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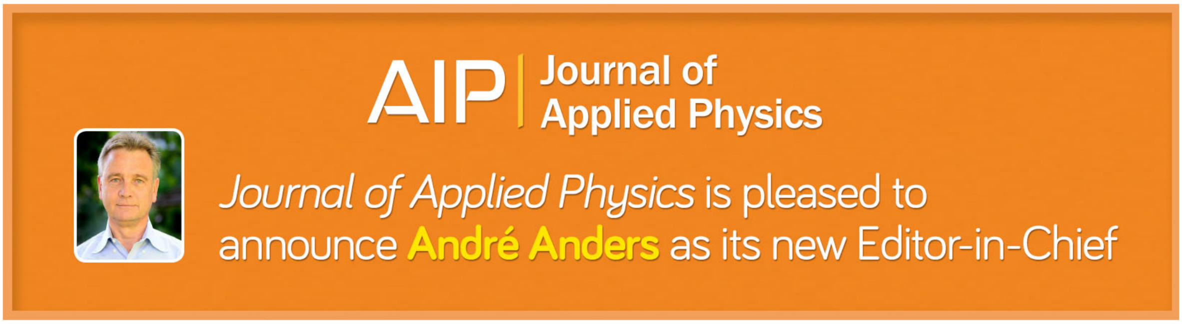

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Electrical and Optical Properties of Mercury Selenide (HgSe)

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HgSe single crystals are grown by zone melting. The compound crystallizes in the zinc-blende structure and splits into (100) planes. For temperatures ranging from 90° to 500°K conductivity, Hall effect and thermoelectric power are measured; above 500°K evaporation of HgSe begins. The lowest carrier concentration of the crystals at 300°K is 3.5×10^{17} cm^{-3}. Only *n*-type conduction is found. The highest mobility at 300°K is 18 500 cm^2/v sec. Magnetoresistance shows that the longitudinal effect is very small compared with the transverse. From the photo emf of the *p*-*n* junction Se/HgSe crystal and from the absorption edge of layers the energy gap of 0.5 to 0.75 ev is obtained. Using the temf and the absorption an estimation of the effective mass leads to 0.04 to 0.07 m_0.

I. INTRODUCTION

ONLY a few facts about the semiconductor HgSe are available. Polycrystalline material and single crystals are known to have a high electron mobility.[1–3] The mobility in HgSe layers is also remarkable. The conductivity of such layers practically does not depend upon temperature.[4] There are contradicting experimental results about the energy gap and little work has been done on the scattering mechanism. We have tried to obtain more information about the HgSe.

II. PREPARATION OF SAMPLES

Even at room temperature, Hg and Se join at the surface to form HgSe. The compound is produced by annealing stoichiometric amounts of the components in evacuated quartz crucibles. The melting point of 960°K is given by Blum and Regel.[1] Rodot,[5] however, finds the point at 1035°K. In spite of the high melting point, the evaporation of the material already begins at 500°K. In a vacuum, it sublimates again as HgSe at the cold sides of the vacuum bell jar. This is pointed out by x-ray investigation. To prevent evaporation, zone melting is carried out under high partial pressure of both components. The purity of Se is 10^{-5} and of Hg 10^{-4}. Before preparing the compound, Hg is distilled three times in a vacuum.

Single crystals obtained by splitting the ingot have an electron concentration of about 5×10^{18}cm^{-3}. By annealing at 500°K for several hours the carrier concentration is lowered; a constant value as low as 3.5×10^{17} cm^{-3} has been reached. Figure 1 shows a sample with a lowest carrier concentration of 1.2×10^{18}cm^{-3}. Annealing

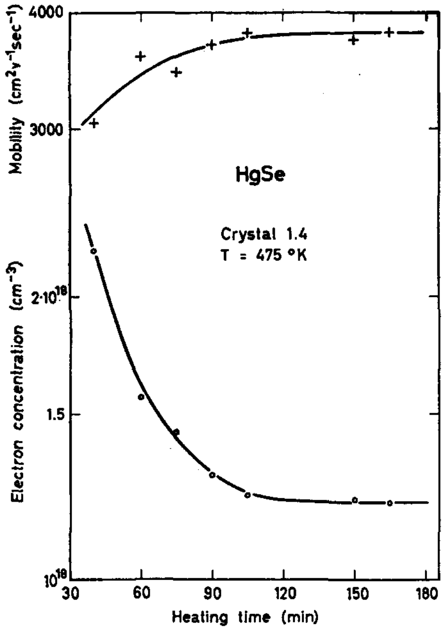

FIG. 1. Variation of electron concentration and electron mobility of a HgSe crystal with annealing time.

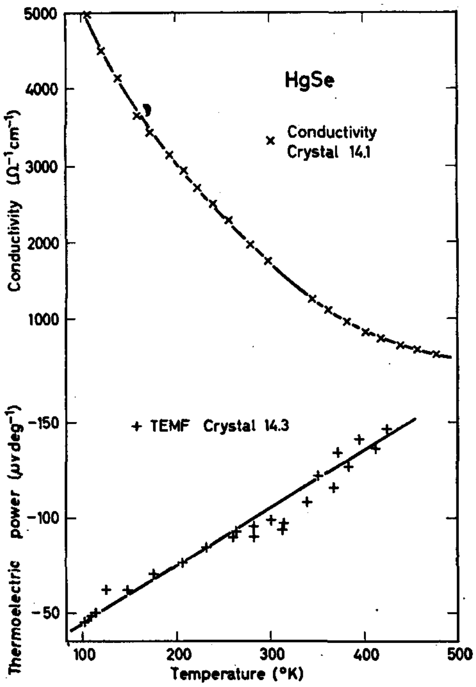

FIG. 2. Conductivity and thermoelectric power of HgSe crystals plotted against temperature.

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[1] A. J. Blum and A. R. Regel, J. Tech. Phys. (U.S.S.R.) **21**, 316 (1951).

[2] T. C. Harman, J. Electrochem. Soc., **106**, 205C (1959).

[3] C. H. L. Goodman, Proc. Phys. Soc. (London) **B67**, 258 (1954).

[4] C. D. Elpat'evskaja, J. Tech. Phys. (U.S.S.R.) **28**, 2676 (1958).

[5] M. Rodot and H. Rodot, Compt. rend. **250**, 1, 1447 (1960).

in air or in a vacuum without any Hg leads to the same effect. However, by a small partial pressure of Hg the electron concentration increases. After annealing, the crystals show a gray coating. It is quite probable that this might be excessive Hg.

We have tried to dope HgSe by adding other elements and by deviations of stoichiometry; but we failed in getting p-type conduction. The method given by de Nobel[6] for CdTe has also achieved no success.

HgSe crystallizes in the zinc-blende lattice, and in splitting generally favors (100) planes. This is confirmed by x-ray investigation. Crystals of about $0.5\times1\times3.5\,\text{mm}^3$ suitable for electrical measurements can be split from the ingot. Cd contacts on the ends of the crystals are created by evaporation. Cd shows practically no influence on the carrier concentration contrary to Ag, Bi, and Sn.

III. EXPERIMENTAL RESULTS

Conductivity and Hall effect are measured on HgSe single crystals. Figure 2 shows that the conductivity decreases as the temperature increases. In Fig. 3 the electron concentration is plotted against reciprocal temperature. These curves supply an activation energy of 0.03 ev. At lower temperatures the concentration, which often varies from test to test, remains at a constant level. The carrier concentration is determined from the Hall coefficient; the mobility is the Hall mobility (Fig. 4). A T^{-a} law holds approximately in two temperature areas. Between 100° and 200°K $a=0.6$ to 0.9; however, between 300° and 500°K $a=3.5$ for all crystals. The temf shown in Fig. 2 increases roughly linearly with temperature and is -100 μv/deg at 300°K. A similar dependence has been observed with HgSe layers.[4]

For three crystals with different orientation, the magnetoresistance is determined at 300°K. One crystal is split from the ingot, the direction of current is [100] and the mobility is 16 200 cm^2/v sec. The other two are grounded with current directions of [110] with mobility of 17 900 cm^2/v sec and [111] with mobility of 17 200 cm^2/v sec, respectively. The electrodes at the ends are built up by evaporation of Cd. In Fig. 5 magnetoresistance is plotted against the angle between current and field. The rotation axes are [010], [1$\bar{1}$0], and [11$\bar{2}$] for current directions [100], [110], and [111], respectively.

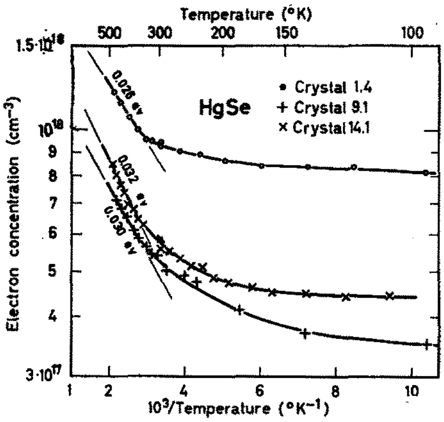

FIG. 3. Electron concentration of HgSe crystals versus reciprocal temperature.

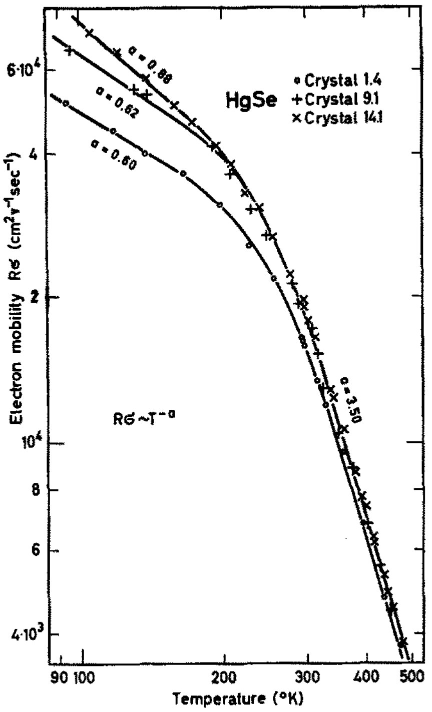

FIG. 4. Hall mobility of the same crystals versus temperature.

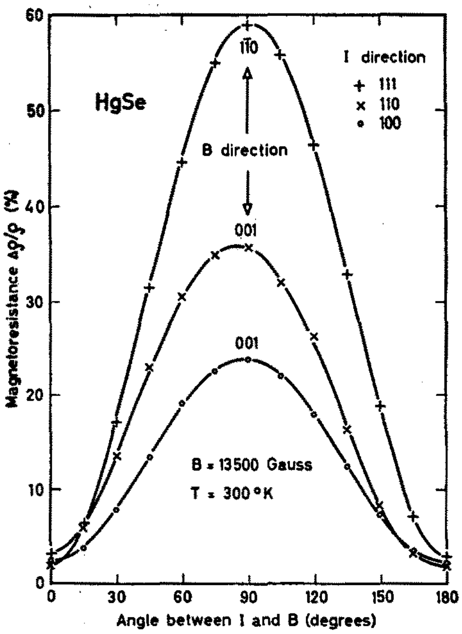

FIG. 5. Variation of magnetoresistance as H is rotated.

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[6] D. de Nobel, Philips Research Repts. 14, 361 (1959).

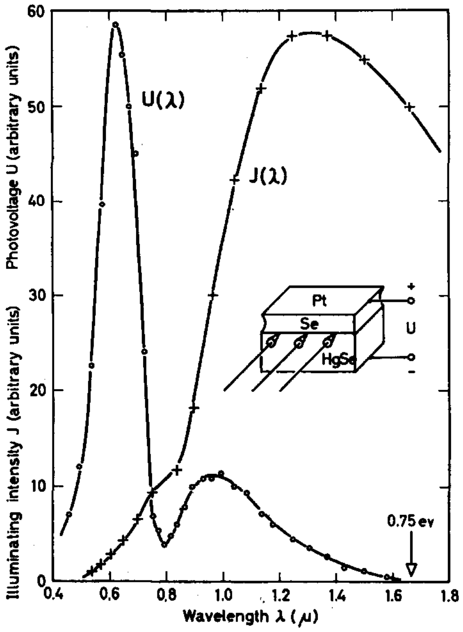

FIG. 6. Dependence of photovoltage and illuminating intensity on wavelength.

The transverse magnetic field depends on the strength of the field and shows a slight parabolic increase from 0 to 5000 gauss and then a linear dependence.

The contact of HgSe with most of the metals shows no barrier layer. A *p-n* junction can be obtained by smearing Se upon a HgSe crystal followed by annealing at 480°K. Se is contacted with Pt to avoid a barrier layer at this side. This cell (Fig. 6) can be used as a rectifier; upon illuminating one side of the junction, a photo emf is observed. These effects can only be obtained when the thickness of the Se layers is more than 50 μ. There is no photo emf at photon energies smaller than 0.75 ev.

The polished slice surfaces of KBr receive HgSe and Cd electrodes through evaporation. (Size of layers 4.5×1.5 cm^2.) The thickness of the layers varies from 0.1 to 2 μ. At 300°K the electrical measurements give values for conductivity ranging from 300 to 1000 $(\Omega\ \text{cm})^{-1}$ and carrier concentrations of 1 to 5×10^{19} cm^{-3}.

We get the absorption coefficient from measurements of transmission and reflectivity of light at these layers over the wavelength range of 1 to 22 μ (Fig. 7). A single crystal with a thickness of 80 μ shows no transmission. A range exists for all layers in which the absorption decreases linearly as the wavelength increases. The center of this linear range corresponds to an absorption coefficient of 10^4 cm^{-1}. If this value is defined as the energy gap ΔE, we calculate for films with different carrier concentrations $\Delta E=0.5$ to 0.7 ev. In Fig. 7 the absorption coefficient of one layer with the concentration of 1.5×10^{19} cm^{-3} (curve a) is shown. The concentration is lowered to 1.13×10^{19} cm^{-3} by annealing for several hours (curve b). The absorption coefficient is proportional to the concentration in the long wavelength tail. Between 5 to 10μ α increases with the law α prop. $\lambda^{3.5}$. The behavior of α at short wavelength (1 to 5 μ) is remarkable. At a constant wavelength the layer with the higher carrier concentration shows the smaller absorption coefficient. The refractive index has a constant value of 2.4 from 5μ to long wavelengths.

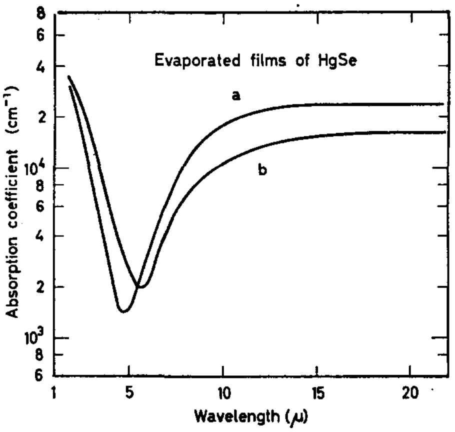

FIG. 7. Absorption coefficient of a HgSe layer, before and after annealing, versus wavelength. Carrier concentrations: curve a, $n=1.55\times10^{19}$ cm^{-3}; curve b, $n=1.13\times10^{19}$ cm^{-3}.

IV. DISCUSSION

There are important relations between the elements and the compounds which crystallize in the diamond and zinc-blende structure within the periodic table of the elements. HgSe can be regarded as an imitation of the gray tin and of the InSb, respectively, as Hg and Se are positioned symmetrically to this element and to the components of the latter compound in the periodic table. InSb has an extremely high electron mobility and indeed, HgSe shows a high mobility also. However it is reduced by the increasing share of the ionic bonding which leads to a stronger interaction of the electrons with the vibrating polar lattice. The change in the nature of the chemical bond can clearly be found in the different splitting of the crystals. The group IV elements split most easily into the (111) planes, as here the lowest number of C–C bonds per unit plane have to be cut. As it was pointed out by Pfister,[7] III-V compounds split into the (110) planes, while with HgSe we always find splitting results into the (100) planes. This change in splitting is caused by the electrostatic power becoming more effective. The energy gap also changes regularly when moving from the group IV elements to the compounds with zinc-blende structure. Goodman[3] predicted $\Delta E=0.7$ ev for HgSe, using the scale of electronegativities. This corresponds well with the value of Sorokin,[8] who calculated $\Delta E=0.7\pm0.10$ ev from the photoelectron emission. Because of the evaporation above

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[7] H. Pfister, Z. Naturforsch. **10a**, 79 (1955).

[8] O. M. Sorokin, J. Tech. Phys. (U.S.S.R.) **28**, 1413 (1958).

500°K and the comparable high carrier concentration, we failed in getting intrinsic HgSe. Regarding the spectral distribution of the photovoltage of the junction Se/HgSe crystal (Fig. 6), there is a great probability that the effect in the infrared is due to band-band transitions within the HgSe. The photovoltage vanishes when the energy of the photons decreases. Thus $\Delta E=0.75$ ev is obtained. The photovoltage shows no distinct threshold, as it is observed with p–n junctions within the same lattice. This is so because there is a continuous junction of two bands with different energy gaps. A photodiffusion voltage in the Se is thought to be responsible for the minimum at 0.8 μ. In this region, the photovoltage consists of a short and a long time effect. Some seconds after illuminating the cell, this long time effect even produces a negative sign of the photovoltage in the region between 0.7 and 0.85 μ. The energy gap, given by the photovoltage, corresponds to a certain degree to ΔE which is obtained from the slope of the absorption coefficient of HgSe layers (Fig. 7). Here, a region of $\Delta E=0.5$ to 0.7 ev has been found, as there is a dependence of ΔE on the electron concentration. At higher concentrations the energy gap increases. This effect is also found in InSb. It is explained by the degeneracy of the electrons in the conduction band. The lower levels of the conduction band are filled progressively by the electrons, so that absorption transitions can only go the higher, empty conduction band levels.

The activation energy of 0.03 ev which was found for the crystals above 300°K, is thought to be due to a donor. It is not yet clear whether it is caused by strange impurities or by excessive Hg. The exact scattering mechanism in HgSe is not known; therefore the electron concentration is calculated by the simple formula $n=f/eR$; $f=1$. This introduced error should be of little significance; f goes to 1 when approaching degeneracy of the electron gas and in the case of increased scattering by optical vibration of the lattice.

Using the experimental data of the thermoelectric power (Fig. 2) for different temperatures, m_n^* is evaluated from the formula

$$\Theta=-k/e[2+\ln 2(2\pi m_n^* kT)^{\frac{3}{2}}/nh^3];$$

$m_n^*=0.04$ to 0.07 m_0 is obtained. The assumptions of the formula, i.e., nondegenerate electron gas and spherical energy surfaces are not fulfilled here. On the other hand, the thermoelectric power is not a sensitive indicator for the scattering mechanism. Calculations based on different scattering mechanisms do not differ significantly. Also in InSb $m_n^*=0.013$ m_0 is obtained by cyclotron resonance experiments. Concerning the mentioned relations to this compound, the value for m_n^*, (about four times larger than in InSb), is quite reasonable, especially since the mobility in InSb is about four times larger than in the HgSe.

Another estimation of m_n^* in HgSe layers can be made by using the infrared absorption between 5 and 10 μ. The increase of the absorption coefficient follows the law α prop. $\lambda^{3.5}$. This means ionized impurity scattering, when you take into account the enlarged theory of Fröhlich.[9] Presuming this mechanism, m_n^* may be evaluated using the data from optical and electrical experiments. These are conductivity, electron concentration, absorption coefficient, and refractive index. The evaluation is carried out as it is shown in[10] and leads to $m_n^*=0.04$ m_0. This corresponds well with m_n^* obtained from the temf, although crystals and layers with a different scattering mechanism are observed. If ionized impurity scattering really would be the exact mechanism, the mobility of the layers should vary prop. $T^{1.5}$. As has been pointed out,[4] there is virtually no dependence on temperature. This is exactly what we find for the mobility in layers. In the theor yof Fröhlich, nondegeneracy is supposed, but degeneracy is indicated by the dependence ΔE (n). When calculated by this method m_n^* does not offer a high degree of accuracy.

Rodot[5] notes that magnetoresistance in HgSe crystals with current in [111] direction is even larger in a longitudinal field than in a transverse field. Our experiments cannot confirm this matter. Three crystals with current in [111], [110], and [100] show a similar dependence of magnetoresistance on the angle between field and current. In the case of a longitudinal field, there is only a very small change in resistance in the three crystals compared with the transverse field. Perhaps there may be a certain deviation from an isotropic conduction, because in the case of current in [111] direction, magnetoresistance is larger than in the other crystals. This is not due to the different mobilities since there is no significant difference between them. Contrary to Rodot we have to assume that the simple spherically symmetrical band centered at $k=0$ gives a better approach than his model. For a transverse field, the dependence of magnetoresistance upon the field is linear already at low fields. This is quite reasonable, when you consider the high mobility in HgSe. The simple theory, which leads to a parabolic dependence, is valid only for $\mu B\ll 1$.

Rodot[5] presents the dependence of the mobility in HgSe single crystals with $n=3.5\times 10^{18}$ cm^{-3}. He finds μ prop. T^{-a}, $a=2$. In polycrystalline HgSe with $n=2\times 10^{18}$ cm^{-3}, $a=2.5$ was found.[4] In a crystal with $n=2.3\times 10^{18}$ cm^{-3}, we determined $a=2.5$ between 200° and 500°K. Purer crystals (5 to 9×10^{17} cm^{-3}) always show $a=3.5$ in this region (Fig. 4). Consequently, the scattering mechanism depends upon the electron concentration. The exponent increases from 2 to 3.5 when the concentration is lowered from 3.5×10^{18} to 5×10^{17} cm^{-3}. At lower temperatures the curve of the mobility is flattened, indicating that a different scattering mecha-

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[9] Y. H. Fan and M. Becker, *Proceeding of the Reading Conference* (Butterworths Scientific Publications, Ltd., London, 1951), p. 132.

[10] K. J. Planker, and E. Kauer, Z. angew. Physik 12, 425 (1960).

nism might have become effective. Because of the relation to InSb, similar scattering mechanisms (as pointed out for InSb by Ehrenreich[11,12]) might be strong in HgSe. The screened polar interaction is thought to be of particular importance since the ionic part of the bond should be larger in HgSe than in InSb and screening effects are likely because of the high density of conduction electrons. On the other hand, intrinsic InSb with a considerably lower carrier concentration has been observed.

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[11] H. Ehrenreich, J. Phys. Chem. Solids 2, 131 (1957).

[12] H. Ehrenreich, J. Phys. Chem. Solids 9, 129 (1959).

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Edge Emission in Zinc Selenide Single Crystals

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Edge emission in single crystals of ZnSe subjected to ultraviolet radiation at low temperatures has been examined in the temperature interval from 4.2° to 77°K. Two distinct edge emission spectra have been found indicating that two different types of single crystals exist. For type I crystals the edge emission spectrum at 4.2°K contains 10 lines located between 4400 A and 4800 A; at 77°K the emission spectrum contains two lines. For type II crystals the edge emission spectrum at 4.2°K contains 14 lines located between 4400 A and 4900 A; at 77°K the emission spectrum contains three lines, one of which is located at the fundamental absorption edge of the crystal. Both crystal emissions show evidence of phonon interaction with the ZnSe lattice and both emissions undergo significant reductions in intensity as the crystal temperature increases from 4.2° to 77°K.

I. INTRODUCTION

SINGLE crystals of ZnSe irradiated with ultraviolet light at low temperature emit a characteristic fluorescence known as edge emission.[1] This emission, appearing on the long wavelength side of the absorption edge of the crystal, is made up of a series of lines and bands whose wavelengths vary between 4400 A and 4900 A. In appearance the edge emission spectrum in ZnSe is similar to the edge emission spectrum in CdS.[2–5] This might be expected since ZnSe, which has the zincblende structure, and CdS, which has the wurzite structure, are similar II–VI semiconductor compounds. The two compounds have fundamental absorption edges in the blue region of the spectrum. A value of 2.554 ev has been reported by Thomas and Hopfield[6] for CdS and the value for ZnSe is 2.83 ev, both values being obtained at 4.2°K. In CdS the emission is made up of a series of lines and bands between 4800 and 5600 A which reflects the longer wavelength absorption edge.

Edge emission in ZnSe has been examined for several samples of single crystals taken from different crystal growth runs. All of the crystals examined were grown from the vapor phase by the same method used to grow single crystals of cadmium sulfide.[7] The samples of ZnSe crystals used for this investigation were made up of a series of yellow rod-shaped crystals. The two distinct edge emission spectra observed for the different samples indicate that two different types of single crystals are present. It is possible that the difference in the two types of crystals may be due to different host lattice defects.

It is the purpose of this paper to report on the nature and structure of edge emission observed in the two

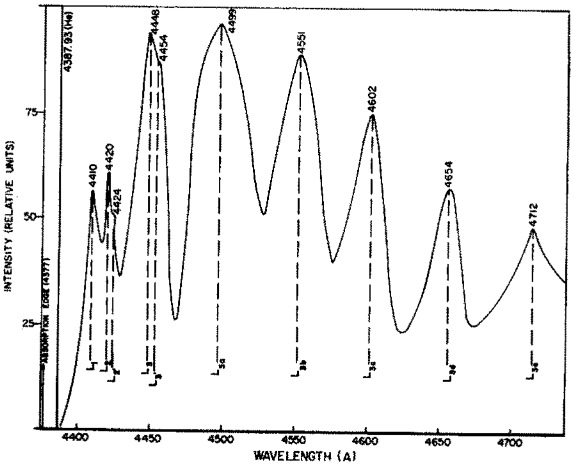

FIG. 1. Edge emission spectrum for type I ZnSe single crystals at 4.2°K.

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[1] F. A. Kroger, Physica 7, 1 (1940).

[2] L. R. Furlong and C. F. Ravilious, Phys. Rev. 98, 954 (1955).

[3] J. J. Lambe and C. C. Klick, Phys. Rev. 98, 909 (1955).

[4] M. Bancie-Grillot, E. F. Gross, E. Grillot, and B. S. Razbirin, Optika i Spektroskopiya 5, 461 (1959).

[5] L. S. Pedrotti and D. C. Reynolds, Phys. Rev. 119, 1897 (1960).

[6] D. G. Thomas and J. J. Hopfield, Phys. Rev. 116, 573 (1959).

[7] L. C. Greene, D. C. Reynolds, S. J. Czyzak, and W. M. Baker, J. Chem. Phys. 29, 1375 (1958).