

Dependence of the Transport Properties of Transition Metal Alloys and Compounds on the Electron Number

Cite as: Journal of Applied Physics **39**, 2208 (1968); <https://doi.org/10.1063/1.1656530>
Published Online: 19 November 2003

J. F. Goff



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

The Irreversible Critical Range in the TiNi Transition

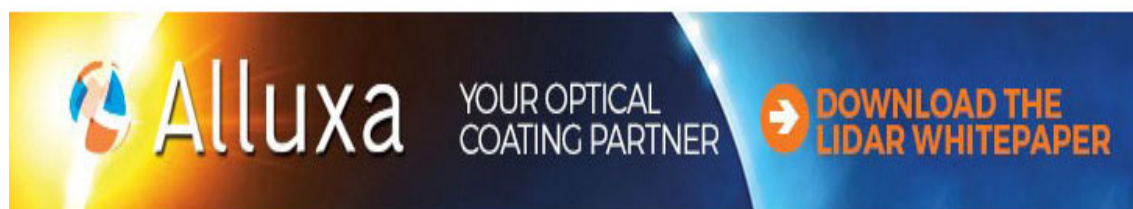
Journal of Applied Physics **39**, 2166 (1968); <https://doi.org/10.1063/1.1656521>

Low-Temperature Transport Properties of Commercial Metals and Alloys. II. Aluminums

Journal of Applied Physics **31**, 496 (1960); <https://doi.org/10.1063/1.1735617>

Ferromagnetism and Superconductivity in $\text{TiFe}_x\text{Co}_{1-x}$

Journal of Applied Physics **38**, 1337 (1967); <https://doi.org/10.1063/1.1709611>



spectrum and the electronic specific heat versus electron per atom ratio (e/a) plot of Beck and co-workers for the bcc first transition series metals and their alloys.¹⁶

If we normalize the pure Ni and Ni in TiNi spectra to the same relative exposure, and assume that these emission spectra are simply proportional to the density of states (with no severe effects from varying transition probabilities), then the area under the pure Ni- M spectrum in Fig. 4 (upper curve), bounded by the bottom of the band, the Fermi energy, and the xy baseline, corresponds to $e/a = 10$. Then, integrating the Ni- M spectrum of TiNi (Fig. 4, lower curve) from the bottom of the band to the low-energy peak, the trough, and the high-energy peak yields areas corresponding to e/a values of 3.9, 6.0, and 7.2, respectively, in surprising agreement with the corresponding values of 4.5, 6.0, and 6.3 taken from the Beck plot. Granting the crudeness involved in neglecting transition probability variation, this result strongly supports the rigid band picture for this e/a range. However, the observed Fe- M spec-

trum, with e/a equal to 8, is single peaked (as currently determined in the ferromagnetic state,¹⁷ with magnetic band splitting present, unknown, and possibly large).

The work on TiNi has not been carried out as yet to the same degree of detail as our work on the pure nickel, that is, with consideration of all of the factors mentioned in the introduction.

ACKNOWLEDGMENTS

The authors wish to thank D. Fickle for the preparation of the NiAl specimen and the 4 at.% Al and 8 at.% Al nickel terminal solid solution specimens. The authors are also grateful for many stimulating discussions with Dr. R. E. Watson and correspondence with Professor N. F. Mott on the interpretation of the spectra, and correspondence with Professor Azaroff concerning an anomaly in the behavior of the Ni-4 at.% Al solid solution. We thank E. C. Snow, J. E. Holliday, and Professor R. J. Liefeld for furnishing results prior to publication.

¹⁶ C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

¹⁷ D. H. Tomboulion and D. E. Bedo, Phys. Rev. **121**, 146 (1960).

Dependence of the Transport Properties of Transition Metal Alloys and Compounds on the Electron Number

J. F. GOFF

U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

A comparison of the transport properties of the elements, compounds, and alloys of the first long period shows many similarities if the electron number is taken as a parameter, although the substances may differ magnetically. This result suggests that their transport band structures are similar. A model for the dependence on electron number of this structure is deduced from the transport properties of some of the nonmagnetic compounds. It is suggested that the model applies to the magnetic substances when they are in their magnetically ordered state.

INTRODUCTION

The analysis of any transport coefficient can be broken into three parts: (1) the states through which energy and charge flow, (2) the scattering which impedes this flow, and (3) the integral which sums these processes over the states. Consequently, one would expect any transport property of a transition metal to be quite complicated because the electronic states are multiband, the scattering processes are expected to be exotic, and the integrals must take into account the possibility of a multiplicity of degeneracy temperatures corresponding to the different bands. The purpose of this paper is twofold. On the one hand it presents an attempt to understand the transport properties of the transition metal compounds TiFe, TiCo, TiNi, and some of their alloys¹⁻³ (hereafter designated by TiX)

by making the admittedly restrictive assumption that their peculiarities are the consequence of their complicated band structure rather than complicated scattering effects. On the other hand it is shown that the transport properties of this system are similar to those of the Cr-X system if they are compared in terms of their electron numbers N (N is the average number of electrons per atom outside of the closed shells). Since the TiX system is in general only paramagnetic⁴ (except for a range of compositions about $N = 6.25$)⁵ while Cr-X is magnetically quite complicated, these purposes reinforce each other; and deductions about the transport band structure of the simpler TiX system should be applicable to the more complicated magnetic ones.

It should be noted that Schröder *et al.*⁶ have concluded

⁴ M. V. Nevitt, J. Appl. Phys. **31**, 155 (1960). See also Erratum, J. Appl. Phys. **31**, 924 (1960).

⁵ B. F. DeSavage and J. F. Goff, J. Appl. Phys. **38**, 1337 (1967).

⁶ K. Schröder, M. J. Yessik, and N. P. Baum, J. Appl. Phys. **37**, 1019 (1966).

¹ J. F. Goff, Bull. Am. Phys. Soc. **10**, 1105 (1965).

² J. F. Goff, Bull. Am. Phys. Soc. **10**, 451 (1965).

³ J. F. Goff, J. Appl. Phys. **35**, 2919 (1964).

TABLE I. Sample parameters.

Sample	Electron No.	Heat treatment	Hall coefficient ¹⁴ ($\times 10^{-4}$ cm ³ /C)		
			4.2°K	77°K	295°K
TiFe	6.00	as cast	+34.8	+29.4	+21.2
TiFe _{0.8} Co _{0.4}	6.20	800°C—2 h in vacuum
TiFe _{0.5} Co _{0.5}	6.25	as cast	-7.1	-5.8	-2.0
TiFe _{0.4} Co _{0.6}	6.30	800°C—2 h in vacuum
TiFe _{0.2} Co _{0.8}	6.40	800°C—2 h in vacuum
TiCo	6.50	as cast	-0.2	-0.3	-0.6
TiCo _{0.5} Ni _{0.5}	6.75	as cast	-2.6	-1.5	-0.4
TiNi	7.00	as cast	+2.7	+2.6	+1.7

from an analysis of the thermoelectric power Q of some Cr-Fe alloys that it was not possible to explain their results by scattering but that changes in band structure must be invoked. In the present case the reason for the presumption that the transport properties of these substances are largely determined by their band structures is again empirical. Beck and co-workers⁷ have measured the electronic heat capacities of these systems and found that they exhibit the same trends in spite of their different magnetic natures. The implication is that they have a dense band which is similar for the same N (this statement is less restrictive than the assumption of a rigid band). Consequently one might well anticipate similarities in the transport properties of the two systems.

There is one cautionary remark. The multiband heat capacity is weighted toward bands of great density and therefore low group velocity. On the other hand, the transport properties are weighted toward bands of great mobility. One would not expect to observe the presence of a dense band in the transport properties unless it served to increase scattering. The fact that no effect of this band has been observed in Q^6 implies that it does not contribute much to scattering. Therefore, the transport measurements reported here augment rather than confirm the work of Beck *et al.*

After a brief description of the experimental factors, the similarities between TiNi ($N=7.00$) and Mn (7.00) and TiFe (6.00) and Cr (6.00) will be outlined to support the contention that these systems have similar transport properties and probably transport bands. Then a similar comparison will be made between TiX and the alloys Cr-X. Finally the dependence on N of the transport band structure of TiX will be deduced.

EXPERIMENTAL

The experimental technique is essentially the same as has been described.³ The principal change is that the temperature gradient in the 4°K and 77°K range is now measured by two Allen & Bradley 100 Ω , 1/10 W carbon resistors. The samples were prepared in the

same way as before except that the brittle samples ($N=6.00$ to 6.50) were ground to shape. The principal sample parameters are given in Table I.

COMPARISONS WITH THE ELEMENTS

It has been pointed out that many of the properties of TiNi (7.00) are similar to those of Mn (7.00).³ Among the transport properties are the sign of the Hall coefficient R (positive), a T^2 dependence of the ideal electrical resistivity ρ_i below 100°K, the temperature dependence of the thermal conductivity, and a large value of the lattice thermal conductivity at low temperatures. In addition there are similarities in the nontransport properties such as the average coefficient of thermal expansion, the melting point, and the formation of a complex structure at low temperatures. More recently Wang *et al.*⁸ have analyzed this structure to have 54 atoms/cell as compared with 58 atoms/cell for α -Mn and also to have comparable lattice constants. The major distinction is that whereas α -Mn is antiferromagnetic below 100°K, TiNi has a temperature-independent Pauli spin paramagnetism.⁵ The effect of antiferromagnetism in α -Mn has been interpreted as changing the symmetry of the lattice and thus causing magnetic Brillouin-zone planes to intersect the Fermi surface.^{9,10} The interesting point is that the transport properties of TiNi resemble those of α -Mn below its Néel temperature, where both chemical and magnetic symmetries are important. It will be seen that TiFe (6.00) and Cr (6.00) resemble each other in this regard.¹¹

Both TiFe and Cr are brittle solids. Their Debye temperatures are $\theta(\text{TiFe})=495^\circ\text{K}$ ¹² and $\theta(\text{Cr})=405^\circ\text{K}$.¹³ Allgaier has pointed out that R is positive for both and is unusually temperature dependent for

⁸ F. E. Wang, W. J. Buehler, and S. J. Pickart, *J. Appl. Phys.* **36**, 3232 (1965).

⁹ D. Griffiths and B. R. Coles, *Proc. Phys. Soc. (London)* **82**, 127 (1963).

¹⁰ R. V. Bellau and B. R. Coles, *Proc. Phys. Soc. (London)* **82**, 121 (1963).

¹¹ J. F. Goff, *Bull. Am. Phys. Soc.* **12**, 348 (1967).

¹² E. H. Starke, C. H. Cheng, and P. A. Beck, *Phys. Rev.* **126**, 1746 (1962).

¹³ I. Estermann, S. A. Friedberg, and J. E. Goldman, *Phys. Rev.* **87**, 582 (1952).

⁷ K. P. Gupta, C. H. Cheng, and P. A. Beck, *Metallic Solid Solutions* (W. A. Benjamin, Inc., New York, 1963), pp. XXV-1 to 12.

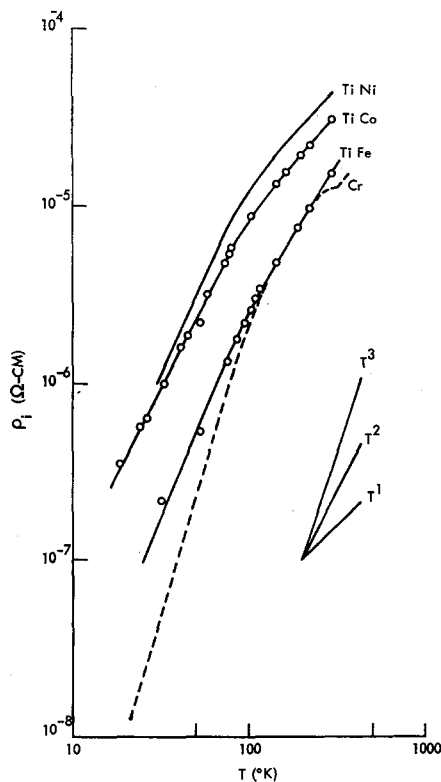


FIG. 1. The ideal electrical resistivity ρ_i vs temperature for representative members of the compound alloy series TiX. The dashed line is taken from the data of Arajs *et al.*

metals.¹⁴ The most striking similarity in their transport properties is the apparent identity of ρ_i in the range between about 150°K and 250°K shown in Fig. 1, where the data for TiFe have been compared with the very accurate data of Arajs *et al.*¹⁵ This congruence is even more striking because the temperature dependence is an anomalous $T^{1.5}$ and therefore can not be a simple Grüneisen-Bloch identity:¹⁶ $\rho_i = (C/4)(T/M\theta^2)$, where M is the average atomic mass and C is a constant. At lower temperatures $\rho_i(\text{TiFe}) \propto T^2$ approximately and $\rho_i(\text{Cr}) \propto T^{3.2}$. At the higher temperatures $\rho(\text{Cr})$ falls below $\rho(\text{TiFe})$ as the Néel temperature is approached. Thus, it appears again that the identity of the two substances seems to require the presence of some sort of magnetic symmetry.

COMPARISON WITH ALLOYS

The above comparison of the compounds TiX with elements apparently confirms the suggestion of Griffiths and Coles⁹ that there should be an equivalency between the effect of chemical and magnetic symmetries on the transport properties. Therefore, it should be possible to compare the higher temperature TiX data with Cr-X

data taken at temperatures well below the various kinds of magnetic transitions that take place below room temperature in that system for $N < 6.5$.

Figure 2 shows $\rho_i(\text{TiX})$ vs N for several temperatures. In Fig. 3 the $\rho_{4,2}(\text{Cr-X})$ data of several authors¹⁷⁻²⁰ have been replotted against N to emphasize the striking similarity of the $\rho(N)$ dependence of the two systems. Both show an initial sharp increase which stops at approximately 6.2. Both decrease until ρ becomes independent of N at $N=6.3$ for a small range and then both decrease further as N increases. The large values of $\rho_i(\text{TiNi})$ are consistent with its similarity to Mn, which is somewhat of a maverick in the first long period.

One should note that $\rho_{4,2}(\text{Cr-Fe})$ does not exhibit a Nordheim plot.²¹ It is possibly for this reason that the data of the different experimenters show such agreement.

THE TiX SYSTEM

There are three striking features of the TiX system. The first, the extremely rapid change in $\rho_i(N)$ between 6.00 and 6.2, has been discussed above. The second is that R^{14} and Q (see Fig. 4), which are positive at the ends of the composition range, become negative over a range of N between approximately 6.2 to 6.9. Finally, the temperature dependence of ρ_i in the inelastic scattering range is very nearly T^2 for all N as is indicated in Fig. 1. It is the presumption of this paper that these features indicate characteristics of multiband transport effects.

It is well known that the sign of R indicates the

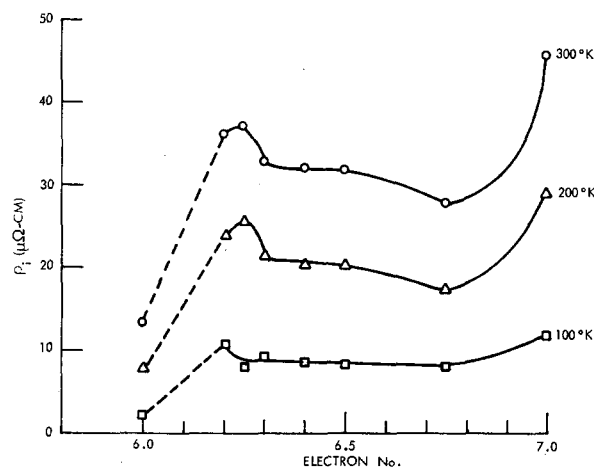


FIG. 2. The ideal electrical resistivity ρ_i vs electron number for the compound alloy series TiX.

¹⁷ N. S. Rajan, R. M. Waterstrat, and P. A. Beck, *J. Appl. Phys.* **31**, 731 (1960).

¹⁸ S. Arajs and G. R. Dunmyre, *J. Appl. Phys.* **37**, 1017 (1966).

¹⁹ J. F. Goff and M. W. Cole, *Bull. Am. Phys. Soc.* **10**, 126 (1965).

²⁰ S. Arajs, G. R. Dunmyre, and S. J. Dechter, *Phys. Rev.* **154**, 448 (1967).

²¹ J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).

¹⁴ R. S. Allgaier, *J. Phys. Chem. Solids* **28**, 1293 (1967).

¹⁵ S. Arajs, R. V. Colvin, and M. J. Marcinkowski, *J. Less-Common Metals* **4**, 46 (1962).

¹⁶ G. I. Meaden, *Electrical Resistance of Metals* (Plenum Press, Inc., New York, 1965).

predominant carrier at the Fermi surface. Thus, the surface is predominantly positive at $N=6.00$ and 7.00 but becomes negative in between. Therefore the change in sign of Q is due to the change in the character of the Fermi surface rather than to a change in scattering mechanisms. However, it is felt that there is still a large positive component of the Fermi surface in this central region for the following reason. The T^2 dependence of ρ , seen throughout the range is usually taken as indicating that there is electron-electron scattering,²² a mechanism that is expected to be quite sensitive to changes in the Fermi surface. Consequently one expects that there must be a positive surface that is relatively unchanged over the whole range which is primarily responsible for ρ . In the central region the negative surface must have enough mobility to override the positive one for the transport coefficients most influenced by the mobility (see the Appendix).

Allgaier¹⁴ has pointed out that R and ρ indicate that there must be a positive band of very large mobility at 6.00 . Therefore, it seems that a transport band model must consist of two positive bands at 6.00 , one of high mobility and the other of only moderate mobility but rather large hole concentration. Between 6.00 and 6.2 , the high mobility band is either filled or suffers a decrease in mobility. Its place is taken by a high mobility negative band.

At the extreme end of the concentration range, at TiNi, a very strange thing happens. Not only is there no indication of multiband effects, that is $Q(T)$ is normal, the magnetic susceptibility is temperature independent,⁵ and $R(T)$ is almost constant¹⁴; but also calculation of the effective mass, Fermi energy, and relative valence of solute Cu on the assumption of a single transport band gives reasonable values.³

CONCLUSIONS

The transport properties of the alloys of the compounds TiFe, TiCo, and TiNi (designated generally as TiX) resemble the properties of the Cr-Fe alloys (and

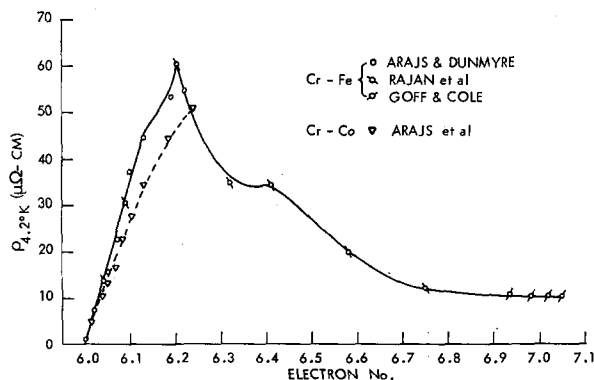


Fig. 3. The electrical resistivity at 4.2°K of Cr-X alloys vs electron number.

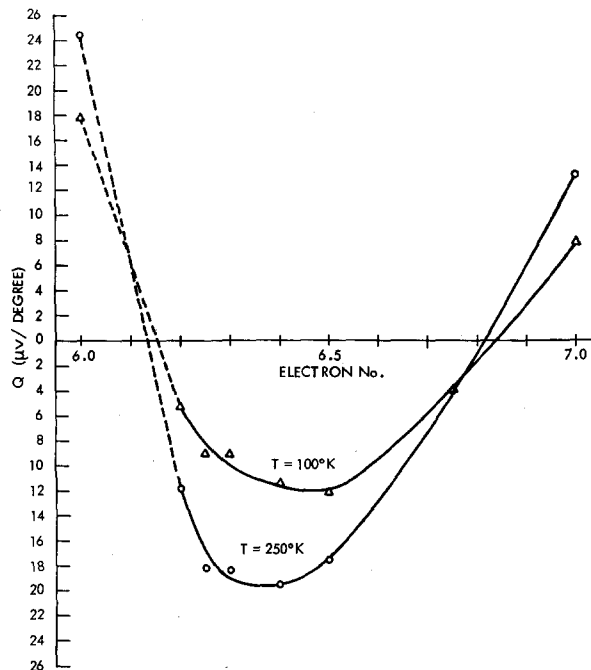


Fig. 4. The absolute thermoelectric power Q vs electron number for the compound alloy series TiX.

to extent of the data, the Cr-Co alloys) when they are in their magnetically ordered state and when they are compared in terms of their electron number N . Since the TiX system is mostly only paramagnetic, its transport properties are much easier to interpret. Any interpretation should be applicable to the more complicated Cr-X systems.

It has been assumed that changes in the transport properties of the TiX system with N indicate changes in its multiband structure rather than changes in scattering processes partly because of the work of Schröder *et al.*,⁶ partly because of the work of Beck *et al.*,⁷ and partly because the similarity of two systems with greatly different magnetic natures implies this interpretation.

The model deduced for TiX consists of a positive band of moderate mobility but of rather large carrier concentration that is relatively unchanged throughout the range of N from 6.00 to 7.00 and a highly mobile positive band of somewhat smaller carrier concentration that exists only in the range from 6.00 to about 6.2 . Beyond 6.2 , this second positive band is supplanted by a highly mobile negative band with a small carrier concentration. The behavior of this negative band is different for the two systems near 7.00 and probably disappears for TiNi.

The transport properties of a multiband system (being weighted differently by the mobilities of these bands) most probably represent different portions of the Fermi surface. The Hall coefficient and the thermoelectric power are weighted much more strongly toward bands of great mobility than is the resistivity. There-

²² N. F. Mott, *Advan. Phys.* **13**, 325 (1964).

fore, the effect of the negative band in TiX is presumed to override the effect of the moderate positive one for values of N between 6.2 and 6.9 for R and Q . In this way it is possible for ρ to be determined by a band which yields the somewhat unusual T^2 dependence over the whole range of N studied but still have a change of sign for the other properties.

This interpretation means that one must look for more subtle changes in the transport properties of the Cr-X system than a gross change in sign of R or Q with composition, because it may happen that the mobility differences among the bands in these other systems are just not enough to give a sign change. While strictly speaking one should compare only the very low temperature Cr-X data with those of TiX, it is intriguing that Schröder and McCain's^{23,24} measurements of R for Cr-Fe and Cr-Ni at 77°K found a positive R that first increased for N up to about 6.1 and then decreased. This is behavior consistent with the model proposed, but of course further work is necessary to be conclusive.

The $\rho_{4.2}$ (Cr-Co) data of Arais *et al.*²⁰ shown in Fig. 3 show the same trend as the Cr-Fe data, although one would not expect an exact comparison because of the different temperature dependences of these data even at these temperatures. In the context of the model proposed, an important effect of alloying Cr with elements to its right in the periodic table is the filling of a highly mobile positive portion of the Fermi surface.

ACKNOWLEDGMENT

I would like to thank W. Buehler for supplying my samples.

APPENDIX

It is to be shown that the multiband transport coefficients are weighted toward bands of high mobility and that it is possible for the signed coefficients to take the sign of a band other than the principal conduction band.

The multiband formulas for the transport coefficients²⁵ simply expressed for the two bands are

Electrical conductivity

$$\sigma = \sigma_p + \sigma_n \quad (1a)$$

Hall coefficient

$$R = (\sigma_p^2 R_p + \sigma_n^2 R_n) / \sigma^2 \quad (2a)$$

Thermoelectric power

$$Q = (\sigma_p Q_p + \sigma_n Q_n) / \sigma, \quad (3a)$$

where p stands for positive and n stands for negative. These formulas can be written in the kinetic formalism where $\sigma_j = n_j e \mu_j$ and $|R_j| = |1/n_j e|$. n_j is the carrier concentration of band j and μ_j is its mobility. In order to put Q into a similar expression it is necessary to assume that the multiband structure can be approximated by a multiplicity of standard bands to obtain a relation between the n_j and the Fermi energy of band j . Assume that Q_j can be expressed by the Mott formula.²⁶ Then $Q_j = \frac{2}{3}(\pi/3)^{2/3}(k/\hbar)^2 T m_j x_j(T) n_j^{1/3} \mu_j$, where k is Boltzmann's constant, \hbar is Planck's constant, m_j is the effective mass of band j , and $x_j(T)$ is the exponent of the energy dependence of the conductivity of the carriers in band j . If there are no exotic scattering mechanisms, then $x_j(T)$ varies from 1 to 3 as a function of T . Formulas (1a)–(3a) are then:

$$\sigma = e(p\mu_p + n\mu_n) \quad (1b)$$

$$R = (e/\sigma^2)(p\mu_p^2 + n\mu_n^2) \quad (2b)$$

$$Q = \frac{2}{3}(\pi/3)^{2/3}(k/\hbar)^2(T/\sigma)[m_p x_p(T)p^{1/3}\mu_p + m_n x_n(T)n^{1/3}\mu_n]. \quad (3b)$$

The denominators have been left in symbolic form because they do not affect the stated problem. It is immediately seen that in terms of the mobility relative to the carrier concentration these coefficients are weighted toward bands of large mobilities in the following sequence: $\sigma \rightarrow R \rightarrow Q$. It has been assumed that variations in m_j and x_j are insignificant.

The conditions such that

$$\sigma_p > \sigma_n \quad (4)$$

$$|\sigma_p^2 R_p| < |\sigma_n^2 R_n| \quad (5)$$

can be found by dividing Eq. (2a) by Eq. (1a) twice.

$$|\sigma_p R_p| < |\sigma_n R_n| \quad (6a)$$

$$|R_p| < |R_n|. \quad (7a)$$

In terms of the kinetic formalism these conditions are

$$|\mu_p| < |\mu_n| \quad (6b)$$

$$p > n \quad (7b)$$

These conditions are physically consistent. The same conditions obtain for Q if the variations of m_j and $x_j(T)$ are neglected.

²³ K. Schröder and C. E. McCain, Phys. Rev. **135**, A149 (1964).
²⁴ C. E. McCain and K. Schröder, J. Phys. Chem. Solids **26**, 1139 (1965).

²⁵ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1954).

²⁶ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 311, Eq. 118.