

Fig. 1. Photoconductivity excitation spectra for CdSe:Mn crystal. Curve A: at room temperature. Curve B: at liquid-nitrogen temperature.

CdSe and CdS have been extensively investigated.¹⁻⁴ One of the outstanding characteristics due to the impurity imperfections in the II-VI compounds is that most impurity ionization energies in these compounds are considerably larger than those found in Ge and Si. Most of the recent investigations are concerned with the impurities with single levels such as the impurity levels induced by Cu, Ag, Sb, and Cl in CdSe and CdS. However, manganese is unlike the other elements of group I and group III in that it often induces very complicated multiple impurity levels in the group-II-VI compounds and also in the Ge and Si systems. The properties of these multiple levels have been most completely investigated only in the case of the Ge:Mn system.^{5,6}

This communication reports the measurements of the photoconductivity and the Mn impurity level in the CdSe:Mn single crystal. The CdSe single crystal is activated by Mn and contains a very high percentage (0.15%) of MnSe. In this experiment the indium electrode contacts have been used and they provide good Ohmic contacts as in the case of CdS crystals.^{7,8} The spectral photoresponse of this sample has been measured at room temperature and liquid-nitrogen temperature by using a dc photoconductivity method. The results are shown in Fig. 1.

As shown in the Fig. 1, the photo-peak of 7000 Å corresponds to the intrinsic excitation of 1.77 eV which is the bandgap of the CdSe single crystal. This value is in excellent agreement with the known bandgap for CdSe measured by the methods of photoconductivity as well as by the luminescence emission.⁹⁻¹¹ The high photo-peak of 9400 Å corresponds to an excitation transition of 1.32 eV from the Mn impurity centers to the conduction band. Here the Mn substitutes for the Cd. Eventually, it should act as a donor⁴ and the present results show that this donor level is deeply located. It is located at (0.45 ± 0.05) eV above the valence

band. This deeply located donor level for the manganese has been observed at least in the case of Ge:Mn.^{4,5} In fact, the manganese in the Ge and also in the group-II-VI compounds forms a complicated impurity with multiple levels and can act as a donor or an acceptor.^{5,12} In the present measurement only one donor level is observed. In order to investigate the possible existence of the Mn multiple levels in the CdSe:Mn one may have to incorporate some kind of compensating impurities to adjust the ionization states of the Mn with multiple levels. At present, this has not been attempted.

It is observed that the Mn-impurity-excited photoconductivity is much greater than that due to the intrinsic transition. This is mainly due to the high concentration of the Mn impurity in the sample. This property of the impurity excitation dominating the spectrum has also been observed by Veith in the case of CdS:Cu.¹³ By increasing the Cu concentration in the CdS, Veith observed a large shift from primarily intrinsic excitation to primarily impurity excitation. In the present case, the thermal quenching of the intrinsic transition in the liquid nitrogen temperature is also observed.

¹ R. H. Bube and L. A. Barton, *J. Chem. Phys.* **29**, 128 (1958).

² F. A. Kroeger, H. J. Vink, and J. Volger, *Phil. Rev. Rep.* **10**, 39 (1955).

³ R. H. Bube, *J. Phys. Chem. Solids* **1**, 234 (1957).

⁴ R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1956).

⁵ R. Newman, H. H. Woodbury, and W. W. Tyler, *Phys. Rev.* **102**, 613 (1956).

⁶ G. A. Morton, E. E. Hahn, and M. L. Schultz, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p. 556.

⁷ C. I. Shulman, *Phys. Rev.* **98**, 384 (1955).

⁸ F. A. Kroeger, G. Diemer, and H. A. Klasens, *Phys. Rev.* **103**, 279 (1956).

⁹ R. H. Bube, *Phys. Rev.* **99**, 1105 (1955).

¹⁰ R. H. Bube, *Proc. IRE* **43**, 1836 (1955).

¹¹ E. F. Gross and V. V. Sobolev, *J. Tech. Phys. (USSR)* **26**, 1622 (1956).

¹² R. H. Bube, *Phys. Rev.* **90**, 70 (1953).

¹³ W. Veith, *Z. Angew. Phys.* **7**, 1 (1955).

Selective Nucleation of the High-Pressure Ices

L. F. EVANS

Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia

(Received 6 July 1967)

One of the problems which hamper the study of the various high-pressure polymorphs of ice is the inability to crystallise the desired polymorph. In his classic work on the phase relationship of the ices, Bridgman¹ found that although ice I, ice III and ice VI could be readily crystallised from the liquid at the appropriate pressure, ice IV and ice V were obtained from the liquid only with great difficulty, their appearance, according to Bridgman, being a matter of "caprice". Thus in the pressure range of about 3500–4500 bar the ice which crystallises from the liquid may be ice IV, ice V, ice VI or mixtures thereof.

Bridgman finally prepared ice V by decompressing ice VI (see Fig. 1), but even this inconvenient route was only sometimes successful, the transformation from ice VI to ice V apparently being dependent on the nature of the containing vessel. The preparation of ice IV was even more capricious because ice IV is a metastable phase which exists wholly within the stability range of ice III and ice V. Bridgman originally postulated ice IV to account for two occasions on which the ice which he obtained at 5000 bar melted at a temperature 1.5°C higher than the established melting point of ice VI. Later when studying the D₂O ices, Bridgman² unequivocally established the existence of

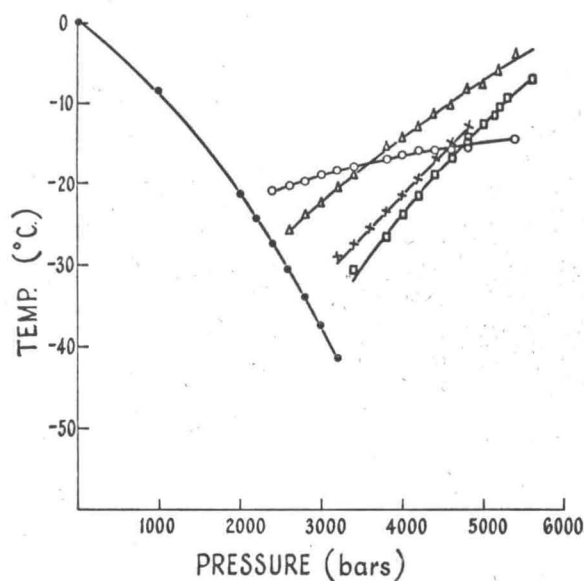


FIG. 1. The solid-liquid equilibrium data for the ice polymorphs—ice I (●), ice III (○), ice IV (×), ice V (Δ), and ice VI (□).

ice IV (D_2O) but found that it could only be formed in an apparatus which had not previously contained ice V (D_2O).

The nucleation of ice I presents no problem, for a large number of organic compounds are known which facilitate the nucleation of ice I.³ However, good organic nucleators for the high-pressure ices are extremely rare, partly because below 0°C there is a strong tendency for organic surfaces to adsorb water in the form of a two-dimensional layer of ice I.⁴ On such an adsorbed layer, the high-pressure ices have difficulty in growing epitaxially, therefore a considerable supercooling is generally required. Nevertheless the present study shows that certain organic compounds do exhibit a preference for nucleating a particular phase of ice, even though the required supercooling is relatively large. By using these nucleators each phase has been crystallised from the liquid at pressures outside the range of thermodynamic stability, and by measuring the equilibrium freezing point during crystallisation the solid-liquid equilibrium curves have been extended beyond the pressure range investigated by Bridgman.

Apparatus: A droplet of water about 2 mm in diameter is suspended on the tip of a platinum/platinum-rhodium thermocouple contained in a high-pressure cell fabricated from beryllium-copper. Pressure is generated by a hydraulic pump via a 10:1 intensifier and separator, the limiting pressure being 6000 bar. The working fluid in the cell is petroleum ether, b.p. = 60°–80°C. The cell is cooled at a steady rate of about 4°C/min and the amplified signal from the thermocouple is recorded continuously. When crystallisation begins the temperature of the thermocouple rises abruptly to the equilibrium freezing point of the phase of ice which is crystallising, and remains at this "plateau temperature" until crystallisation is complete. Where two phases have the same equilibrium freezing point the phase which is crystallising is identified by raising the pressure slightly during crystallisation thus obtaining, from the step in the plateau, the derivative of the equilibrium freezing point with respect to pressure.

If the phase which has crystallised subsequently transforms to a more stable phase the transformation is signalled by a temperature spike resulting from the abrupt release of the heat of transformation. Similarly, if during the crystallisation of the first phase, a second phase begins to crystallise, a stepped plateau is formed. The phase which is finally formed is confirmed by heat-

TABLE I. Nucleators for high-pressure ices.

Nucleator	Preferred ice phase	Supercooling (°C)	Pressure range (bar)
α -phenazine	I	4	1–3200
phloroglucinol dihydrate	I	6	1–3200
8-hydroxy-quinoline	III	18	2800–4800
benzoin	III	21	3000–4600
<i>p</i> -amino hippuric acid	IV	13	3800–4200
<i>l</i> (leucine	IV	11	3200–4000
phenol tetra-bromo-phthalein	IV	14	3800
tetra-chloro-phthalic anhydride	IV	7	3200–4000
<i>l</i> -asparagine	VI	5	4400–4800
benzamide	V	14	2600–4200
	V	21	3200–3600
	IV	16	4200–4600
adipic acid	V	22	3400–4600
2,4 dinitro-diphenylamine	VI	13	3800–5000
haematoxylin	VI	10	4000–5000
cholic acid	VI	11	3800–4600
anisoin	VI	16	5600

ing the cell and noting the melting point, this being the temperature at which an arrest appears in the trace of temperature vs time.

The accuracy of the thermocouple-recorder system is shown, by calibration, to be $\pm 0.5^\circ\text{C}$. The plateau temperature for ice I at atmospheric pressure is $0 \pm 0.5^\circ\text{C}$, thus establishing that in spite of the relatively small size of the water droplet and heat leakage along the thermocouple wires, the thermocouple measures the true melting point. Pressures accurate to ± 50 bars are measured on a 7-kbar Budenburg gauge.

To test a particular organic compound as an ice nucleator the compound is freshly crushed under water and a drop of the resultant slurry is placed on the thermocouple.

Results and Discussion: As reported by Bridgman,¹ ice V is difficult to nucleate from the liquid in the absence of a specific nucleator, the experience being that between 2400 and 4000 bar ice III is obtained, whereas above 4000 bars ice VI is generally obtained.

No evidence has been found for Bridgman's alleged "memory effect" for ice V, i.e., the ability of ice V (but not ice VI) to nucleate from the liquid once ice V had been previously formed in the apparatus. However it is known that memory effects arise from adsorbed films⁴ or from the retention of ice in crevices⁵; therefore one expects the phenomenon of "memory" to be a function of apparatus rather than being an intrinsic property of ice V.

When selective nucleators are present in the water droplet it is possible to nucleate, at will, all the phases of ice except ice II and ice VII, the former being notoriously difficult to nucleate from the liquid,² the latter requiring pressures beyond the limit attainable in the present apparatus. In Table I are listed the most selective of the organic nucleators together with the pressure range in which selectivity is found. Of particular interest is the confirmation of Bridgman's claim that a wholly unstable phase, ice IV, exists within the stability region of ice III and ice V. The melting-point curve of ice IV is depicted in Fig. 1 together with the extension into regions of instability, of the melting-point data of ices I, III, V, and VI.

The melting-point data of all the ices except ice I are, on the average, about 1°C lower than the data reported by Bridgman, but taking into account the uncertainty of pressure and tem-

perature values both in the present work and in the work of Bridgman, the present results are in substantial agreement with those of Bridgman.

It may be of interest to those engaged in the preparation of the various phases of ice to note that ice V and ice VI can be prepared at pressures much lower than are indicated by the equilibrium phase diagram, thus allowing these ices to be prepared in relatively simple high-pressure apparatus. It is also possible to prepare ice IV at will, but ice IV transforms to one of the stabler forms if stored for a few minutes at about -30°C . Probably this transformation could be delayed indefinitely by rapidly chilling the ice IV in liquid air, a procedure which has been used to maintain other phases of ice in a nonequilibrium state.⁶

Good nucleators for ice I have generally been found to have lattice spacings which correspond to the lattice spacings of ice I,³ therefore it is of interest to look for a similar relationship between the other ice polymorphs and their respective nucleators. The nucleation of ice III by benzoic acid affords this opportunity since the structures of both ice III (tetragonal, $a=c=6.80 \text{ \AA}$ ⁷) and benzoic acid (monoclinic, $a_0=18.75$, $b_0=5.72$, $c_0=10.46$, $\beta=105^{\circ}50'$ ⁸) are known. No obvious similarity is apparent between these structures but in view of the rather large supercooling (21°C) close similarity should perhaps not be expected.

¹ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **47**, 441 (1911).

² P. W. Bridgman, *J. Chem. Phys.* **3**, 597 (1935).

³ N. Fukuta, *J. Atmos. Sci.* **23**, 191 (1966).

⁴ L. F. Evans, *Nature* **213**, 384 (1967).

⁵ D. Turnbull, *J. Chem. Phys.* **18**, 198 (1950).

⁶ R. L. McFarlan, *J. Chem. Phys.* **4**, 253 (1936).

⁷ W. B. Kamb and S. K. Datta, *Nature* **187**, 140 (1960).

⁸ M. Prasad and J. Shanker, *J. Indian Chem. Soc.* **13**, 123 (1936).

Erratum: Reflection and Transmission of Electromagnetic Waves by a Moving Uniaxially Anisotropic Medium

[38, 870 (1967)]

S. W. LEE AND Y. T. LO

Antenna Laboratory, University of Illinois, Urbana, Illinois

The lower bound of the critical angle when $\nu > (\mu_0\epsilon_2)^{-1/2}$ in Table I should read as

$$\theta_c > \sin^{-1} \{ (\epsilon_2/\epsilon_1)^{1/2} [1 + (\epsilon_0/\epsilon_1)^{1/2} \beta] / [1 + (\epsilon_2/\epsilon_0)^{1/2} \beta] \}.$$

Erratum: Measurement of Atomic-Stopping Cross Sections at Low Energies

[38, 3660 (1956)]

W. WHITE AND R. M. MUELLER

Nuclear-Chicago Corporation, Des Plaines, Illinois

In the second paragraph on page 3660 replace "With beam currents of 10-100 mA, . . ." by "With beam currents of 10-100 nA, . . ."