Nester and Kingery 1963). Nester and Kingery's work deals with glasses of nominal composition from 50 to 90% of V_2O_5 , the other constituents being BaO and P_2O_5 . Activation energies W in (60) for various samples were as in the table, which shows also the high-frequency dielectric constant (κ_∞):

W (eV)	0.295	0.33	0.392	0.418	0.443
κ_∞	4.05	3.72	3.35	3.22	3.15
$W\kappa_\infty$	1.2	1.2	1.3	1.3	1.4

The static dielectric constants κ were very temperature dependent and in the range 15 to 50. Taking κ to be large and therefore negligible the constancy of the product $W\kappa_\infty$ seems to be quite strong evidence that the activation energy is of polaron type and W_D not large. A value of r_p equal to about 2 Å is obtained by comparing with the observed activation energies, which is rather larger than that deduced for NiO. Nester and Kingery compare their activation energies with theory in a slightly different way, using the formula:

$$W = A\kappa_p.$$

They assume $\kappa = \kappa_\infty + 4$ and find the following agreement between the formula and experiment, A being chosen to give agreement for the first glass:

κ_∞	W_{calc}	W_{obs}	V^{5+} (p.c.)	V^{4+} (p.c.)
4.05	0.25	0.295	47	3.37
3.72	0.333	0.333	38	7.3
3.35	0.392	0.392	31	9.8
3.22	0.414	0.418	24	11.8
3.15	0.430	0.443	16.9	15.2

These values, if one sets $A = e^2/r_p$, are compatible with $r_p \sim 1$ Å, as for NiO.

We next turn to the factor $\exp(-2\alpha R)$ in (60). This assumes non-adiabatic hopping and may be absent for glass containing a high concentration of vanadium, for which the adiabatic approximation will be appropriate. To test this behaviour a plot is given in figure 19 (due to Banks) of $\log_{10} \rho$ as a function of distance between the ions, which does not seem to show that $\log \rho$ is proportional to R , the mean distance between the ions; these are for more dilute glasses. Hansen's (1965) results

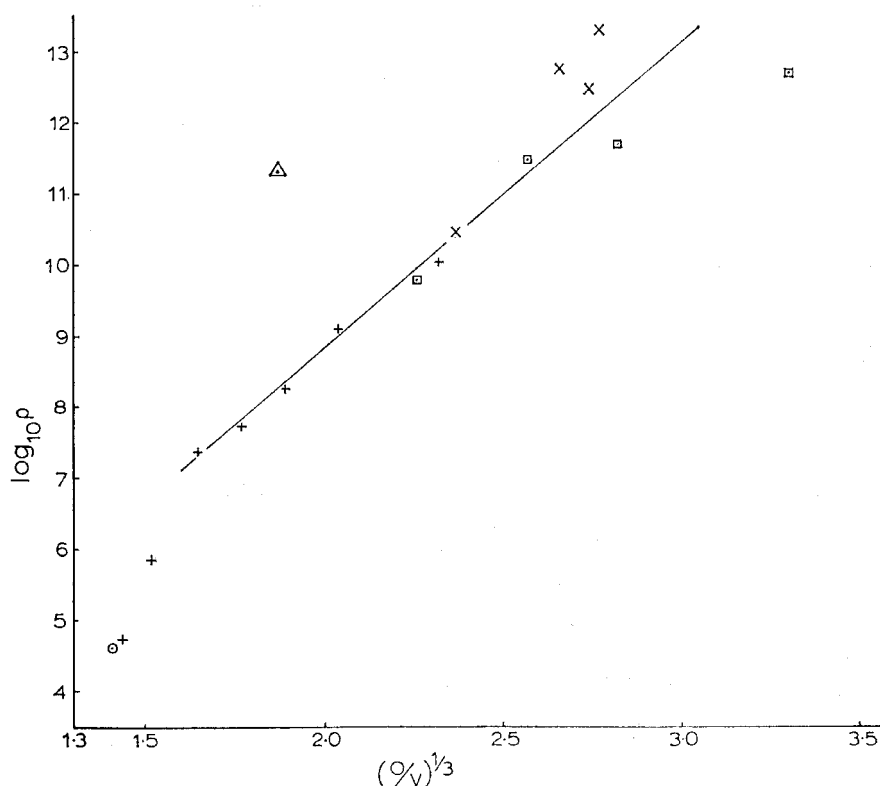


Figure 19. Log (resistivity) for vanadate glasses as function $(O/V)^{1/3}$, where O is the proportion of oxygen and V of vanadium (Banks, unpublished).

on glasses containing iron show a rapid change of $\log \rho$ with iron concentration, but the activation energy changes too.

Next we note the dependence on frequency of σ at low temperatures (figure 20). It is possible that we have here the onset of the phenomenon described by Pollak (section 14) namely jumps over large distances, so that the tunnel factor $\exp(-2\alpha R)$ plays a role. On the other hand τ is here so large that we doubt if the condition $\omega\tau \sim 1$ would be satisfied. The alternative explanation of Killias (1966) (see section 3) may well be valid, that W_H varies with distance R between centres. For d.c. conductivity the electron chooses the easiest paths between ions, but these paths will include some 'hops' for which R is large. These are not important in a.c. conductivity. Thus rather lower activation energies may be involved in a.c. conductivity.

A drop in the observed activation energy W at low temperatures has been observed by various authors (Schmid 1968, Owen (private communication)); the results of Schmid (1968), are illustrated in figure 21. These of Schmid show in particular that W apparently tends to zero at low temperatures. As regards the term W_D , we have no *a priori* means of investigating its magnitude. There may be a contribution from a variable arrangement of ions surrounding each vanadium side, and another from the random field due to fluctuations in charge.

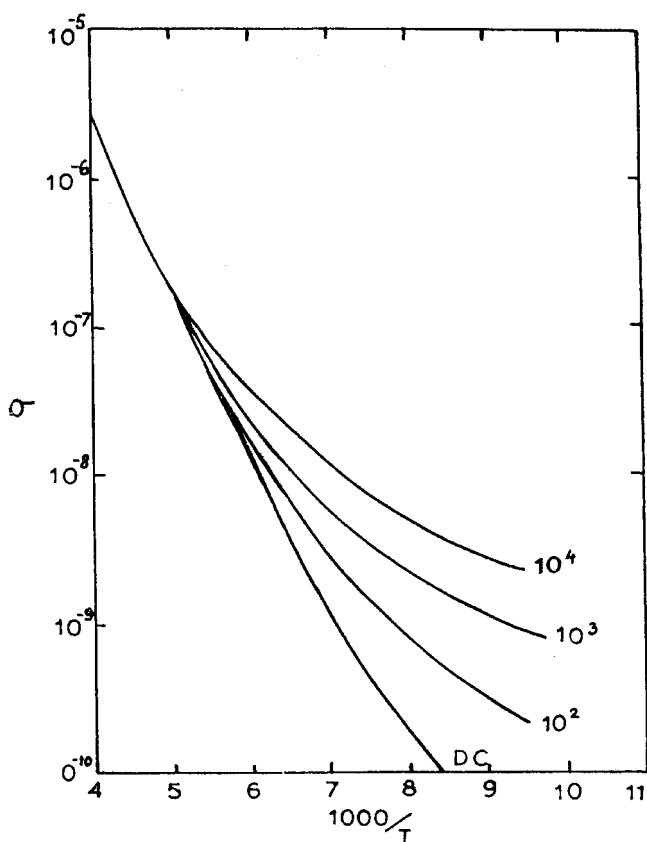


Figure 20. Conductivity (σ in $\Omega^{-1} \text{ cm}^{-1}$) of vanadate glass as a function of temperature at various frequencies (in Hz) (Nester and Kingery 1963). The glass contained 47% of V^{5+} and 3.37% of V^{4+} .

In principle the apparent disappearance of W_D at low temperatures observed by Schmid might be due to either of the effects described in section 13 for impurity conduction.

Drake and Scanlan (1969) have reported measurements on glasses containing 40% of CuO and Cu_2O , and finds a very large activation energy W ($\sim 1 \text{ eV}$). This is too large to be explained by polaron hopping and it is clear that the ligand field environment is different for Cu^+ and Cu^{2+} ions, part of W being the excitation energy of carriers from one kind of site to the other. On the other hand these glasses can be switched to a state of high conductivity with a low activation energy about 0.015 eV . Not only do the environments of the sites become identical, but there seems to be no polaron energy, probably because of the much greater radial extension of the wave function of the copper ions in comparison with vanadium.

Recently Kennedy and Mackenzie (1969) have prepared sputtered amorphous films of VO_2 and V_2O_3 . These behave quite differently from the glasses, even from those rich in vanadium oxides. The conductivity is of metallic order of magnitude (10^2 – $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$), but increases with T like a semiconductor with activation energy in the range 0.02 – 0.05 eV . They do not show the switch to a high-resistivity phase characteristic of the crystals. This behaviour can perhaps be understood on the

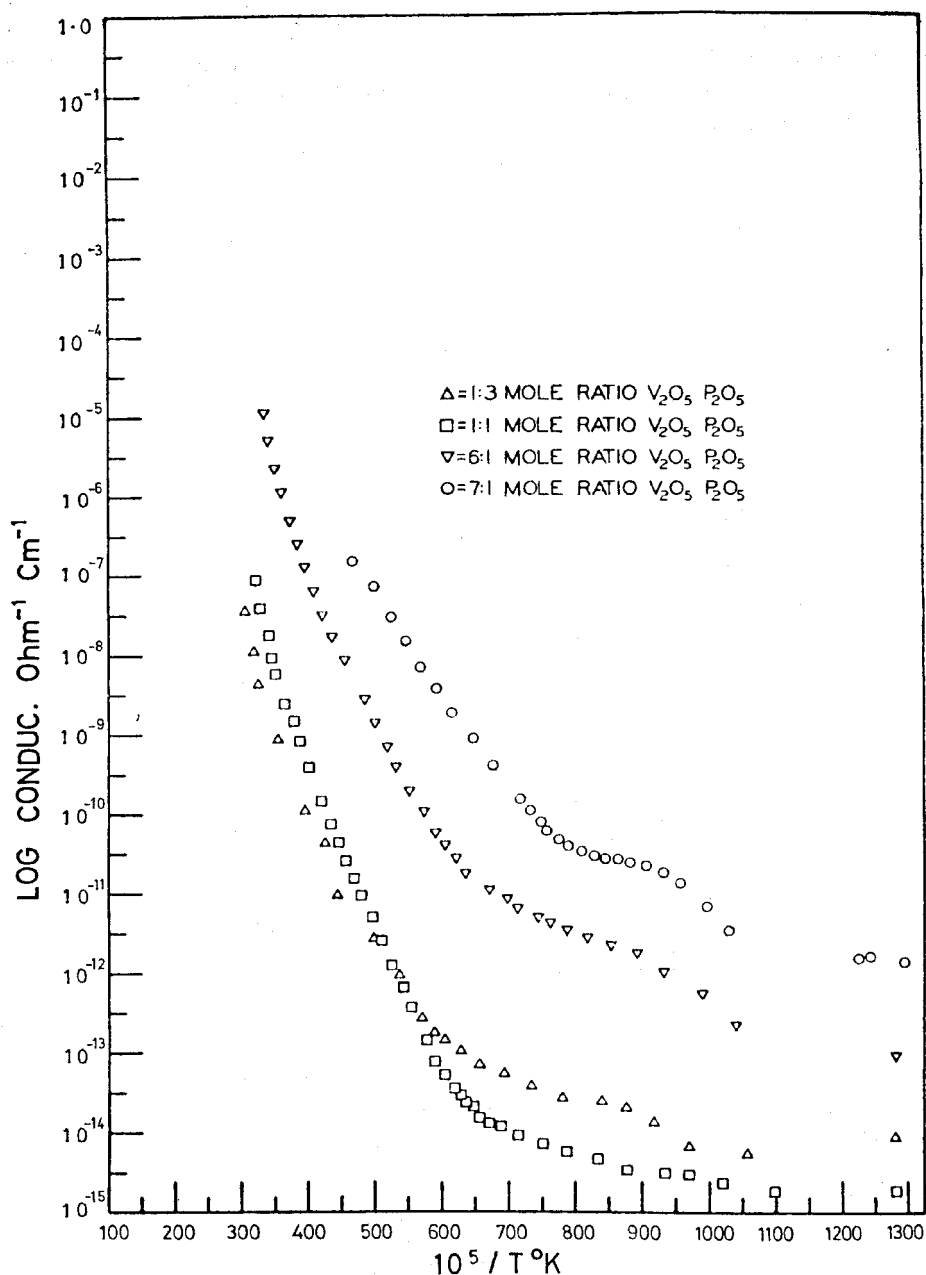


Figure 21. Log (conductivity) as a function of $1/T$ for four typical V_2O_5 - P_2O_5 glasses (Schmid 1968).

basis of a rather speculative model put forward by one of us (Mott 1969b). High-temperature VO_2 and V_2O_3 is thought to be a Mott-Hubbard insulator (like NiO) but with a small band gap, so that it is near the metal-insulator transition, but there is a small overlap between the two bands, so that the material behaves like a semi-metal. This means that the carriers are (in VO_2) V^{3+} ions; whereas in glasses containing a

mixture of V^{5+} and V^{4+} they are V^{4+} ions. The latter may be expected to form a small polaron; the observed hopping energies of at least 0.25 eV give for γ perhaps 10 and thus very large effective masses m_p of order 10^4 – $10^5 m$. In crystalline VO_2 the value is probably nearer to $10m$ and this suggests that $\exp(\gamma) \sim 5$, so that γ is of order 2, so the hopping energy (which has not been observed) could be 0.05 eV at the temperatures above $\frac{1}{2}\Theta$ at which it should set in. In the amorphous films the random fields, though small, should be enough to produce Anderson localization, and the polaron hopping energy of order $W_H \sim 0.05$ should be observed until it begins to fall away below $\frac{1}{4}\Theta$.

16. Some other crystalline materials

16.1. Titanates, tantalates and cobaltites

The titanates and tantalates have high dielectric constants and we expect the electrons to move in comparatively narrow d bands. Tight-binding calculations of the band structure in $SrTiO_3$ (Kahn and Leyendecker 1964) indicate that $J \sim 0.1$ eV, corresponding to a rigid-band mass of $\sim 3m_0$. $SrTiO_3$ and $KTaO_3$ show metallic behaviour at low temperatures at small levels of doping ($2 \times 10^{17} \text{ cm}^{-3}$). Mott (1969b) has proposed elsewhere that in these materials the electron forms a polaron small enough for the attractive force to a donor to be very small ($= e^2/\kappa r^2$) as in (27). At the same time the enhancement of the polaron mass of free carriers is not sufficient to prevent a metallic state forming. This requires $m_p < 10m$ for the free carriers.

Thermopower and conductivity measurements on doped $LaCoO_3$ indicate an activated mobility. Mühlstroh and Reik (1967) have interpreted absorption in the near infra-red in terms of small polarons and find $\gamma \sim 5$, $m_p \sim 50m$, $W_H = 0.17$ eV and $J \sim 0.2$ eV. At liquid helium temperatures they observe much structure in the absorption between 8 and 13 microns, at frequencies corresponding to two-phonon summation bands.

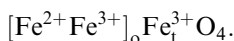
16.2. Ferrites and garnets

The ferrites are derived from Fe_3O_4 by substituting divalent and trivalent metal ions for iron. Structurally they form cubic close-packed oxygen lattices with the metal ions in octahedral and tetrahedral sites. Usually the Fe^{2+} ions show a preference for octahedral sites and electron transport is ascribed to Fe^{2+} - Fe^{3+} exchange between these sites, as in ferric and ferrous oxides. A number of authors have used a hopping model to describe the semiconducting properties but there have been few detailed studies on single crystals.

The ferrites and garnets differ from FeO and Fe_2O_3 in the following ways: (i) the distribution of cations on the octahedral sites is usually random; this should lead to a term $\exp(-W_D/kT)$ in the conductivity; (ii) the distance between octahedral sites can be large, and if direct tunnelling has a low probability the electron may move indirectly via a tetrahedral site; this would introduce an activation energy into the mobility, equal to the difference between the energies of the two sites; (iii) some Fe^{2+} ions may occupy the tetrahedral sites, where they could distort the oxygen environment, giving an additional W_D term on the octahedral sites.

(a) Fe_3O_4 and Li ferrite

Magnetite (Fe_3O_4) has the inverse spinel structure in which the Fe^{2+} ions and half the Fe^{3+} ions are randomly distributed in octahedral sites. The remaining Fe^{3+} ions are in tetrahedral sites as in the following formula, where o stands for octahedral and t for tetrahedral sites:



Below 119 K the cations in octahedral sites are ordered in alternating layers of Fe^{2+} and Fe^{3+} ions and the conductivity shows an activation energy of 0.15 eV. One of us (Mott 1967, 1969b) has described this state as an analogous 'Wigner crystallization', the crystallization being due to the Coulomb repulsion between electrons. Above the ordering temperature the conductivity shows little variation with temperature (figure 22) and the drift mobility is $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, assuming 0.5 free electrons per iron atom. Recent data by van Daal and Bosman (1967) show the same value of the mobility for electrons in Fe_2O_3 ; it is almost independent of temperature up to $\sim 1000 \text{ K}$. The iron atoms in this oxide occupy slightly distorted octahedral sites but the shortest distance between them is almost the same (3 \AA) as in Fe_3O_4 . Thus the mobility data suggest a narrow band conduction mechanism, with high effective mass due to polaron formation, and the possibility of a small hopping energy at high temperatures as in NiO.

In contrast the electron mobility in many ferrites shows an activation energy of 0.1–0.3 eV. Elwell *et al.* (1969) have investigated lithium ferrite

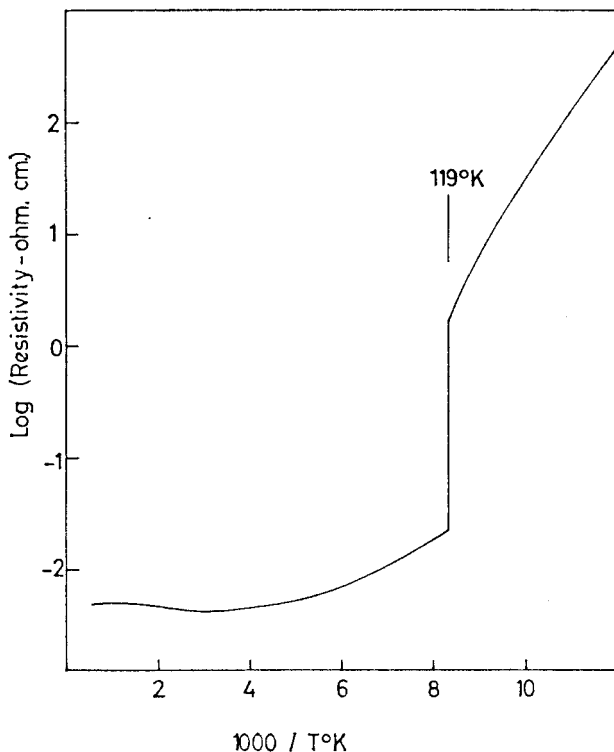


Figure 22. Log (resistivity) of Fe_3O_4 (Tannhauser 1962).

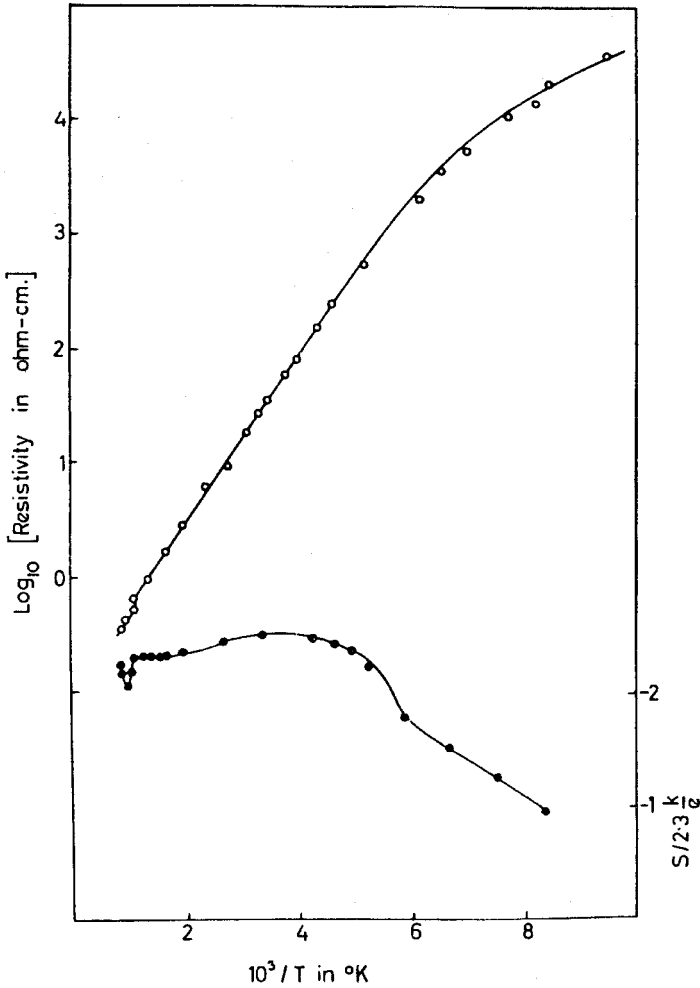
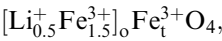


Figure 23. Electrical properties of ordered Li ferrite ($\text{Li}_{0.5}\text{Fe}_{1.5}\text{O}_4$) after Elwell *et al.* (1969).
Resistivity ○; thermopower ●.



a material in which Li^+ and Fe^{3+} ions on the octahedral sites are *ordered*. Thermopower measurements on single crystals (figure 23) indicate a constant carrier concentration between 200 and 850 K, which is due to the residual Fe^{2+} ions. The conductivity and hence the mobility show an activation energy W of 0.14 eV. It seems unlikely that this is a polaron hopping energy (W_H) for the following reasons. The jump distance between iron atoms in octahedral sites is essentially the same as in Fe_3O_4 , so that W_H according to formula (23) should not differ from $\frac{1}{2}W_p$ for one rather than the other. Also, the activation energy in Li ferrite does not fall off with temperature as expected for polaron hopping. The observed decrease in W below 200 K (figure 24) is most probably due to the onset of impurity conduction, since the thermopower also changes in this region.

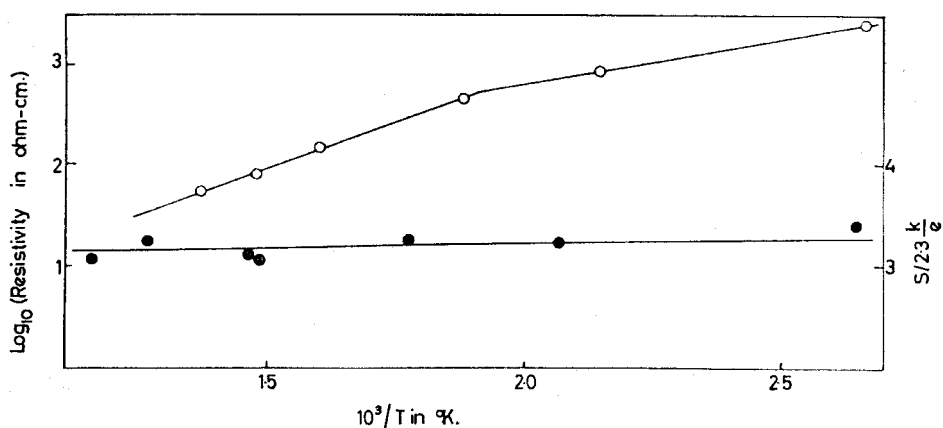


Figure 24. Electrical properties of YIG containing 4 at.% Hf^{4+} (Elwell and Dixon 1968). Resistivity \circ ; thermopower \bullet .

An alternative explanation is that the activation energy W is a disorder term of type W_D arising from the Fe^{2+} ions. The concentration of these ions in the Li ferrite sample is about 1 at.%, and according to the Miller–Abrahams formula (section 13) this would give a disorder energy of ~ 0.05 eV. The distribution of the Fe^{2+} ions is unknown, but if some of them enter the smaller tetrahedral sites, the oxygen environment is distorted (Banerjee *et al.* 1967) and this could give an additional random potential energy in the octahedral sites.

The distribution of Fe^{2+} ions in titanium spinels of the form $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($0 < x \leq 1$) has been studied by Banerjee *et al.* (1967) using Mossbauer spectra and other methods. In this material random pairs of Fe^{3+} ions are replaced by $\text{Ti}^{4+}\text{--Fe}^{2+}$ combinations. For $x < 0.2$, the Fe^{2+} ions enter the octahedral sites only, but for $0.2 < x < 0.8$ both tetrahedral and octahedral sites are occupied and the observed values of W are in the range 0.1–0.15 eV. For $x > 0.8$, iron atoms in mixed valence states are present on tetrahedral sites only and W is larger (0.2 eV). Comparable activation energies (0.2–0.3 eV) for tetrahedral site hopping were found by Verwey *et al.* (1947) in $\text{Fe}_3\text{O}_4\text{--MgCr}_2\text{O}_4$.

(b) Co and Ni ferrites

Jonker (1959) has made a detailed study of Co ferrite (CoFe_2O_4). This material has the inverse spinel structure in which the Co^{2+} ions and half the Fe^{3+} ions are randomly situated in the octahedral sites thus:



Stoichiometric material of this composition has a high resistivity, but samples can be prepared with a considerable excess of iron or cobalt, and these show n and p -type conduction. In Fe rich material some of the Co^{2+} ions are replaced by Fe^{2+} ions and this gives rise to electron transport through the *disordered* Fe^{3+} ions in octahedral sites. Conversely in Co rich material some of the Fe_o^{3+} is replaced by Co^{3+} giving hole conduction through Co sites. Thus n and p -type conduction are observed in the one system, which can be regarded as a mixed crystal of Fe_3O_4 and Co_3O_4 . Jonker studied samples in which up to 10% of the valence states were altered. For all these, except those close to the composition of (61), he found that (i) the activation energy

E for conduction was almost independent of carrier concentration, and (ii) the thermopower was independent of temperature between 300 and 450 K.

Assuming that the electron and hole concentrations were equal to the concentrations of Fe^{2+} and Co^{3+} , so that E is to be equated to a hopping energy W , he found

$$\mu_D \sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \quad W = 0.2 \text{ eV} \quad \alpha' = 1 \quad \text{for electrons}$$

and

$$\mu_D \sim 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \quad W = 0.5 \text{ eV} \quad \alpha' = 6 \quad \text{for holes.}$$

The temperature-independent values of α' were calculated from the Seebeck data using (31) with P equal to half the density of octahedral sites. These data refer to sintered specimens and the effect of grain-boundary resistance is unknown. Recently, Elwell *et al.* (private communication) have repeated some measurements on single-crystal ferrites and found very similar results.

The activation energy and mobility for electron and hole motion in the Co ferrite is in marked contrast with the mobility data for Fe_3O_4 and n -type Fe_2O_3 discussed earlier, and in p -type CoO (van Daal and Bosman 1967). In the simple oxides, μ_D in each case is of order $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and is almost independent of temperature up to ~ 1000 K. Qualitatively, the difference in the ferrite may be due to the following.

- (i) A term W_D in W due to the random potential fluctuations of the Co^{2+} and Fe^{3+} ions in the octahedral sites.
- (ii) An increase in the polaron hopping energy W_H due to the greater jump distance and reduction in the number of overlap integrals. The separation of the octahedral sites is similar to Fe_3O_4 , but in the ferrite only half of them are available for each type of carrier.

It is impossible at present to estimate the disorder hopping energy W_D with any certainty, but if we use the Miller-Abrahams formula which makes this quantity equal to about $0.4e^2\kappa^{-1}R^{-1}$ one finds a value of about 0.1 eV. The observed value of W for electrons in Co ferrite is only slightly larger than in Li ferrite. This suggests that if conduction is entirely through octahedral sites the disordered Co^{2+} ions do not contribute much to W_D . In the absence of data on the temperature dependence of W we cannot comment on the possibility of a polaron hopping energy.

An alternative hypothesis is that electron tunnelling between octahedral sites is more difficult than in Li ferrite because the jump distance is greater. Thus the electron may move between these sites by jumping indirectly over a tetrahedral site as envisaged in figure 10. The discussion at the end of section 8 shows that such a model could explain the temperature-independent thermopower.

For hole conduction in Co ferrite, W and α' are much larger than for electrons. Jonker (1959) points out that Co^{2+} is in the normal high spin state (following Hund) but Co^{3+} is an exception and usually forms a low spin state (diamagnetic) state in spinels. Thus a hopping transition may be a multielectron process involving an excited state and an additional activation energy (E'). For this model, as for that which postulates jumping over tetrahedral sites, no extra term of the form $\alpha' = E'/kT$ need appear in the thermopower.

In a comparative study on single crystals of Ni ferrite, Elwell *et al.* (1966) find

$$W = 0.28 \text{ eV}, \quad \mu_D \sim 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \quad \text{and} \quad \alpha' = 1 \quad \text{for holes.}$$

Here both the Ni^{2+} and Ni^{3+} ions are in the high spin state and charge transfer is presumably a single electron process as in NiO.

(c) Garnets

Some other magnetic oxides show a thermopower which is remarkably independent of temperature, as in glasses containing transition metal ions (compare section 15). Figure 24 shows data by Elwell and Dixon (1968) on single-crystal yttrium iron garnet with Fe^{2+} ions. Pure YIG, or $\text{Y}_3\text{Fe}_5\text{O}_{12}$, is cubic and contains Fe^{3+} ions in octahedral and tetrahedral sites in the ratio 2:3. The resistivity shows an exponential decrease with temperature from which they infer an activated mobility with $W = 0.19$ eV below the Curie temperature, which is 560 K, and 0.34 eV above. However recent measurements by Turner (private communication) show that the activation energy is constant from 500 K down to ~ 80 K suggesting that W is not simply a polaron hopping energy, since $\Theta \sim 700$ K. Since the thermopower indicates a constant carrier concentration, we again infer that W is due to jumping between non-equivalent sites or excitation *over* a higher state as in figure 10.

In YIG the iron atoms on octahedral sites form a body-centred cubic lattice and the nearest neighbour distance is relatively large (5.7 \AA). Thus an electron hopping in the octahedral sites may move most easily by jumping indirectly through a tetrahedral site. Below the Curie temperature, an additional energy may be required to produce a spin reversal in this process. But the observed change in W above T_C (figure 24) is too large and has the wrong sign to be explained by this effect.

At the level of doping used here (~ 4 at.%) it seems likely that a term of type W_D would also be present. Also, there is strong evidence in Si doped YIG (Hunt 1966) that the Fe^{2+} ions in octahedral sites occupy four types of magnetic site, which are crystallographically equivalent but differ slightly in energy because of the ferrimagnetic coupling.

Pure YIG is highly transparent in the infra-red between 1.1 and 4.5 microns, but *n*-type samples doped with Si^{4+} ions show an additional temperature-dependent absorption, which increases with frequency (Wood and Remeika 1966, LeCraw *et al.* 1965). This is attributed to $\text{Fe}^{2+} - \text{Fe}^{3+}$ charge transfer near the donor impurity. Similar characteristics are observed in *p*-type material and qualitatively the absorption is like that observed in Li doped NiO in the near infra-red (Austin *et al.* 1968).

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