ELECTRICAL CONDUCTIVITY OF CADMIUM SULFIDE UNDER HIGH PRESSURE AND HIGH TEMPERATURE

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The electrical resistance of single crystal cadmium sulfide was measured at pressures up to 40 kb and at temperatures up to 700°C in a cubic compact anvil high pressure apparatus.

Both the atmospheric wurtzite phase and the high-pressure rock salt phase are semiconductors. In the high-resistivity samples used the electrical resistance increased with pressure both in the wurtzite and in the rock salt phases. From the measurements of electrical resistance as a function of temperature a band gap of about 2.5 eV is obtained for the wurtzite phase. For the rock salt phase a band gap of about 0.8 eV is obtained.

Introduction

The semiconducting properties of group IV elements, III–V compounds, and II–VI compounds have received a great deal of attention. The study of electrical properties, for instance, of these semiconductors at high pressures have contributed to the understanding of the conduction mechanisms in terms of the pressure coefficients for energy gaps between the valence band maxima and the conduction band minima. Recently several investigators have reported the electrical[1)2)] and optical[3)–6)] properties of cadmium sulfide under high pressure but under room temperature condition. So far as the present authors know, no work has been reported concerning the effect of high pressure and high temperature on electrical properties of cadmium sulfide, except that of Samara and Giardini[7)] only at 250°C.

In the present work an investigation of the electrical conductivity (up to 40 kb) of single crystal CdS at room and elevated temperatures was carried out. The temperature dependence of the conductivity of the wurtzite and the high-pressure rock salt phases was investigated and the estimates of the widths of the energy gaps were obtained.

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Experimentals

The cadmium sulfide samples used were cleft from a high purity single crystal produced from the melt.

The experimental procedure was the same as in the work previously described.[8] In a few experiments the Pt-PtRh (10) thermocouples were used in place of Chromel-Alumel thermocouples because the latter were apt to pinch off at extremely high pressures. For the Pt-PtRh (10) thermocouples temperatures were measured using the values from the standard tables. The corrections of the measured temperatures for the effect of pressure on the e.m.f. of the thermocouples were made in accordance with the results reported by Hanneman and Strong.[9]

The energy gaps were estimated by the measurements of the temperature dependence on electrical conductivity at constant pressures. The temperature was held constant (for 10 min to 2 hr) at each value until no change in resistance could be observed. The isobars of resistance as a function of temperature were measured at two different pressures in the wurtzite phase and two pressures in the rock salt phase.

Results and Considerations

Energy gap

Since CdS is a semiconductor both in the wurtzite and rock salt structures, the electrical resistance R, in the intrinsic region of conduction, is given by

$$R = R_\infty \exp(E_g/2kT) \tag{1}$$

where E_g is the energy gap, k is the Boltzmann's constant, T is the absolute temperature, and R_∞ is an essentially temperature-independent constant. Thus, the slope of $\log R$ versus $1/T$ curves yields the energy gap. Fig. 1 shows the isobars of $\log R$ versus $1/T$. The data in Fig. 1 yield for the band gap of wurtzite structure a value of $E_g = 2.48$ eV at 2.5 kb and $E_g = 2.52$ eV at 12.7 kb, giving the pressure coefficient

$$\frac{dE_g}{dp} = 4.0 \times 10^{-6} \text{eV/bar}.$$

The values are favorably compared with the value of about 2.5 eV obtained from optical work.[5][4] Gutsche[6] measured the absorption of single crystals of CdS parallel and perpendicular to the crystal axis under hydrostatic pressure to $12,000$ kg/cm², finding a pressure coefficient of energy gap

$$\frac{dE_g \perp C}{dp} = 4.4 \pm 0.3 \times 10^{-6} \text{eV/bar},$$

$$\frac{dE_g //C}{dp} = 3.9 \pm 0.3 \times 10^{-6} \text{eV/bar}.$$

8)   J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *This Journal*, **36**, 59 (1966)

9)   R. E. Hanneman and H. M. Strong, *J. Appl. Phys.*, **36**, 523 (1965), *ibid.*, **37**, 612 (1965); E. T. Peter and J. J. Ryan, *ibid.*, **37**, 933 (1965).
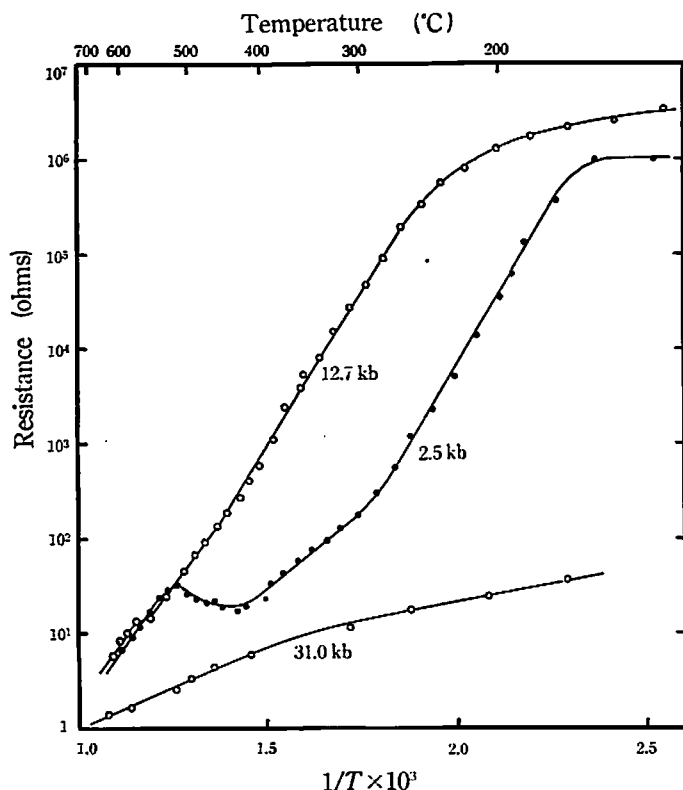
Fig. 1   Resistance *versus* $1/T$ isobars

Glyamov *et al.*[10] also reported the pressure dependence of E_g for CdS of $4.5 \sim 4.6 \times 10^{-6}$ eV/bar under hydrostatic pressure. The observed increase in E_g with pressure in the present work is in agreement with the hitherto reported data.

Hopfield *et al.*[11] have shown that the conduction band minimum and the valence band maximum in hexagonal CdS both occur at the center of the Brillouin zone. However, Cardona[12] has suggested using the **k·p** method that the valence band maximum may not be at the center of the Brillouin zone.

For the rock salt phase the data in Fig. 1 yield a value of $E_g=0.78$ eV at 31 kb. Drickamer *et al.*[3,4] reported the value of E_g as 1.7 eV, finding the pressure coefficient zero. Samara and Giardini[7] reported $E_g=1.3$ eV, dE_g/dp being equal to 1×10^{-6} eV/bar. The discrepancy may be partly due to the fact that the sample is polycrystalline in the rock salt phase. Because of the experimental difficulties such as shorting, deteriotation of the thermocouples, etc., only a few data were successfully obtained in the rock salt phase. The 30 kb isobar showed the same feature as that shown in Fig. 1.

10)   K. Glyamov, N. A. Tikhomirova and V. M. Fridkin, *Fiz. Tverdogo Tela*, **7**, 1037 (1965)
[*English transl.: Soviet Phys.—Solid State*, **7**, 834 (1965)]
11)   D. G. Thomas and J. J. Hopfield, *Phys. Rev.*, **116**, 573 (1959)
      D. G. Thomas, J. J.Hopfield and M. Power, *ibid.*, **119**, 570 (1960)
      J. J. Hopfield, *J. Appl. Phys.*, **32**, 2277 (1961)
12)   M. Cardona, *J. Phys. Chem. Solids*, **24**, 1543 (1963)

It is interesting to compare the pressure dependence of the band gap with its temperature dependence.[13] The temperature dependence of the energy gap of hexagonal CdS have been reported by several workers. Measurements of the dependence of the absorption on wave length have indicated[14]-[17] that the absorption edge shifts to longer wave lengths at the rate of about 1 Å/deg for increasing temperature. Measurements of photoconductivity have also indicated[18][19] approximately a 1 Å/deg shift in absorption edge. Bube[20] determined the temperature dependence of the forbidden band gap for CdS from the measurements of photosensitivity as a function of wave length. With rise in temperture E_g decreases, dE_g/dT being equal to -5.2×10^{-4} eV/deg. The temperature dependence of the band gap which is due to the thermal expansion of the lattice may be estimated from the formula,

$$\left(\frac{dE_g}{dT}\right)_a = -\frac{\alpha}{\beta}\frac{dE_g}{dp}, \qquad (2)$$

where β is the isothermal compressibility of the crystal and α is the expansion coefficient. Assuming that for CdS, $\beta = 1.82 \times 10^{-6}$ bar^{-1} obtained from the data of Samara and Giardini,[7] $\alpha = 1.70 \times 10^{-5}$ deg^{-1},[21] and $dE_g/dp = 4.0 \times 10^{-6}$ eV/bar obtained from the present work, $(dE_g/dT)_a = -3.7 \times 10^{-5}$ eV/deg. This value is one order of magnitude smaller than the experimentally observed one. In CdS the temperature dependence of the energy gap cannot be accounted solely in terms of the thermal expansion of the lattice. It is necessary to include a term which represents the explicit temperature dependence of the energy gap arising from the electron-lattice interaction. As known in CdS, scattering of electrons at room temperature is caused by interaction with longitudinal optical phonons.[22][23] The temperature dependence of the energy gap through the interaction of electrons with optical phonons has been discussed independently by Muto and Oyama[24] and by Fan.[25] According to Fan,

$$\Delta E_g = -\frac{\pi(ee^*)^2\hbar^{1/2}}{a^3 M\omega_l^{3/2}}\left[\left(\frac{2m_n{}^*}{\hbar^2}\right)^{1/2} + \left(\frac{2m_p{}^*}{\hbar^2}\right)^{1/2}\right]\left(\frac{1}{e^{\hbar\omega_l/kT}-1}+1\right) \qquad (3)$$

where e is the charge of the ions, e^* the effective charge of the ions, $\hbar$ the Planck's constant divided by 2π, k the Boltzmann's constant, a the nearest neighbors distance, M the reduced mass, ω_l the frequency of longitudinal optical phonon, and $m_n{}^*$ and $m_p{}^*$ are the electron and hole effective masses, respectively. A value for $dE_g/dT = -2.2 \times 10^{-4}$ eV/deg is obtained at 298°K with data for

13) T. S. Moss, "Optical Properties of Semi-conductors", pp. 53–46, Butterworths, London (1959)
14) F. A. Kröger, *Physica*, 7, 1 (1940)
15) G. Höhler, *Ann. Physik*, 4, 371 (1949)
16) R. Seiwert, *ibid*, 6, 241 (1949)
17) H. Radelt, *Z. Naturforsch.*, 15a, 269 (1960)
18) E. A. Niekisch, *Ann. Physik*, 8, 291 (1951)
19) R. Caspary and H. Müser, *Z. Physik*, 134, 101 (1952)
20) R. H. Bube, *Phys. Rev.*, 98, 431 (1955)
21) "American Institute of Physics Handbook", 2nd ed., McGraw Hill Book Co., Inc. New York (1963)
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23) R. Groth and R. Memming, *Phys. Status Solidi*, 1, 650 (1961)
24) T. Muto and S. Oyama, *Progr. Theoret. Phys. (Kyoto)*, 5, 833 (1950)
25) H. Y. Fan, *Phys. Rev.*, 82, 716 (1951)

$e^*=0.97e$ taken from Suchet,[26] $\omega_l=5.7\times10^{-13}$ sec^{-1} taken from the report of Collins,[27] and $m_n^*=$ $0.20m_e$ and $m_p^*=0.7m_e$ reported by Hopfield and Thomas.[28] This value is of the same order as the experimentally observed one by Bube.

Electrical resistance

At constant temperature the electrical resistance increases in the wurtzite phase of CdS. Pressure affects the conductivity through the changes in the carrier density in either conduction or valence bands, and through changes in mobilities.

For an intrinsic semiconductor the conductivity is given by

$$\sigma=e(n\mu_n+p\mu_p), \qquad (4)$$

where μ_n and μ_p are the mobilities of electron and hole, and e is the charge. The densities n and p of the carriers are given by

$$n=p=2(2\pi kT/\hbar^2)^{3/2}(m_n m_p)^{3/4}\exp(-E_g/2kT), \qquad (5)$$

where m_n and m_p are the electron and hole effective masses respectively, and E_g is the band gap. The conductivity is thus,

$$\sigma=2e(\mu_n+\mu_p)\left(\frac{2\pi kT}{\hbar^2}\right)^{3/2}(m_n m_p)^{3/4}\exp(-E_g/2kT). \qquad (6)$$

The resistivity is given by

$$\rho=\frac{1}{e(\mu_n+\mu_p)}\times\frac{1}{2A}\exp(E_g/2kT). \qquad (7)$$

where

$$A=\left(\frac{2\pi kT}{\hbar^2}\right)^{3/2}(m_n m_p)^{3/4}.$$

The fractional change in effective masses with pressure is approximately the same as the fractional change in E_g.[29][30] It is of the order of 10^{-6} bar^{-1} as shown above. The variation of mobilities depends on the scattering mechanism, the order of variation being equal to 10^{-6} bar^{-1}.[31] Accordingly, the predominant effect on the conductivity must be due to E_g. By differentiating equation (7) and neglecting the smaller terms

$$\frac{\partial\ln\rho}{\partial p}\simeq\frac{1}{2kT}\frac{\partial E_g}{\partial p}. \qquad (8)$$

The resistance in equation (1) is represented by

26) J. P. Suchet, *J. Phys. Chem. Solids*, **16**, 265 (1960)

27) R. J. Collins, *J. Appl. Phys.*, **30**, 1135 (1959)

28) J. J. Hopfield and D. G. Thomas, *Phys. Rev.*, **122**, 35 (1961)

29) R. W. Keyes, *Phys. Rev.*, **99**, 490 (1955)

30) A. A. Averkin and P. G. Dermenzhi, *Fiz. Tverdogo Tela*, **8**, 103 (1966) [*English transl.: Soviet Phys.— Solid State*, **8**, 79 (1966)

31) W. Paul, "High Pressure Physics and Chemistry", edited by R. S. Bradley. pp. 299–354, Academic Press, London and New York (1963)

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$$R = \rho \frac{l}{S}, \tag{9}$$

where l is the length and S is the cross-sectional area of the samples. If the dimensional changes in l and S with pressure are neglected

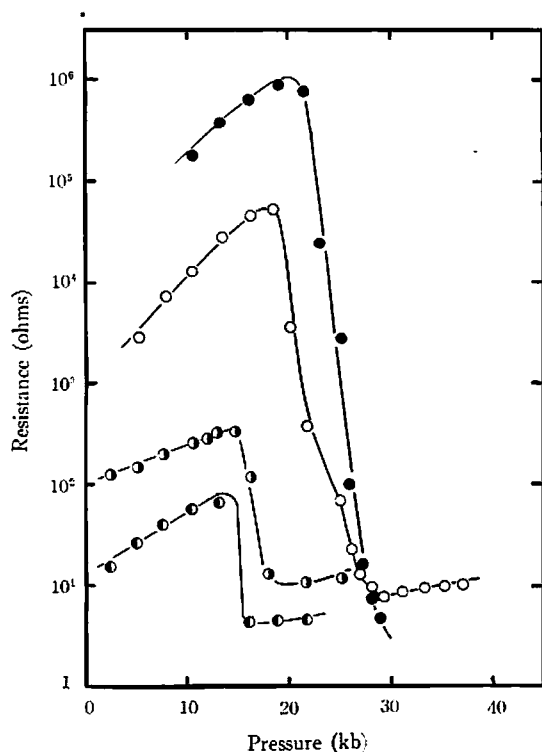$$\frac{\partial \ln \rho}{\partial p} \approx \frac{\partial \ln R}{\partial p}. \tag{10}$$

Fig. 2 Resistance *versus* pressure isotherms
●: 100°C
○: 200°C
◐: 400°C
◑: 500°C

Equation (10) and Fig. 2 give the experimental value equal to 8.7×10^{-5} bar^{-1} at 400°C.

With equation (8) it follows

$$\frac{\partial \ln \rho}{\partial p} \approx 3.4 \times 10^{-5}\,\text{bar}^{-1}$$

which is in agreement with the observed values.

Below about 200°C the measured conductivity is extrinsic. In a simple one-donor-model it would be given by[32]

$$\sigma = e\mu(N_C N_D)^{1/2}\exp\left(-\frac{E_C - E_D}{2kT}\right), \tag{11}$$

thus

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32) See for example, N. B. Hannay, "Semiconductors", edited by N. B. Hannay. pp. 1–49, Reinhold Publishing Co., New York (1959)

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$$\rho = \frac{1}{e\mu}\frac{1}{(N_C N_D)^{1/2}}\exp\left(\frac{E_C - E_D}{2kT}\right),\tag{12}$$

where $N_C = 2\left(\frac{m^*kT}{2\pi\hbar^2}\right)^{3/2}$, N_D is the concentration and $E_C - E_D$ is the ionization energy of the donor level. Equation (12) gives

$$\frac{\partial\ln\rho}{\partial p} = -\frac{\partial\ln\mu}{\partial p} - \frac{3}{4}\frac{\partial\ln m^*}{\partial p} + \frac{1}{2kT}\frac{\partial(E_C - E_D)}{\partial p}.\tag{13}$$

The first two terms have values of the order of $10^{-6}\,\text{bar}^{-1}$ and can be neglected, compared with $\partial\ln\rho/\partial p$. A hydrogen-like model of the donor gives[33]

$$(E_C - E_D) = \frac{e^4 m^*}{2\hbar^2\epsilon^2} \sim E_g{}^2\tag{14}$$

and so

$$\frac{\partial(E_C - E_D)}{\partial p} \approx 2\frac{\partial E_g}{\partial p}.\tag{15}$$

Thus,

$$\frac{\partial\ln\rho}{\partial p} \approx \frac{1}{kT}\frac{\partial E_g}{\partial p}.\tag{16}$$

Equation (16) gives the value of $1.2\times10^{-4}\,\text{bar}^{-1}$ at 100°C, which is fairly in agreement with the values obtained from Fig. 2. at 100°C, $2.0\times10^{-4}\,\text{bar}^{-1}$.

The increase in resistance of the rock salt phase with increasing pressure is consistent with previous investigations.[1][7] The rate of increase with pressure is very small compared with other works. This may be partly due to the high polycrystallinity in the rock salt phase.

Acknowledgment

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33) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals", 2nd. ed., pp. 68–108, Clarendon Press, Oxford, (1950)