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メタデータ	言語: English 出版者: 公開日: 2011-12-27 キーワード (Ja): キーワード (En): 作成者: INOUE, Masasi メールアドレス: 所属:
URL	http://hdl.handle.net/10098/4730

EPR Studies on Mn^{2+} in Sintered Compounds

$\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{CdS}_{1-x}\text{Se}_x$ *

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(Received Feb. 18, 1972)

For further understanding of a mixed system in II-VI compounds, the EPR experiments have been made on the Mn^{2+} (0.02%)-doped sintered powders of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{CdS}_{1-x}\text{Se}_x$ ($x=0, 0.25, 0.50, 0.75, 1.0$) over the temperature range from 77 to 500 K. Attention has been paid on the variation of the hyperfine interaction constant A with composition and its temperature dependence. These properties are found different between the two mixed systems, because of the difference in the crystalline environment. A qualitative discussion for a mixed system is made on the basis of the current information.

1. INTRODUCTION

Experimentally, a number of physical properties of a mixed crystal from II-VI compounds have been found to be changed with composition from those of the original components. Theoretical treatment is not, however, so simple because of the irregular distribution of foreign atoms over the crystal, although many attempts have been made from rather simplified models and approximations to account for the experimental results. For instance, Verleur and Baker¹⁾ have developed a model to understand the infrared reflectivity spectra of $\text{CdS}_{1-x}\text{Se}_x$ mixed crystals, whose main features are the dependence of the phonon frequencies and strengths on concentration x and on the short-range clustering of the cations around the anions. Chang and Mitra²⁾ have, on the other hand, studied the behavior of the long-wavelength optical phonons by the modified random-element-isodisplacement model to predict whether a given mixed crystal exhibits "one-mode" or "two-mode" type. The similar criterion is also investigated numerically for the one-dimensional model by Matsuda and Miyata.³⁾ These studies are mainly concerned with the change of the crystal lattice vibration (mostly optical branch) with composition.

At the same time, it is of current interest for many researchers to study the crystalline environment in the mixed crystal. One of the useful tools for this purpose is the electron paramagnetic resonance (EPR) experiment. So far the EPR studies have been reported on Mn^{2+} in powder $\text{ZnS}_{1-x}\text{Se}_x$,⁴⁾ $\text{Zn}_{1-x}\text{Cd}_x\text{S}$,⁵⁾ and single crystal

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$\text{CdS}_{1-x}\text{Se}_x$.⁶⁾ In a previous paper,⁷⁾ we have reported the EPR studies on Mn^{2+} in the mixed single crystal $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ ($0 \leq x \leq 0.25$) and proposed a simplified model to predict the overall change in the EPR parameters (g -value, hyperfine interaction constant A , and crystalline field constant a) for this mixed system as well as other II-VI compounds. These parameters are well described in terms of the effective distance between the magnetic ion and the anion, which is defined by taking account of the ionic radii of each ions and the lattice constant of the host crystal. Moreover, it should be noted that the bonding and chemical nature of semiconductors as well as insulators have recently been a focal point of interest for many solid state physicists;⁸⁾ *i. e.*, effective charge, ionicity, and electronic charge densities.^{9)–11)}

In view of these circumstances, the similar EPR experiments for Mn^{2+} in sintered mixed compounds $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{CdS}_{1-x}\text{Se}_x$ have been made for further understanding of physics of a mixed system. Although single crystals are preferable, as in the previous work for $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$,⁷⁾ the samples used in the present study are sintered powder specimens, partly because the preparation technique is simple, and partly because the hyperfine interaction constant A is independent on the crystal orientation. In this paper are reported the experimental results about the composition dependence of the constant A and its temperature dependence, and are compared with the previous model⁷⁾ and with the existing theory to study the different crystalline environment in the two mixed systems. For both systems the temperature dependence of the EPR signals has also been measured to get information about the Mn^{2+} concentration and hence about the charge transfer mechanism associated with the Mn^{2+} -states in the energy band. These will be reported in another paper.²²⁾

2. EXPERIMENTAL

The samples were prepared in the following way. The original sintered powders of CdS and ZnS , both of 5-nine purity, produced by Gould Laboratories (Cleveland), were mixed in a mortar in a desired ratio to make the mixed compounds $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x=0, 0.25, 0.50, 0.75, 1$) with MnCO_3 powder, where the Mn concentration was calculated to an amount of 0.02%. As in the previous work on $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$, the samples with 0.05% Mn showed broadened EPR lines and the hyperfine structures could not be resolved due to the strong exchange interaction between the Mn^{2+} ions, as discussed by Ishikawa.⁵⁾ The mixed powders were then pressed into a disk shape, and heated for 24 hours at $750^\circ\sim 800^\circ\text{C}$ in N_2 gas flow. The same procedure was employed for the system $\text{CdS}_{1-x}\text{Se}_x$, but in this case the starting materials were single crystals with $x=0.25, 0.50, 0.75, 1$, of 5-nine purity, produced by the same company, which were crashed into powders and pressed. Of course, the samples without heat-treatment did not show any EPR signals. Measurements were carried out over the temperature range from 77 to 500 K by using the same apparatus and the results were analyzed as in the previous study.⁷⁾

3. RESULTS AND DISCUSSION

1) Hyperfine interaction constant vs. composition

The experimental values of the hyperfine interaction constant A at 77 K for the two systems are shown as a function of the composition x in Figs. 1 (a) and (b), respectively. For comparison the data from Deigen *et al.* for the same system is also given, which they obtained with the single crystals prepared by a sublimation method.⁶⁾ These results are to be compared with the simplified prediction⁷⁾ that the EPR parameters for Mn^{2+} in II-VI compounds are characterized more clearly by the effective distance than usual ionicity. If this model is applied to the present mixed systems $Cd_{1-x}Zn_xS$ and $CdS_{1-x}Se_x$, then the effective distance for the composition x may be written as

$$d_{eff}(x) = (1-x)d_{CdS}(A-B) + xd_{ZnS}(A-B) + R_{Mn} - (1-x)R_{Cd} + xR_{Zn}, \dots\dots\dots(1)$$

and

$$d_{eff}(x) = (1-x)d_{CdS}(A-B) + xd_{CdSe}(A-B) + R_{Mn} - R_{Cd}, \dots\dots\dots(2)$$

respectively. The values $d_{ZnS}(A-B)$, $d_{CdS}(A-B)$, and $d_{CdSe}(A-B)$ are the inter-atomic distance of the anion and cation of ZnS ,¹²⁾ CdS ,¹³⁾ and $CdSe$,¹⁴⁾ while R_{Mn} , R_{Cd} , and

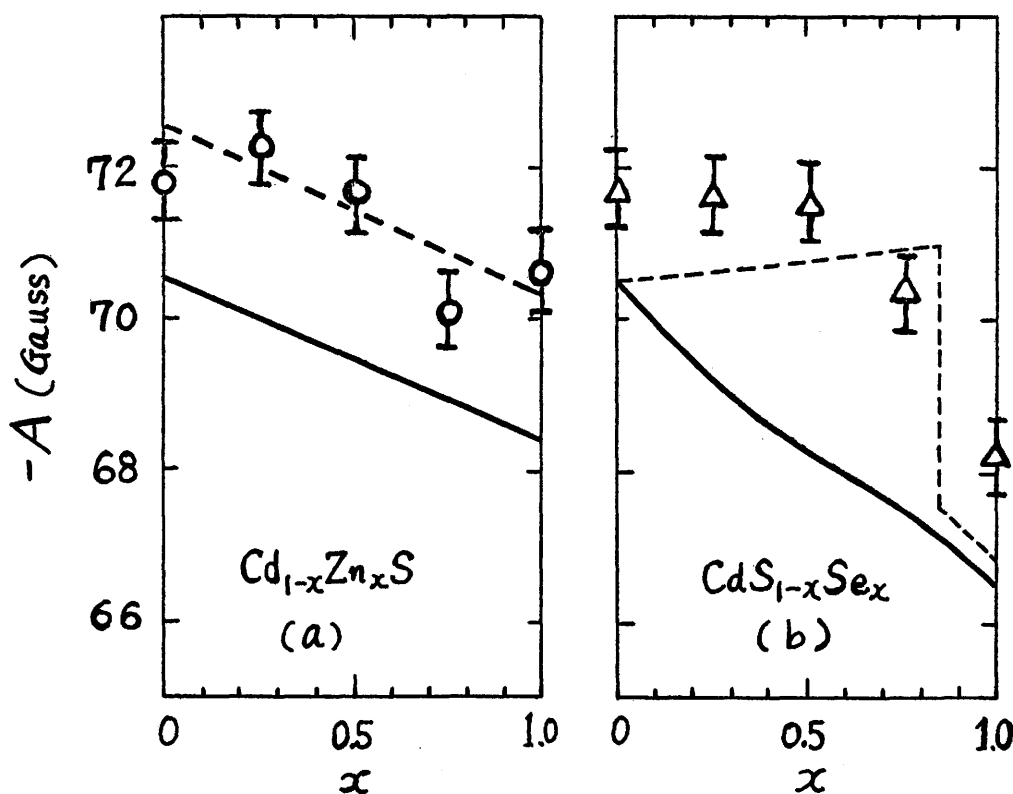


Fig. 1. The hyperfine interaction constant against the composition x for (a) $Cd_{1-x}Zn_xS$ and (b) $CdS_{1-x}Se_x$. The solid lines are the predicted curves from data of II-VI compounds.¹⁵⁾ In Fig. 1 (b) the observed values by Deigen, *et al.*⁶⁾ are indicated by a dotted line.

R_{Zn} are the ionic radii of the cations Mn, Cd, and Zn, respectively. With the use of the data for the constants A obtained with II-VI single crystals, compiled in Title's Tables 6.1 and 6.2,¹⁵⁾ we can now estimate the values A for the mixed systems by an interpolation procedure. The estimated values are demonstrated in Fig. 1 by the solid lines.

The samples used are polycrystalline powders, and the observed values are a little larger than the predicted lines. In the case of $Cd_{1-x}Zn_xS$, the constants A decrease almost linearly with x , while in $CdS_{1-x}Se_x$ there is a drastic change at $x=0.7\sim 0.8$ in contrast with the predicted curve. The overall behavior of the system $CdS_{1-x}Se_x$ is, however, similar to that found with single crystals by Deigen, *et. al.* Although the hyperfine interaction constants are in general less sensitive to the crystalline environment than the crystalline field constant a , comparison of Fig. 1 (a) with (b) indicates that the constants A are more dependent on the change of the anion than that of the cation. However, there is no possible mechanism to account for the drastic change at $x=0.7\sim 0.8$ in the system $CdS_{1-x}Se_x$. As pointed out by others,^{4), 6)} we are to arrive at a dubious conclusion that it is due to the stronger chemical affinity of Mn ions with S ions. To our knowledge, there are no experimental evidence except the constants A which shows such a drastic change at the composition $x=0.7\sim 0.8$ in $CdS_{1-x}Se_x$.

2) Temperature dependence of the constant A

Little is known about the temperature dependence of the hyperfine constant A for II-VI compounds as well as its mixed system, except for ionic crystals such as CaF_2 and $NaCl$ etc. From this measurement for $Cd_{1-x}Mg_xTe$ we have estimated the variation of the Debye temperature with x .⁷⁾ The similar measurements were carried out for the present two mixed systems and the constants A were also found to decrease with temperature. In Fig. 2 are shown the ratios of the observed values A at 100 to 500 K as a function of x , which is equal to the coefficient B in a simplified expression of the temperature-dependent hyperfine constant, $A(T)=A_0-BT$. Fig. 2 shows that the coefficient B of CdS is smaller than those of the counterparts ZnS and $CdSe$, and that the x -dependence of B is different between the two systems.

The results may be compared with the theoretical calculation developed by Huang for the case of Mn^{2+} in octahedral symmetry, in which the Van Vleck orbit-lattice interaction is used to calculate the

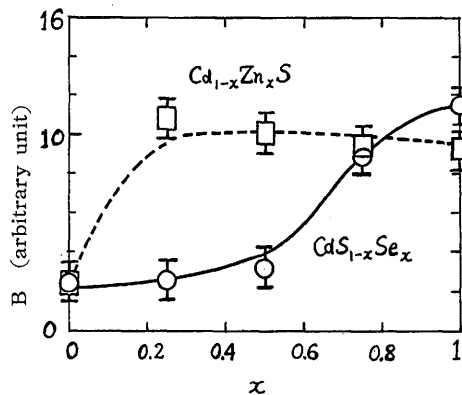


Fig. 2. The coefficient B of the temperature-dependent hyperfine constant in a simplified form of $A(T)=A_0-BT$ for the two systems against x .

phonon-induced hyperfine interaction constant of Mn^{2+} in alkali halides.¹⁶⁾ According to this theory the coefficient B is approximately expressed as

$$B \propto (e \cdot e_{eff})^2 / \rho R^3 \theta_D^3, \quad \dots\dots\dots(3)$$

where e is the charge of the bonding electron of the paramagnetic ion, e_{eff} the effective charge of an anion, ρ the density, R the anion-cation distance, θ_D the Debye temperature. For comparison, let us first take the ratio of B between the two components. Numerical values of each compounds are given in Table I, and the value $d(\text{A-B})$ is used as R . For ZnS and CdS, we then have $B_{\text{ZnS}}/B_{\text{CdS}} \approx 1.42$, where we assume e and e_{eff} to be same for ZnS and CdS. Similar comparison between CdS and CdSe gives the ratio $B_{\text{CdSe}}/B_{\text{CdS}} \approx 1.70$, where the anion is different; S and Se. Since there are no data for e_{eff} available, we take here the value e_{eff} as the local effective charge e_l obtained empirically; $e_{\text{Se},l} = 6.5 \times 10^{-10}$ for Se and $e_{\text{S},l} = 5.5 \times 10^{-10}$ (esu) for S.¹⁾ This is based on the first suggestion by Brodsky and Burnstein that the effective ionic charge in II-VI compounds has a local and non-local portion.¹⁷⁾

As mentioned in the introduction, there are recently many works on the chemical nature of the bonding such as ionicity and effective charge, *e. g.*, Szigeti's charge¹⁸⁾ and Callen's charge.¹⁹⁾ If we use simply the Szigeti's charge e_s^* as e_{eff} , then the above ratios become $B_{\text{ZnS}}/B_{\text{CdS}} \approx 1.73$ and $B_{\text{CdSe}}/B_{\text{CdS}} \approx 1.04$. As seen from Fig. 2, these rough estimations show that the use of e_l is better than e_s^* . It is also seen that the values of B for ZnS and CdSe are about four times as large as that of CdS, but the above estimation indicates they are 1.42 and 1.70 times as large as CdS, respectively. This discrepancy can be easily compensated by taking a different scale factor for each compounds, as done for CaF_2 (scale factor=2.4) and BaF_2 (scale factor=9) to fit the experimental values with the calculated values.²⁰⁾

Furthermore, it is of interest to estimate the optical phonon contribution to the hyperfine interaction constant by the Huang's calculation. This is evaluated by the ratio of the zero-point contribution of acoustic to optical phonon as

$$C_{op}(\text{O})/C_{ac}(\text{O}) \propto \theta_D \rho \sum_r (\nu_{rB})^{-1} / M, \quad \dots\dots\dots(4)$$

where M is the atomic mass of the crystal and ν_{rB} the optical phonon frequency at the Brillouin zone boundary for the r -th optical branch. If we assume here ν_{rB} to be constant for all compounds, we get for ZnS and CdSe relative to CdS, respectively,

$$\left(\frac{C_{op}(\text{O})}{C_{ac}(\text{O})} \right)_{\text{ZnS}} / \left(\frac{C_{op}(\text{O})}{C_{ac}(\text{O})} \right)_{\text{CdS}} \approx 1.4, \quad \left(\frac{C_{op}(\text{O})}{C_{ac}(\text{O})} \right)_{\text{CdSe}} / \left(\frac{C_{op}(\text{O})}{C_{ac}(\text{O})} \right)_{\text{CdS}} \approx 0.7,$$

Table 1. Numerical values used in the calculation.

	Inter-atomic distance $d(\text{A-B})$ (Å)	Debye temperature θ_D (K)	Density ρ (gr/cm ³)	Szigeti's charge e_s^*/e
ZnS	2.34	246	4.04	0.96
CdS	2.52	214	4.82	0.89
CdSe	2.62	170	5.81	0.83

which means the zero-point optical phonon contribution in ZnS is larger than in CdSe relative to CdS. This relative difference may also be compared with the magnitude of the longitudinal optical phonon energies $\hbar\omega_l$ (in eV);²¹⁾ 0.044 (ZnS), 0.038 (CdS), and 0.027 (CdSe).

Hitherto we have confined ourselves to the discussion of the extreme cases; *i. e.*, comparison of the coefficient B between the two groups ZnS vs. CdS and CdSe vs. CdS. Now turn our attention to the mixed systems. The observed composition-dependence of B is different between the two systems, as seen in Fig. 2. However, theoretical evaluation for these behaviors seems to be complicated, which is one of the current problems for physics of the mixed crystal. As reported frequently, to predict the behaviors let us here also apply the interpolation method to all physical quantities Q in Eq. (3), where Q stands for the inter-atomic distance $d(A-B)$, density ρ , Debye temperature θ_D , and effective charge $e_{eff}(=e_i)$. That is, the quantities $Q(x)$ for a given mixed crystal with the composition x will be written as, *e. g.*, in the case of $CdS_{1-x}Se_x$,

$$Q(x) = (1-x)Q_{CdS} + xQ_{CdSe}, \quad \dots\dots\dots(5)$$

where Q_{CdS} and Q_{CdSe} are those of the constituent semiconductor CdS and CdSe, respectively. The same is applied to the system $Cd_{1-x}Zn_xS$, where the effective charge is assumed to be constant. From these values we can calculate the relative change in the coefficient B for the two groups from Eq. (3), where we neglect the scale factor. The results are shown in Fig. 3, in which a monotonic increase in the relative values of B is seen with the composition x .

Several factors are, therefore, to be pointed out why the estimated behaviors based on the Huang's calculation do not fit with the observed ones as follows.

1) Our samples are sintered powders, heated in N_2 gas flow, and thus there may possibly exist a large number of lattice defects in the specimens; *i. e.*, crystal imperfection, which may in turn give rise to some change of the lattice vibration from an ideal arrangement of the anions and cations or stoichiometric array of the atoms.

2) The discrepancy is seen larger for $Cd_{1-x}Zn_xS$ than for $CdS_{1-x}Se_x$. The assumption that the effective charge of the anion in $Cd_{1-x}Zn_xS$ is constant over the whole composition, seems incorrect. Is there any other experimental evidence which demonstrates the difference in the crystalline environment, especially of the anion in $Cd_{1-x}Zn_xS$?

3) Eq.(3) involves other quantities besides the effective charge, for which we have so far employed the interpolation proce-

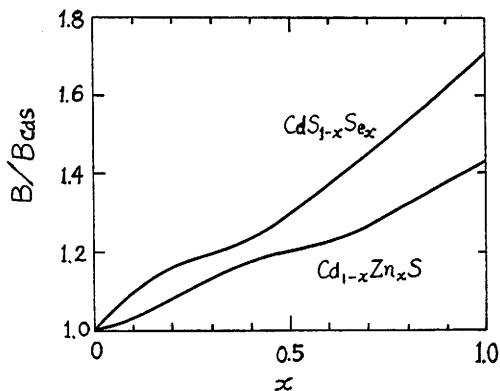


Fig. 3. The predicted behavior of the coefficient B with x normalized by the value of CdS, calculated by Eq. (3) with the values given in Table 1.

ture. This method may not always be correct to study the mixed system, though it is a sort of approach to the problem. Unfortunately, little has been investigated on the composition dependence of each quantities.

4) Our observed data are compared with the Huang's calculation, which is based on the Van Vleck orbit-lattice interaction for Mn^{2+} in the octahedral coordination and is verified to agree with the data of ionic crystals. However, the situation is different in II-VI compounds, where the Mn^{2+} ion is in the tetragonal symmetry.

5) In connection with the different behaviors between the two mixed systems $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and $\text{CdS}_{1-x}\text{Se}_x$, it is noted that the former belongs to the "one-mode" type and the latter to the "two-mode" type by Chang and Mitra's classification.²⁾ In order to understand the observed behaviors of the composition dependence of the hyperfine interaction constant and its temperature dependence, it is desired to study both theoretically and experimentally on the lattice vibration and chemical nature of the crystals for II-VI compounds as well as its mixed systems.

Acknowledgements

The author would like to thank Professor E. Tatsumoto (Hiroshima University) for many discussions of this problem and much useful advice. Thanks are due to Professor C. Y. Huang for the generous hospitality extended to me and for valuable suggestions, F. J. Rachford, K. Sugawara, and W. Jennings for their help of the EPR measurements at the Department of Physics, Case Western Reserve University. He is also grateful to Professor H. Yagi for his continuing encouragement throughout this study and to the Ministry of Education of Japan for its financial support during his stay at the Department of Physics, Case Western Reserve University. This work will also be submitted to J. Phys. Soc. Japan.

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