dependence of ϵ_2 may determine whether the process is due to a band formed by positively charged impurity ions or the excited states of the neutral impurity. It may also be of interest to determine if ϵ_2 and ϵ_1 have a linear relation also for other acceptors in Ge and for p-Si. The experimental results indicate that ϵ_3, in this concentration region, is a function of the effective Bohr radius although the detailed process leading to ϵ_3 has not been established.

The investigation of the transition to metallic conduction yields the stress dependence of the effective Bohr radius. The form of the stress dependence indicates the importance, at high concentrations, of the potential energy term which can be neglected at low concentrations.

The low-stress behavior of the resistivity indicates that the effective Bohr radius is initially decreasing with increasing stress, due to the change in the relative contributions of the two valence bands to the impurity wave function.

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Paramagnetic Resonance of $^8S_{7/2}$ Ions in CdSe and CdTe

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Paramagnetic-resonance measurements for Gd^{3+} in CdSe and CdTe are reported. The resonance parameters for Gd^{3+} are compared with those of the isoelectronic ion Eu^{2+} in the same crystals. The b_n^m parameters characterizing the splitting of the $^8S_{7/2}$ ground state are much larger for Gd^{3+} than for Eu^{2+} in both CdSe and CdTe. The g values for Gd^{3+} are significantly lower than those for Eu^{2+}. The presently available theories of the splitting of the $^8S_{7/2}$ state are considered in the interpretation of these results.

INTRODUCTION

In this paper paramagnetic resonance measurements for Gd^{3+} in the II-VI compounds CdSe and CdTe are reported. Measurements for the isoelectronic ion Eu^{2+} in these crystals have previously been reported.[1]

The literature has very few references to measurements on rare-earth ions in semiconducting crystals. One is led to speculate whether this is due to a lack of previous interest or due, perhaps, to difficulties in incorporating rare-earth ions in these materials. No difficulty was encountered in incorporating Eu or Gd into CdSe and CdTe. However, only negligibly small amounts of Eu or Gd were obtained in ZnSe and ZnTe. This is probably due to the smaller size of the Zn ion as compared to the rare-earth ions.[2,3] The Cd ion, on the other hand, is comparable in size to those of the rare-earth ions.[3] The resonance measurements for Eu and Gd in CdSe and CdTe, as will be shown, provide some information concerning the surroundings of the rare-earth ion. The information is not without ambiguity because of the presently inadequate understanding of the splitting of the $^8S_{7/2}$ state.

Information concerning the surroundings of the rare-earth impurity is obtained from the effect of the crystalline field of the surrounding ions on the electronic ground state of the rare-earth ion. The crystalline field removes some of the degeneracy of the ground state and leads to splittings which for most rare earths are in the optical range (100 to 1000 cm^{-1}). Paramagnetic resonance measurements carried out in the microwave region are therefore limited to the lowest lying level. The measurement of the g tensor of this level is sufficient to determine the symmetry of the rare-earth site, but provides insufficient data to determine the magnitudes of the radial parameters characterizing the crystalline field. In certain cases where the spin lattice relaxation is via an Orbach process,[4] the position of the next highest level may be determined by a measurement of variation of the spin-lattice relaxation time with temperature.

One advantage of working with Eu^{2+} or Gd^{3+} is that they have splittings of their ground states which are in the microwave rather than the optical range. All the data concerning the splittings may therefore be obtained by paramagnetic resonance techniques. There is however, at present, some difficulty in interpreting the splitting of the ground state. The $4f^7$ configuration

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of Eu^{2+} and Gd^{3+} consists of a half-filled *f* shell and has a $^8S_{7/2}$ ground state. An *S* state cannot be split by the action of the crystalline field alone. The splitting is a result of higher order perturbations involving spin-orbit coupling or spin-spin coupling as well as the crystalline field.[5] It is possible to construct several perturbations of this kind and there has been considerable effort to determine both experimentally and theoretically which are the dominant perturbations.[6] It is helpful in this regard to carry out studies on the same ion in several isomorphic crystals[1] or else to study a group of isoelectronic ions in the same crystal.[7] In either case, the number of parameters that vary from sample to sample is held to a minimum and differences in the resonance spectra are more easily correlated with the few varying parameters. Comparative studies of this type can be used to obtain at least a qualitative understanding of the crystalline field whereas a single measurement, because of uncertainties in the theoretical understanding of the *S*-state splitting, would by itself be much less helpful.

The measurements reported here on the isoelectronic ions Eu^{2+} and Gd^{3+} in CdSe and CdTe allow some conclusions regarding the nature of the perturbation causing the ground-state splitting to be made.

The Theory of the Spectrum

The Gd^{3+} ion both in CdSe and CdTe was found to have the symmetry of the Cd^{2+} ion for which it substitutes. This indicates that the negative charge compensating the extra positive charge on the Gd^{3+} ion is not within a few lattice spacings of the Gd^{3+} ion. The spin Hamiltonians to be used for Gd^{3+} in these lattices are therefore identical to those for Eu^{2+}.[1] The splittings that result from these Hamiltonians and the expressions for the allowed transitions between the split levels have previously been given in the literature. In the notation to be used in this paper, the expressions appropriate for the cubic symmetry of CdTe have been given by Baker *et al.*[8] Those appropriate for the hexagonal symmetry of CdSe have been given by Low and Zusman.[9] The splittings of the ground state are characterized by the parameters b_n^m. Since the splitting arises from the high-order perturbations referred to earlier, an exact relation between the b_n^m and the radial crystalline field parameters $A_n^m\langle r^n\rangle$ requires a knowledge of the nature of the perturbations involved.[10] Either the spin-orbit coupling ζ or the spin-spin coupling V_{ss} will also be involved in the splitting.

EXPERIMENTAL

The single crystals of Gd-doped CdSe and CdTe were grown by J. A. Kucza. The CdSe crystals were vapor grown. Gd was added in the form of Gd_2Se_3. The CdTe crystals were grown from the melt in the presence of excess tellurium in order to lower the melting point. Gadolinium metal was added to the melt.

Experiments were carried out at 77 and 4.2°K.

RESULTS

The paramagnetic resonance parameters determined at 77°K for Gd^{3+} are given in Table I for CdSe and Table II for CdTe. Included for comparison are the results obtained for Eu^{2+} in these crystals.[1] The signs of the parameters were determined from a study of the relative intensities of the fine structure lines at 4.2°K. (In the case of Gd^{3+} in CdTe, the lines were saturated at 4.2°K and the sign of b_4 was not determined. From the spacings of the lines at 77°K it was shown that b_4 and b_6 have identical signs.)

There are two features to be noted in the results of Table I and Table II. The *g* values for Eu^{2+} are almost equal in CdSe and CdTe, as are the two *g* values for Gd^{3+}. However, the *g* values for Eu^{2+} are significantly higher than those for Gd^{3+}. The dominant parameter in the ground-state splitting, b_4 for CdTe and b_2^0 for CdSe, is over three times as large for Gd^{3+} as it is for Eu^{2+} in these two crystals. The significance of these results will now be discussed.

DISCUSSION OF THE RESULTS

The ability to detect environmental changes due to incorporation of Eu^{2+} and Gd^{3+} in CdSe and CdTe will depend on how accurately the resonance parameters *g* and b_n^m can be theoretically predicted. Our understanding of the splitting of the $^8S_{7/2}$ state is far from complete and this leads to some uncertainty in interpretation of the results. A brief review of the theory of the splitting of the $^8S_{7/2}$ state will be given including possible effects on the splitting due to covalency in the bonding.

The $^8S_{7/2}$ state cannot be split by action of the crystalline field alone. Watanabe[5] first suggested, following his explanation of the splitting of the $^6S_{5/2}$ ground state of the $3d^5$ configuration, that the splitting might arise from a higher order perturbation involving the simultaneous action of the crystalline field and either the spin-orbit or spin-spin coupling. For a particular symmetry it is possible to construct several nonzero perturbations. For cubic symmetry possible perturbations

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TABLE I. Paramagnetic-resonance parameters for Eu^{2+} and Gd^{3+} in CdSe at 77°K.

	g	b_2^0	b_4^0	b_6^0	b_4^3
			10^{-4} cm^{-1}		
Eu^{2+}	1.9914±0.0007	+239.7±2.0	−2.75±0.09	+0.24±0.09	11.7±5.0
Gd^{3+}	1.985 ±0.002	+805.5±1.0	+6.91±0.4	+0.36±0.3	17.5±1.5

have been given by Low[11] and Lacroix[12] and for axial symmetry by Hutchinson *et al.*[6] In both symmetries the perturbations they give depend either linearly or quadratically on the crystalline field potential.

In order to calculate the relative magnitudes of the various possible perturbations it is necessary to calculate first the crystalline field potentials. Since these depend on high inverse powers of the separation of charges in the lattice, an accurate knowledge of the electron-charge distribution in the lattice is required. The accuracy to which electronic charge distributions are determined by x rays is not sufficient for accurate calculation of crystalline potentials.[13] Therefore, experimentally, rather than use the absolute value of the splitting of the $^8S_{7/2}$ state to determine the dependence of the splitting on crystalline potential, variations in the splitting with changes in lattice size are used. Variations in lattice size occur with changes in temperature[6] or may result from application of a hydrostatic pressure.[14] It is also possible to examine the splitting of Eu^{2+} or Gd^{3+} in a set of isomorphic compounds of varying lattice dimensions.[6]

The results obtained to date[6] indicate that in a few cases a single perturbation appears to be the dominant one, but in general for both cubic and axial symmetries, more than one perturbation is necessary to explain the splitting of the ground state. In addition, the pressure experiments of Rimai *et al.*[14] on $SrTiO_3$ doped with Eu^{2+} and Gd^{3+} show that in this lattice the ground-state splitting depends on approximately the fifth power of the crystalline field potential, indicating that more complicated perturbations than those proposed by Low[11] and Lacroix[12] may be necessary in certain cases.

Because of the difficulties encountered in deciding which perturbations are dominant in the splitting of the $^8S_{7/2}$ state, no attempt has been made as yet to determine the effects of covalency on the splitting. Kondo,[15] in his consideration of the splitting of the somewhat analogous case of the $^6S_{5/2}$ ground state of the $3d^5$ configuration, presented a theory in which the covalency in the bonding is considered. In this theory Kondo does not treat the effects of the surrounding ions via the mechanism of a crystalline field potential. Instead he considers the direct interaction between the electrons of the $3d^5$ configuration and the electrons on the surrounding ligand ions, the interaction proceeding via the spin-spin and spin-orbit coupling. In consideration of these interactions the overlap of the wave functions and the covalency of the bonding is taken into account. Kondo's theory is able to account for the ground-state splitting of Mn^{2+} in the alkali halide lattices.

The extension of Kondo's theory to the $^8S_{7/2}$ state of the $4f^7$ configuration is not straightforward. In addition to a parameter characterizing the degree of covalency in the bonding, a second parameter is necessary to account for the shielding of the $4f^7$ electrons by the $5s^25p^6$ electrons. One can predict without carrying out the actual calculations that the shielding will tend to reduce somewhat the effects due to covalency so that as the covalency in the bonds is increased, the ground-state splitting should also increase but not as rapidly as for the $3d^5$ configuration of Mn^{2+}.[16]

The other parameter of interest in this discussion is the g value. The g values that have been measured for Eu^{2+} and Gd^{3+} in all lattices are always less than the free-electron value 2.0023 expected for a pure $^8S_{7/2}$ state. The deviation from the free-electron value has been explained[5,8] as arising from a departure from Russell Saunder coupling. This causes excited $J=\frac{7}{2}$ states of the $4f^7$ configuration to be admixed into the ground $^8S_{7/2}$ state. The amount of admixture α_i of the ith excited state is given by

$$\alpha_i=K_i\zeta/W_i, \tag{1}$$

where K_i is a numerical constant, ζ the spin-orbit coupling parameter, and W_i the energy separation of the ith state from the $^8S_{7/2}$ state. The g value of the admixed ground state is given by

$$g=(1-\sum_i \alpha_i^2)g(^8S)+\sum_i \alpha_i^2 g(W_i), \tag{2}$$

TABLE II. Paramagnetic-resonance parameters for Eu^{2+} and Gd^{3+} in CdTe at 77°K.

	CdTe		
	g	b_4	b_6
		10^{-4} cm^{-1}	
Eu^{2+}	1.9917±0.0005	−7.66±0.10	−0.12±0.14
Gd^{3+}	1.9869±0.0003	(−)24.07±0.06	(−)0.26±0.06

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where $g(^8S)$ and $g(W_i)$ are the g values of the $^8S_{7/2}$ state $(=2.0023)$ and the W_i states, respectively. Since the $g(W_i)$ are always less than the g value for the free electron and α_i^2 is a number less than unity, the g value as given by Eq. (2) is always less than that of the free electron.

Since the bonds in CdSe and CdTe are partially covalent it is relevant to consider what effect covalency has on the g value. For the $3d^5$ configuration Fidone and Stevens[17] suggested that the covalent bonding would mix some of the ligand wave functions with that of the $3d^5$ electrons and result in an altered g value. Experiments have shown[2,16] that for the $3d^5$ configuration the Δg that results from covalency is positive. Watanabe[18] has in fact calculated that a positive Δg is expected from the admixed ligand wave functions.

No calculations have as yet been made for the $4f^7$ configuration. The screening of the $5s^25p^6$ electrons would have to be considered.

Effects due to covalency have been experimentally observed in $4f^n$ configurations other than $4f^7$. Low[19] has reported covalent effects on the g values of $Dy^{3+}(4f^9)$ and $Yb^{3+}(4f^{13})$ in CaO. Much larger effects have been observed for Yb^{3+} in ZnTe and CdTe.[20] In all these cases the g values are reduced from the values expected for a cubic field in an ionic crystal.

The b_n^m Values

The results obtained for Eu^{2+} and Gd^{3+} in CdSe and CdTe will now be considered. There is a pattern in the g and b_n^m values that is similar in both CdSe and CdTe. In both crystals the principal parameter in the splitting b_2^0 or b_4, is some three times larger for Gd^{3+} than it is for Eu^{2+}. Also in both crystals the g values for Gd^{3+} are significantly lower than those for Eu^{2+}.

The ratios of g and b_n^m values for Eu^{2+} and Gd^{3+} in CdSe and CdTe are different from those found in other crystals in which Eu^{2+} and Gd^{3+} have been measured in the same symmetry. Measurements exist in the alkaline earth fluorides,[21] chlorides,[22] and oxides,[23] as well as in $SrTiO_3$.[14] In these crystals the g values of Eu^{2+} and Gd^{3+} are equal to each other within experimental error. In the alkaline earth fluorides and chlorides,[21,22] the b_4 for both Eu^{2+} and Gd^{3+} vary approximately linearly with crystalline field potential and b_4 for Gd^{3+} is slightly less in magnitude than b_4 for Eu^{2+} in these crystals. In the alkaline earth oxides[23] the evidence is that more than one perturbation is responsible for the ground-state splitting. Under these circumstances the ratio of the splitting of Gd^3 to Eu^{2+} might be expected to vary from crystal to crystal and this is found to be the case in CaO and SrO.

Since the perturbations responsible for the splitting of the $^8S_{7/2}$ state in CdSe and CdTe may not be identical to those in the alkaline earth halides and oxides there is no reason why the ratios of the splitting of Gd^{3+} to Eu^{2+} in CdSe and CdTe should bear any relation to the ratios found in the halides and oxides. It is, however, interesting that in both CdSe and CdTe the splitting of the Gd^{3+} ground state is some three times that of Eu^{2+}. Possible explanations as to why this is so may be obtained by considering first the splitting in CdSe. If one compares the splitting of Eu^{2+} in CdSe[1] with that of Eu^{2+} in the isomorphic crystal CdS[24] than it can be shown[1] that the dominant perturbation in the splitting of Eu^{2+} in CdSe is given by

$$b_2^0 \sim \frac{-12\zeta^3 A_2^0\langle r^2\rangle}{5W_P^2W_D}, \tag{3}$$

where ζ is the spin-orbit coupling constant, $A_2^0\langle r^2\rangle$ is the radial factor in the second-order term of the crystalline field potential, and W_P and W_D are the energies of the $^6P_{7/2}$ and $^6D_{7/2}$ levels relative to the $^8S_{7/2}$ ground state. If Eq. (3) is the dominant perturbation for Gd^{3+} as well as for Eu^{2+} in CdSe then one must decide which parameters in Eq. (3) are altered sufficiently in going from Eu^{2+} to Gd^{3+} to account for the three times larger b_2^0 for Gd^{3+}.

The parameter ζ will be considered first. In their summary of data for trivalent rare earths Dieke and Crosswhite give 1581.1 cm^{-1} for the value of ζ for Gd^{3+}.[25] The value for ζ for Eu^{2+} has not as yet been measured. However, according to McClure and Kiss[26] the value of ζ does not change much with the state of ionization since the major contributions to this effect occur near the nucleus. If one uses the value of ζ for Eu^{3+} as given by Dieke[25] then the ratio $\zeta(Gd^{3+})/\zeta(Eu^{3+})$ is 1.20. This ratio is somewhat less than would be required to quantitatively account for the variation of b_2^0 from Gd^{3+} to Eu^{2+}. Because of the approximations involved in considering ζ, it is worthwhile to consider whether the other parameters in Eq. (3) vary in going from Gd^{3+} to Eu^{2+}.

The value of $A_2^0\langle r^2\rangle$ will certainly be different for Eu^{2+} and Gd^{3+}. The Eu^{2+} ion is larger than the Gd^{3+} ion.[3] The electronic charge on the Eu^{2+} ion is therefore closer to the charges on the neighboring anions and a larger $A_2^0\langle r^2\rangle$ is therefore expected for Eu^{2+} ion because of its larger ionic size. This effect cannot explain a larger b_2^0 for Gd^{3+}. The value of $A_2^0\langle r^2\rangle$ may, however, be affected by the extra positive charge on the Gd^{3+} ion.

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The extra positive charge at the Gd^{3+} site may symmetrically pull in the negative charges on the neighboring anions leading to a larger $A_2^0\langle r^2\rangle$ for Gd^{3+}. Such an effect has been observed in the alkaline earth fluorides[21] but was quite small.

There is another possible difference between Eu^{2+} and Gd^{3+}. This is because of the possibility that a trivalent rare-earth ion in the II-VI compounds may be an ionized shallow donor level. This has been shown to be true for Nd^{3+} in CdTe.[27] If Gd^{3+} is an ionized donor level in CdSe then the parameters W_P and W_D in Eq. (3) will be smaller than usually found for Gd^{3+} in insulating crystals and b_2^0 would as a result be increased. In order to check the positions of the energy levels of Gd^{3+} in CdSe an attempt was made to observe the fluorescent spectrum of Gd^{3+} but without success.

The effects of the environment on the parameters ζ, $A_2^0\langle r^2\rangle$, W_P, and W_D are not known with sufficient accuracy to decide quantitatively which of these varies enough in going from Eu^{2+} to Gd^{3+} to account for the larger b_2^0 observed for Gd^{3+}. Qualitatively as has been shown it is possible for all these parameters to vary in a way that would predict a larger b_2^0 for Gd^{3+}.

The discussion has so far considered the splitting parameter b_2^0 for Eu^{2+} and Gd^{3+} in CdSe. A similar discussion would apply for the parameter b_4 for Eu^{2+} and Gd^{3+} in CdTe. The perturbations that have been suggested by Low[11] and Lacroix[12] as responsible for the splitting of the $^8S_{7/2}$ state in a cubic field, involve ζ to as high as the fourth power, the crystalline field parameter $A_4^0\langle r^4\rangle$, and the energy separations of higher excited states such as W_P and W_D. Differences in these parameters for Eu^{2+} and Gd^{3+} in CdTe could account for the larger value of b_4 observed for Gd^{3+} in CdTe.

The *g* Values

The results in Table I and Table II show that in both CdSe and CdTe the g value of Gd^{3+} is significantly lower than that of the isoelectronic ion Eu^{2+}. This contrasts sharply with the results obtained in all other cases in which Eu^{2+} and Gd^{3+} have been observed in the same symmetry in the same crystal.[14,21–23] In these crystals the g values of Eu^{2+} and Gd^{3+} are very close to one another.

From Eq. (2) the departure of the g value from the free electron value, Δg is seen to be proportional to α_i^2 where α_i is the admixture of the ith excited $J=\frac{7}{2}$ state in the $^8S_{7/2}$ state. From Eq. (1) α_i^2 is proportional to ζ^2 and a larger ζ for Gd^{3+} as compared to Eu^{2+} will lead to a larger Δg for Gd^{3+}. The differences in ζ for Eu^{2+} and Gd^{3+} cannot completely account for the larger Δg observed for Gd^{3+} in CdSe and CdTe. Similar differences in ζ probably exist in the alkaline earth fluorides and yet the Δg's for Eu^{2+} and Gd^{3+} are approximately equal in these crystals. Equation (1) also shows that α_i^2 is proportional to $(1/W_i)^2$ where W_i is the energy separation of the ith excited state from the $^8S_{7/2}$ state. If one invokes the argument presented in consideration of the b_n^m parameters, that Gd^{3+} may be a donor in CdSe and CdTe and as a result the W_i would be less in these crystals as compared to insulating crystals, then α_i^2 would be larger for Gd^{3+}.

From Eq. (2) Δg would also be larger for Gd^{3+} and this would explain the lower g values of Gd^{3+}.

Little is known about the contribution to Δg that would result from the admixture of the ligand wave functions into the $^8S_{7/2}$ states as a result of covalency in the bonding.

In summary, the relative values of b_n^m and g for Eu^{2+} and Gd^{3+} in CdSe and CdTe are unique in these crystals. There are several qualitative explanations that can account for the observed values. Finding which explanation is most likely will require further measurements on rare-earth ions in semiconducting materials, particularly on the effects of covalency on the rare-earth ion.

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