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.[3,9-11] 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 donor[4] 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 accepter.[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. Kroger, 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

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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, Bridgman[1] 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, Bridgman[2] unequivocally established the existence of