triplet state transitions. Since spectrophotofluorometers are now in wide use and can so easily be adapted to the measurement of fluorescence polarization, this technique should now be readily available to many laboratories.

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References and Notes

1. G. Weber, in *Advances in Protein Chemistry* (Academic Press, New York, 1953), vol. 8, p. 416.
2. S. F. Velick, *J. Biol. Chem.* **233**, 1455 (1958).
3. P. P. Feofilov, *The Physical Basis of Polarized Emission* (Consultants Bureau, New York, 1961).
4. C. R. Singleterry and L. A. Weinberger, *J. Am. Chem. Soc.* **73**, 4574 (1951).
5. R. F. Steiner and H. Edelhoch, *ibid.* **83**, 1435 (1961).
6. R. L. Bowman, P. A. Caulfield, S. Udenfriend, *Science* **122**, 32 (1955).
7. T. Azumi and S. P. McGlynn, *J. Chem. Phys.* **37**, 2413 (1962).
8. J. E. Stewart and W. S. Galloway, *Appl. Opt.* **1**, 421 (1962).
9. C. H. Palmer, *J. Opt. Soc. Am.* **42**, 269 (1952).
10. M. N. McDermott and R. Novick, *ibid.* **51**, 1008 (1961).
11. American Instrument Co., Silver Spring, Md.
12. Electro Instruments, San Diego, Calif.
13. R. F. Chen, *Biochem. Biophys. Res. Commun.* **17**, 141 (1964).
14. Polished quartz strain-free discs 19 mm in diameter and 1.6 mm thick were obtained from Polacoat, Inc., Blue Ash 42, Ohio.
15. Obtained from the Polymer Research Division, Polaroid Corp., Cambridge, Mass.
16. A. S. Makas, *J. Opt. Soc. Am.* **52**, 43 (1962).
17. L. Szalay, L. Gáti, B. Sárkány, *Acta Phys. Acad. Sci. Hung.* **14**, 217 (1962).
18. P. P. Feofilov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **9**, 317 (1945).
19. National Aniline Division, Allied Chemical Corp., New York, N.Y.
20. V. P. Klochkov and B. S. Neporent, *Opt. Spectry. USSR, English Transl.* **12**, 125 (1962); *Opt. i Spektroskopiya* **14**, 812 (1963) (in Russian).
21. G. Weber, *J. Opt. Soc. Am.* **46**, 962 (1956).
22. R. J. Argauer and C. E. White, *Anal. Chem.* **36**, 368 (1964).
23. F. Perrin, *Ann. Phys. Paris* **12**, 169 (1929); V. L. Levshin, *Z. Physik* **26**, 274 (1924).
24. W. F. Harrington, P. Johnson, R. H. Ottewill, *Biochem. J.* **62**, 569 (1956).
25. Armour Co.
26. D. J. R. Laurence, in *Methods in Enzymology*, S. P. Colowick and N. O. Kaplan, Eds. (Academic Press, New York, 1957), vol. 4, p. 174.
27. C. S. Chadwick and J. E. Fothergill, in *Fluorescent Protein Tracing*, R. C. Nairn, Ed. (Livingston, Edinburgh and London, 1962), p. 4.

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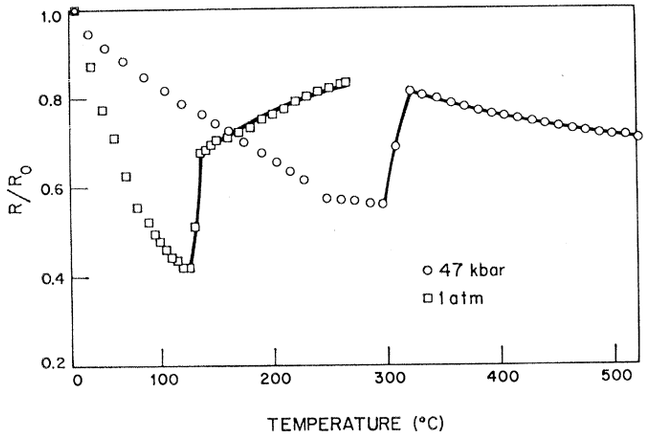
Pressure Dependence of the Alpha-Beta Transition Temperature in Silver Selenide

Abstract. *The pressure dependence of the α-β transition temperature in Ag_2Se was determined by observing the temperature at which the sharp change in resistivity occurs when Ag_2Se is transformed from the low-temperature orthorhombic to the high temperature body-centered-cubic form. The transition temperature increased from 133°C at 1 atmosphere to 298°C at 47 kilobars. The value of ΔH_t, the heat of transformation, of 2.19 kcal/mol measured calorimetrically agreed well with the value calculated from dT/dP of the transition.*

The silver and copper chalcogenides have well-characterized (*1*, *2*) polymorphic transitions to cubic structures at elevated temperatures. A sharp change in resistivity occurs when Ag_2Se is transformed from the low-temperature orthorhombic form (*3*, *4*) (α-Ag_2Se) (*5*) to the high-temperature body-centered-cubic form (β-Ag_2Se). Under atmospheric pressure, this transition occurs at about 133°C. Pressure dependence of the transition temperature up to 47 kb was determined by resistance measurements. The samples were polycrystalline cylinders and rectangular parallelepipeds cut from an ingot prepared by the horizontal Bridgman technique and then cooled slowly through the transition region. The sample had carrier concentrations of about 2×10^{18} cm^{-3} at 77°K. Measurements of resistivity versus temperature were made at atmospheric pressure by a four-lead method. At higher pressures, measurements were made in the tetrahedral-anvil press by a two-lead method previously used to investigate the P-T diagram of InSb (*6*). The high pressure cells were calibrated with the Bi I-II (25.4 kb) and the Tl I-II (37 kb) transitions (*7*). The four-lead method was also used to measure resistance at room temperature as a function of pressure to 40 kb. No appreciable change in resistance was observed. X-ray powder patterns taken at more than 45 kb also showed no phase change at room temperature.

Typical data for relative resistance versus increasing temperature are given in Fig. 1 for atmospheric pressure and 47 kb. At all pressures the resistance increased sharply over a range of 10° to 20°C when the samples were heated through the transition point (Fig. 1). Baer *et al.* (*8*) also observed an increase in resistivity on heating a sample which had been converted to the low-temperature form by cooling from a temperature a little above transition. This treatment is similar to those used in preparation and measurement of our samples. In experiments on samples



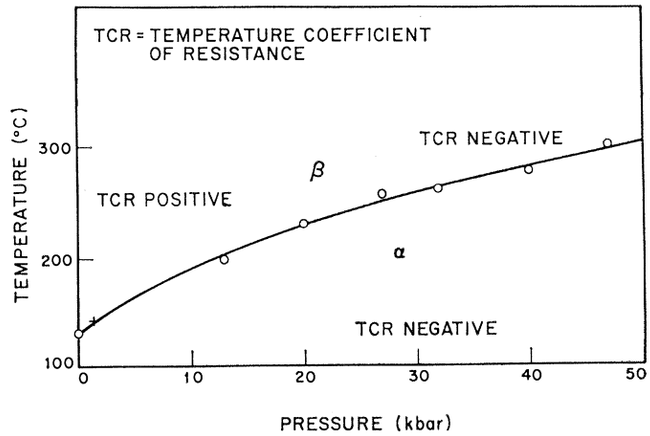


Fig. 1 (left). Relative resistance (R/R_0) versus temperature for Ag_2Se at atmospheric pressure and at 47 kb. At atmospheric pressure, resistivity in ohm-cm is equal to $(1.02 \times 10^{-3}) \times (R/R_0)$. Fig. 2 (right). Temperature of α-β transition in Ag_2Se versus pressure. Cross indicates data of Roy *et al.* at 1115 atm (*9*).

converted by cooling slowly from 700° to 900°C, Baer *et al.* (*8*) observed a decrease in resistivity on heating through the transition point. A decrease in resistivity was also observed by Junod (*2*). To explain their results, Baer *et al.* (*8*) have proposed two modifications of the low temperature phase. At atmospheric pressure the sign of the temperature coefficient of resistivity is negative for α-Ag_2Se and positive for β-Ag_2Se. This change in sign is observed for pressures up to about 15 kb, but at higher pressures the temperature coefficient is negative for both phases (Fig. 1). At most pressures the $\beta \rightarrow \alpha$ transition on cooling occurred 15° to 25°C lower than did the $\alpha \rightarrow \beta$ transition on heating.

Transition temperatures (obtained from graphs of resistance plotted against temperature, as temperature increases) are plotted against pressure in Fig. 2. For each pressure the transition temperature was taken as the temperature at which the resistance began to rise steeply. Roy *et al.* (*9*) observed an increase of 8.0°C in the transition temperature at 1115 atm with differential thermal analysis (DTA). As shown in Fig. 2, this point falls on the smooth curve connecting my data. The increase in transition temperature with pressure is consistent with crystallographic evidence that β-Ag_2Se (*2*) is less dense than α-Ag_2Se (*1, 3, 4*). [The face-centered tetragonal α-phase proposed by Junod (*2*) had lattice parameters which gave a molar volume which is inconsistent with the experimental data.]

The heat of transformation (ΔH_t) has been calculated from the pressure data by applying the thermodynamic relation $(dT/dp) = T\Delta V_m/\Delta H$. The initial slope of the curve of the transition temperature plotted against pressure from the data of Roy (*9*) is $dT/dp = 7.0$°C per kilobar. The transition temperature is 406°K. The molar volumes (V_m) of the α and β phases calculated from lattice parameter data are 35.57 cm^3/mol (*3*) and 37.36 cm^3/mol (*2*), respectively. The ΔH_t calculated from these values is 2.5 kcal/mol. Roy *et al.* (*9*) obtained $\Delta H_t = 1.678$ kcal/mol by using a molar volume for the low-temperature phase calculated from their measured density of 8.14 g/cm^3. The molar volume used in my calculation corresponds to a density of 8.29 g/cm^3.

Since the present calculated ΔH_t did not agree with reported values (1.68, 1.61 kcal/mol) determined from heat capacity measurements (*8, 10*), a calorimetric measurement of ΔH_t was made with a Perkin-Elmer Model DSC-1 differential scanning calorimeter (*11*). In this apparatus the sample and a standard are sealed in aluminum foil, heated or cooled at a constant rate, and the differential power necessary to keep the sample and standard temperatures equal throughout the run are recorded and integrated. For the measurements on Ag_2Se the calorimeter was calibrated by melting-freezing runs on high purity indium metal ($T_m = 156.6$°C, $\Delta H_m = 0.78 \pm 0.02$ kcal/g-atm). The $\alpha \rightarrow \beta$ transition on heating began at 132.5°C and the $\beta \rightarrow \alpha$ transition on cooling began at 113°C, in good agreement with the temperatures observed in the resistivity measurement. The ΔH_t for Ag_2Se was 2.19 kcal/mol.

In calculating the ΔH_t from pressure data the values of $V^{\alpha}{}_m$ and $V^{\beta}{}_m$ were obtained from lattice parameters measured at 298° and 443°K, respectively. Therefore, the value of ΔV_m used in the calculation is greater than the actual value at the transition temperature. Use of the value of ΔV_m at 406°K would reduce ΔH_t and improve its agreement with the result obtained calorimetrically. Roy *et al.* (*9*) made such a correction by measuring the increase in lattice parameter of the cubic high temperature phase with increasing temperature and by assuming the same expansion coefficient for the low temperature phase. However, they gave no data which could be used to correct the present calculations.

An unpublished (*12*) DTA resulting in $\Delta H_t = 2.36 \pm 0.59$ agrees better with the ΔH_t values obtained in this study than with the values from heat capacity measurements. The discrepancy between the heat capacity results and those obtained by other methods may be due to the existence of the two modifications of the low temperature phase proposed by Baer *et al.* (*8*). This difference of about 0.7 kcal/mol may be heat of ordering which they discussed, but for which they assigned no value.

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References and Notes

1. P. Rahlfs, *Z. Physik Chem.* **B51**, 157 (1935).
2. P. Junod, *Helv. Phys. Acta* **32**, 567 (1959); *ibid.*, p. 581.
3. R. Simon, R. C. Bourke, E. H. Lougher, *Advanced Energy Conv.* **3**, 481 (1963).
4. J. B. Conn and R. C. Taylor, *J. Electrochem. Soc.* **107**, 977 (1960).
5. The designation of α for the low temperature phase is consistent with the practice in M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, ed. 2, 1958).
6. R. E. Hanneman, M. D. Banus, H. C. Gatos, *J. Phys. Chem. Solids* **25**, 293 (1964).
7. M. D. Banus and S. D. Nye, *Rev. Sci. Instr.* **35**, 1319 (1964).
8. Y. Baer, G. Busch, C. Fröhlick, E. Steigmeier, *Z. Naturforsch.* **17a**, 886 (1962).
9. R. Roy, A. J. Majumdar, C. W. Hulbe, *Econ. Geol.* **54**, 1278 (1959).
10. M. Bellati and S. Lussana, *Atti Ist. Veneto* Ser. 6, **7**, 1051 (1888–89).
11. Equipment used through the courtesy of J. Justin, Perkin-Elmer Co., Norwalk, Conn.
12. B. M. Kulwicki, thesis, University of Michigan (1963).
13. I thank A. J. Strauss for the samples of Ag_2Se, for many helpful discussions, and for critically reviewing this manuscript, and A. R. Leyenaar for the x-ray determination.
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Screw Dislocations in Graphite

Abstract. *Graphite contains varying concentrations of screw dislocations whose Burgers vector parallels the* c *axis. Single crystals of natural graphite contain very few such dislocations; furthermore, their Burgers vector always exceeds 450 angstroms. Pyrolytic graphites annealed above 3000°C contain abundant screw dislocations, ranging from 10^6 to 5×10^8 per square centimeter in two different samples prepared by somewhat different methods. The Burgers vectors of these screws are predominantly 3.35 angstroms.*

A decoration technique has been developed (*1, 2*) which can render individual lattice vacancies in graphite visible for electron microscopy. The method consists of cleaving the crystal to a thickness of a few hundred angstrom units, etching in a gas (usually a mixture of O_2 and Cl_2) which expands surface vacancies to any desired diameter without increasing their depth, and finally decorating with minute amounts of gold. This method reveals other lattice defects besides vacancies, and in particular can be used to identify screw dislocations by the extra surface step which originates on the dislocation (*1*). I now report that the screw dislocations can actually be "unravelled" by suitable etchants like carbon dioxide which react faster at linear than highly curved surface steps. After the core of the screw has been etched away, the remaining