The effect of high hydrostatic pressure on the silver azide electrical conductivity

G.M. Diamant, A.E. Saprykin and Yu.Yu. Sidorin

Kemerovo State University, Krasnaya 6, Kemerovo 650043 (U S S R)

Abstract

A study on the influence of high hydrostatic pressure on the electrical conductivity of silver azide single crystals at the ranges of temperature 263–373 K and pressure $10^5 - 4 \times 10^8$ Pa is described Motional and formation activation volumes for intrinsic defects and activation energies of the processes have been determined The theoretical estimates of the activation volumes in terms of Zener strain-energy model have been made, and were found to be in reasonable agreement with the values obtained from the experiment The results support the view that silver azide has Frenkel disorder, transport in single cyrstals is generally ionic at low voltage, extrinsic under normal conditions, and occurs by the motion of interstitial ions Conduction becomes intrinsic at temperatures above ~ 330 K There are some differences between the data obtained for single crystals and those published for powder samples, which is probably related to the peculiarities of the powders

Introduction

A study of the mechanism of silver azide solid-state decomposition under external energy factors necessitated the examination of the crystal structure intrinsic defect participation in each reaction stage. Thus lattice disorder, the intrinsic defect concentration, their role in the transport processes and characteristics of the ionic charge carriers have been studied [1–4]. One effective research method of the intrinsic defect formation and motion processes in ionic crystals requires the use of high hydrostatic pressures [5]. The dependence of ionic conductivity on the hydrostatic pressure enables us to define directly the degree of strain volume lattice relaxation related to intrinsic defect formation and migration processes; the latter would improve our understanding of the ionic transport mechanism and enable the nature of the disorder in a crystal to be determined [5].

The effect of the hydrostatic pressure on the electrical conductivity of silver azide has been investigated previously [6–8]. In these studies the

electrical conductivity activation volumes both in extrinsic and intrinsic regimes were determined and it was suggested that charge transfer in the ohmic part of a current–voltage characteristic is ionic. The measurements in [6,8] were carried out on samples as pellets pressed from AgN_3 powder. Such samples are known to have a number of notable pecularities owing to the presence of barriers at the grain boundaries, the developed surface, the partial decomposition when pressed etc. Therefore the data of [6,8] are different from those obtained for single crystals [7].

Here we describe the influence of high hydrostatic pressure on the electrical conductivity of silver azide single crystals at temperatures between 263 and 373 K and at pressures 10^5–4×10^8 Pa. The activation volumes for intrinsic and extrinsic conduction, and the activation energies for the processes have been estimated. Theoretical estimations of the activation volumes have been made from the Zener strain-energy model [5,9].

Theoretical background

The ionic conductivity activation volume ΔV can be determined from the dependence of the sample resistance on the pressure by the relationship [5]

$$\Delta V = kT\left[\left(\frac{\partial \ln R}{\partial P}\right)_T + \left(\frac{\partial \ln \nu}{\partial P}\right)_T\right] \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, R is the sample resistance, P is the pressure, ν is the vibrational frequency of ion jump attempts. The second term in eq. 1 is generally neglected since the estimates and the direct measurements of dependence of the phonon frequency on pressure indicate that the correction is only a few per cent [5.8].

In cases where one mobile species in the extrinsic and intrinsic regimes predominates, the activation volumes become [5]

$$\Delta V_{\rm I} = \Delta V_{\rm m}, \quad \Delta V_{\rm II} = \Delta V_{\rm m} + \tfrac{1}{2}\,\Delta V_{\rm f} \tag{2}$$

where $\Delta V_{\rm I}$ and $\Delta V_{\rm II}$ are the activation volumes of conductivity in the extrinsic and intrinsic regimes, respectively, $\Delta V_{\rm m}$ and $\Delta V_{\rm f}$ are motional and formation activation volumes of defects, respectively.

A realization of different types of conduction in the sample by varying the temperature or by doping makes it possible to define the activation volumes of the processes from the corresponding slopes on the plot of $\ln \sigma$ against P. A comparison of $\Delta V_{\rm f}$ with the molar volume $V_{\rm M}$ enables us to determine the type of structural disorder. If $\Delta V_{\rm f}$ is similar in value to $V_{\rm M}$ the crystal lattice has Schottky disorder, and if $\Delta V_{\rm f}$ is less than $V_{\rm M}$ 'Frenkel' defects are present [5].

The Zener strain-energy model and the Grüneisen approximation [5,9,10] has been used to obtain a theoretical estimate of the activation volumes.

This model shows that [5]

$$\Delta V = \frac{2\left(\gamma - \frac{1}{3}\right) X \Delta H}{1 + 2\beta\left(\gamma - \frac{1}{3}\right)T} \tag{3}$$

where X is the isothermal compressibility, β is the volume thermal expansivity coefficient, ΔH is the enthalpy of the corresponding process and γ is the Grüneisen parameter. The latter can be calculated from the expression [9,10]

$$\gamma = \frac{\beta}{XC_p\rho - T\beta^2} \tag{4}$$

where C_p is the specific heat at a constant pressure and ρ is the density

Experimental

Silver azide crystals were grown from the AgN_3 solution in ammonium hydroxide by slow evaporation of ammonia. The available conditions for crystallization were chosen. Depending on the ammonia concentration in water and its evaporation rate, either (i) single crystals of $3 \times 3 \times 1$ mm having the most developed face (001) and the side faces (110) (sample of type A) or (ii) needle-shaped crystals having a mean size $5 \times 0.2 \times 0.05$ mm, a growth direction [001], the most developed face (100), the side faces (110) (samples of type B), were grown. The investigated crystals of both types had a perfect habit and no volume defects were revealed by optical microscopy Colloidal silver paste served as the electrical contacts to the sample. The current flow direction for the crystals of type A was along [110], and along [001] for those of type B. The distance between contacts was 1.5 mm for the type B samples.

The experiments were carried out in a hydrostatic high pressure chamber of the piston-and-cylinder type, the temperature was adjusted and stabilized. A dielectric oil of conductivity $< 10^{-13}$ ohm^{-1} cm^{-1} was used as the pressure-transmitting medium. The pressure measurements were made by a calibrated manganin gauge.

In all cases no hysteresis of the pressure dependence of conductivity was observed, which indicates both the high perfection of crystals and good mechanical qualities of the electrical contacts.

Results and discussion

Figure 1(a, b) depicts the dependence of the conductivity σ on the pressure expressed as lg σ versus P at various temperatures for single crystals of silver azide of type A and B, respectively. The conductivity of
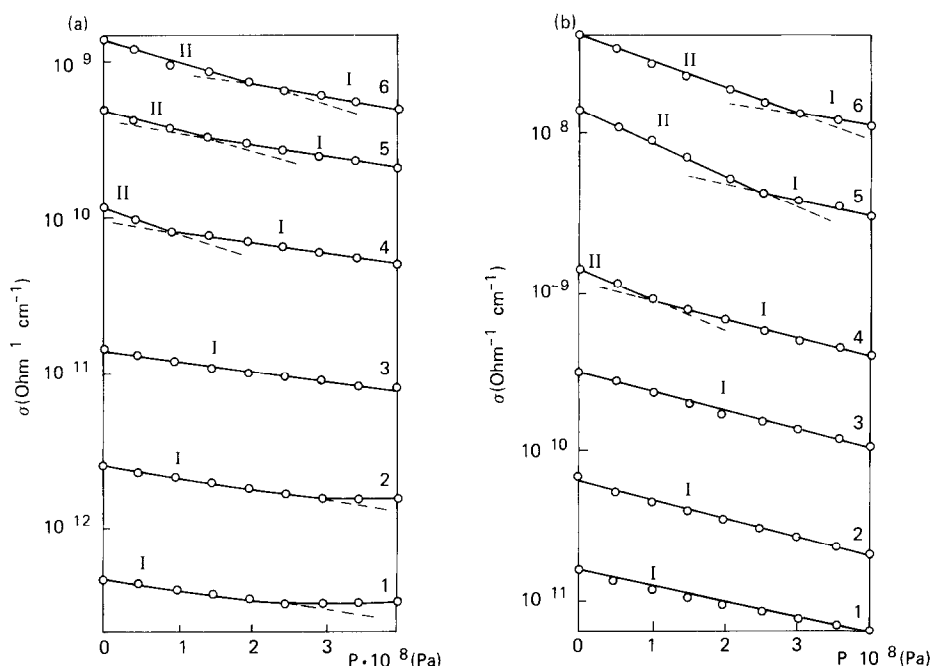
Fig 1 Dependence of the conductivity as a function of pressure for AgN_3 a single crystal of type A (a) at 261 K (1), 281 K (2), 303 K (3), 333 K (4), 353 K (5), 373 K (6), for a single crystal of type B (b) at 277 K (1), 292 K (2), 308 K (3), 323 K (4), 353 K (5), 368 K (6) Regions I and II correspond to extrinsic and intrinsic conduction respectively

each sample was calculated for constant values of geometrical size measured at atmospheric pressure. At temperatures above 333 K for type A samples (Fig. 1a) and above 323 K for type B samples (Fig. 1b) the dependence on pressure of σ was shown by the two rectilinear regions I and II of differing slopes.

The temperature dependence of the conductivity at atmospheric pressure (Fig. 2) plotted as $\lg(\sigma T)$ against $1/T$ is a straight line which also shows a change in the slope. The gradient change on the plot is associated with the transition from an extrinsic regime (region I) to an intrinsic one (region II) as the temperature increases [5]. Thus, the change in slope, which appears with an increase in pressure, of the plot of the pressure dependence of conductivity over a range of high temperatures (Fig. 1) is related to the transition from intrinsic conduction to that which is extrinsic. In the case of lower temperatures the conduction is extrinsic over the whole pressure range. The presence of a horizontal region of the plot of σ against P for the samples A at 261 K and at 281 K (Fig. 1a) is probably connected with the transition to the electronic component of conductivity, owing to the lower activation energy for the electronic component of charge transfer compared to the ionic one.
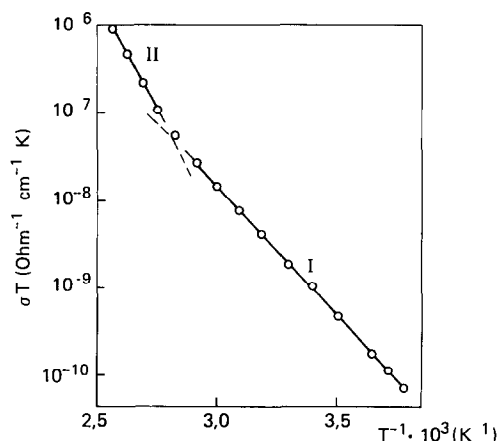
Fig. 2 The electrical conductivity of a single crystal of silver azide as a function of temperature. The regions I and II correspond to extrinsic and intrinsic conduction respectively

Other workers [8] have suggested that the transport in the extrinsic regime occurs by the movement of cation vacancies, because the chief impurity in the powder was found to be iron at 70 ppm. We determined the degree of impurity of single crystals of AgN_3 by emission spectral analysis in an AC arc. The major impurities in the experiments were found to be silicon and magnesium, but their concentrations were less than 10^{-3} percent. We think that the charge transfer in the extrinsic regime is by the interstitial cations. The assumption is supported by data for silver azide powder samples doped with Pb^{2+} or Cd^{2+} [3,4]. The conductivity was found to decrease with the as more positive charge was introduced, so that the results were consistent with mobile interstitial cations in an extrinsic regime. In the intrinsic regime charge transport occurs by the movement of both interstitial ions and cation vacancies, but the motility of the latter is much smaller and so its contribution to the conductivity can be disregarded [8].

The activation volumes of σ were estimated from the slopes of regions I and II of the $\sigma(P)$ plot (Fig. 1) by eq. 1. The values obtained enabled us to calculate ΔV_m for the Ag^+ interstitials, and to calculate ΔV_f for the AgN_3 defects from eq. 2; 3.9 ± 0.6 cm^3 mol^{-1} for ΔV_m and 12.5 ± 1.6 cm^3 mol^{-1} for ΔV_f for crystals of type A, and 6.8 ± 0.2 cm^3 mol^{-1} for ΔV_m and 12.5 ± 2.4 cm^3 mol^{-1} for ΔV_f for crystals of type B. These values are consistent with the activation volumes of the corresponding processes for silver halides [5,11], which are ionic conductors having properties close to that of silver azide.

The formation activation volumes obtained for the various silver azide samples are in good agreement with each other, which confirms that the same type of mobile species is active in the extrinsic and intrinsic conduction regimes for the samples. The formation activation volume is several

times lower than the silver azide molar volume of 29.4 cm³ mol⁻¹ This result undoubtedly, confirms the Frenkel disorder in AgN₃ described previously [3,4]. The motional activation volume magnitude for A is significantly larger than that for B, the difference between the ΔV_m values is too large to be attributed to experimental error. This discrepancy for single crystals is likely to be associated with a different transport mechanism of their most mobile defects. The latter is probably due to either anisotropy of the properties of silver azide or a surface conduction effect because of the much thinner B samples. The larger crystal conductivity of type B as compared with that of type A (Fig 1) is probably due to the same factors.

From the slopes of regions I and II of the lg(σT) versus $1/T$ (Fig. 2) we obtained the conductivity activation energies in the extrinsic and the intrinsic regimes, which are given by.

$$E_1 = \Delta H_m, \quad E_{II} = \Delta H_m + \tfrac{1}{2} \Delta H_f \tag{5}$$

where ΔH_m is the motional enthalpy and ΔH_f is the defect formation enthalpy. Equations 5 gave values of ΔH_m and ΔH_f of 0.56 and 0.72 eV, respectively.

The $\sigma(P)$ dependences obtained in our experiments for single crystals differ greatly from the data taken from ref. 6,8 in which the experiments were carried out on powder pellets. In the latter case the conductivity was intrinsic at atmospheric pressure over the given temperature range, and extrinsic conductivity occurred only at the pressures above 1.5 GPa. Here we deduce from Figs 1 and 2 that conductivity is extrinsic at room temperature and becomes intrinsic at temperatures above ~ 330 K; pressure-induced transition from intrinsic to extrinsic conduction in this temperature range occurs at considerably lower pressures. The dependence of conductivity on temperature, and the activation energies determined during our studies do not agree with those reported by other workers [8]. These discrepancies are probably because of the properties of the powder samples used [6,8] as mentioned above.

The theoretical values of both defect motional and formation activation volumes and Grüneisen parameter have been determined by use of the strain-energy model and the experimental data (eqs 3 and 4, respectively). The following characteristics and parameters of silver azide have been used in calculations: $X = 3.8 \times 10^{-11} m^2 \ N^{-1}$ [12], $C_p = 4.9 \times 10^2 \ J \ kg^{-1} \ K^{-1}$ [13]; $\rho = 5.1 \times 10^3 \ kg \ m^{-3}$ [14]; $\beta = 1.71 \times 10^{-4} \ K^{-1}$ (our laboratory data) The calculated values are: $\Delta V_m = 5.6 \ cm^3 \ mol^{-1}$, $\Delta V_f = 7.2 \ cm^3 \ mol^{-1}$ and $\gamma = 2$. The estimated activation volumes are in good agreement with the experimental data. In addition the Grüneisen parameter and the calculated activation volumes are close to those for silver halides [5,11].

Conclusion

The conduction of silver azide single crystals has been shown to be mainly ionic as is the case in powder pellets [6,8]. However, unlike latter, conduction is extrinsic under the normal conditions. That the ion transport mechanisms and the conductivity for crystals of type A and B differ is probably attributable to anisotropy of silver azide properties or to the surface conductivity effect in B because it is thinner. The activation volumes, as were calculated from the strain-energy model and the Grüneisen approximation have been shown to be consistent with the observed values and analogous estimations for silver halides, which verifies the correctness of the experimental results, and the assumptions and conclusions made. The data obtained provide new information on the processes of the intrinsic defect motion and formation in silver azide and will be of considerable help in working out the mechanism of solid state decomposition of the compound investigated.

Acknowledgements

References

1 B E. Bartlett, F.C. Tompkins and D A Young, Proc R Soc A, 246 (1958) 206
2 D A Young, Br J Appl. Phys, 15 (1964) 499
3 Yu A Zakharov and A A Kabanov, Russ J Phys Chem, 38 (1964) 1567
4 Yu.A Zakharov, V K. Gasmaev, S P Baklykov and Yu R Moreyns, Russ J Phys Chem., 52 (1978) 2076
5 G A Samara, Solid State Phys., 38 (1984) 1
6 C S. Rees and M M Chaudhri, in Proc 2nd Intern Conf Conduction and Breakdown in Solid Dielectrics, Erlangen, July 7–10, 1986, New York, 1986, pp 466–470
7 G M Diamant and Yu.Yu Sidorin, in Proc All-Union Conf Physical Processes in light-sensitive systems based on silver salts, October 10–14, 1986, Vol II, Kemerovo, 1986, pp. 108–109
8 C S Rees and M.M Chaudhri, J Phys C Solid State Phys, 20 (1987) 4097
9 W Paul and D.M Warschauer (Eds), Solids under Pressure, McGraw-Hill Book Company, Inc, N Y, San Francisco, Toronto, London, 1963
10 P P Pavinskii, Introduction to Solid State Theory, Izdatelstvo Leningradskogo Universiteta, Leningrad, 1979, p 116
11 A N Munn, I V Munn and V P Sivkov, Russ Solid State Physics, 15 (1973) 142
12 Yu A Zakharov, L V Kolesnikov and A E Cherkashin, Izv Akad Nauk SSSR, Neorg Mater, 14 (1978) 1283
13 F.P. Bowden and A D Yoffe, Fast Reactions in Solids, Butterworths Scientific Publications, London, 1958
14 L.I. Bogal, Chemistry and Technology of Primary Explosives, Mashinostrojenije, Moskva, 1975