# Exchange Interaction of $Eu^{2+}$-$Sm^{2+}$ and $Mn^{2+}$-$Sm^{2+}$ in Samarium Chalcogenides Observed by Electron Paramagnetic Resonance

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Electron paramagnetic resonance of $Eu^{2+}$ in various samarium chalcogenides and $Mn^{2+}$ in SmTe have been observed. The $g$ values are shifted by as much as 10% from their usual values near $g=2$. The large $g$ shifts are described in terms of the impurity-samarium exchange interactions.

The magnetic and transport properties of the samarium monochalcogenides have been of considerable interest in recent years.[1-6] In this paper we report on EPR studies of SmS($Eu^{2+}$), SmSe($Eu^{2+}$), and SmTe($Eu^{2+}$, $Mn^{2+}$). These studies indicate unusually large $Eu^{2+}$-$Sm^{2+}$ and $Mn^{2+}$-$Sm^{2+}$ exchange interactions which vary from one host crystal to another. In the theoretical discussion of the $Eu^{2+}$-$Sm^{2+}$ exchange interactions, it is pointed out that promotion of $4f$ electrons to the nearby $5d$ band plays an important role in the interaction. Since the separation of the $5d$ band from the $4f$ band varies from one host crystal to another, the experimentally observed variation of the $Eu^{2+}$-$Sm^{2+}$ exchange from host to host may be correlated with the $4f$-to-$5d$ separation. The possibility of the existence of $Sm^{2+}$-$Sm^{2+}$ exchange in the host crystals is also discussed.

The EPR of $Eu^{2+}$ ($4f^7\,{}^8S_{7/2}$ ground state) has previously been observed in a number of diamagnetic hosts.[7] The $g$ value of this paramagnetic ion is usually about 1.99. The small differences between the observed $g$ values and the free electronic value of 2.0023 are normally attributed to second-order spin-orbit interactions. Samarium chalcogenides which contain divalent samarium ions are rather special hosts, for the $Sm^{2+}$ ion has a ground state with $J=0$ ($4f^6\,{}^7F_0$) and an excited state ${}^7F_1$ not too far above it (~300 $cm^{-1}$). This excited state because of its proximity and $J$ value is readily admixed into the ground state by a magnetic field and the ion is slightly paramagnetic (Van Vleck paramagnetism[8]). Exchange interactions between $Eu^{2+}$ and $Sm^{2+}$ spins will act like a magnetic field on the $Sm^{2+}$ ions. The $Sm^{2+}$ ions adjacent to $Eu^{2+}$ ions will therefore be polarized and this will appear as a $g$ shift of the $Eu^{2+}$ EPR spectrum. Similar but much smaller $g$ shifts have been previously observed by Hutchings, Windsor, and Wolf[9] for $Fe^{3+}$ and $Gd^{3+}$ in europium gallium garnet, where the $Eu^{3+}$ ions (isoelectronic with $Sm^{2+}$) also have $J=0$. In the samarium chalcogenide hosts the exchange interactions are orders of magnitudes greater than and of opposite sign to those in europium gallium garnet. In the chalcogenides there appears to be a correlation with the activation energy between the $4f$ levels and the unoccupied $5d$ conduction band. This energy is much smaller than is found in the garnets. We have also observed the spectrum of $Mn^{2+}$ ($3d^5\,{}^6S_{5/2}$) in SmTe. The $Mn^{2+}$ $g$ shift in this case is unusually large ($g=1.885$) and suggests that the $Mn^{2+}$-$Sm^{2+}$ exchange interactions (antiferromagnetic) are opposite in sign from those of $Eu^{2+}$-$Sm^{2+}$. The mechanism which produces the $g$ shifts also appears to cause a line broadening in the observed spectra.

So far we have not been able to resolve a superhyperfine structure due to $Sm^{2+}$. Its observation would be valuable in interpreting the results in that it would enable us to determine whether the exchange effects are primarily with nearest or next nearest neighbors.

The samarium monochalcogenides used in this study were prepared from the elements. The crystals have the rock-salt structure and were grown from synthesized materials by heating in a sealed tungsten crucible to 2300°C and slowly cooling to room temperature. The crystals were found to contain 30 ppm Eu as an unintentionally added impurity. The resulting crystals were cleaved parallel to the cubic axes. The EPR measurements were performed at $X$-band frequency at temperatures of 4.2 and 77°K. The magnetic fields were varied in the (100) and (110) planes.

The EPR spectra of SmS($Eu^{2+}$), SmSe($Eu^{2+}$), and SmTe($Eu^{2+}$) were found to have an angular dependence characteristic of an $S$-state ion in a cubic crystal field.[10] The spectrum for SmSe($Eu^{2+}$) in which both the fine and hyperfine structure are clearly resolved is shown in Fig. 1. SmS($Eu^{2+}$), which shows the largest $g$ shift, has broader lines and the fine and hyperfine structures are not completely resolved. This probably results from the unresolved superhyperfine structure caused by the exchange interactions with $Sm^{2+}$

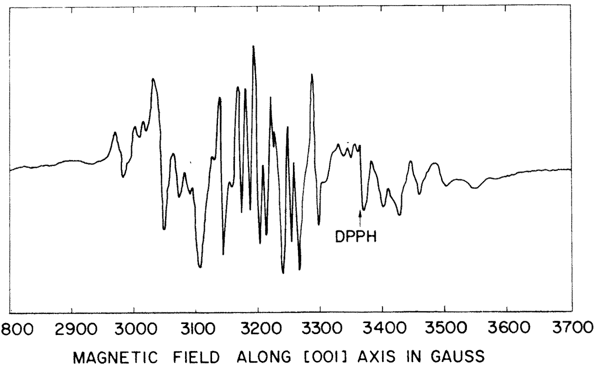

FIG. 1. The spectrum of SmSe(Eu$^{2+}$) at 4.2°K with the magnetic field along [001] axis.

ions. The fine structure of the Mn$^{2+}$ ions in SmTe was too small to be measured.

The measured EPR parameters are given in Table I. They consist of the $g$ factors, the fine-structure parameter $b_4$, and the hyperfine-structure parameter $A$. Also included are the excitation energies $E_i$ of the Sm$^{2+}$ $f$ electrons to the lower $5d$ sub-band.[11] These energies correspond to the second absorption peaks reported by Jayaraman *et al.*[1,5] The first absorption peaks reported in Refs. 1 and 5 are probably due to excitonic peaks or impurities as discussed in Ref. 5. The separations $\Delta$ of the $J=0$ and $J=1$ levels of the Sm$^{2+}$ ion in the various hosts are also given. These are derived from the Van Vleck susceptibilities reported in Ref. 5.

The most significant features of the data in Table I are the large $g$ shifts from $g\approx 1.99$, the value usually observed. The $g$ shifts for Eu$^{2+}$ correspond to a ferromagnetic interaction. The magnitudes of the $g$ shifts increase as the excitation energies $E_i$ decrease. For SmTe(Mn$^{2+}$) the $g$ shift corresponds to an antiferromagnetic interaction.

The problem to be considered is how a Eu$^{2+}$ ion which is $4f^7\,{}^8S_{7/2}$ polarizes an Sm$^{2+}$ ion which has a ground state $4f^6\,{}^7F_0$ and a low-lying excited state with $J=1$. The simplest assumption is that there is an exchange interaction between the spins of the two ions of the form $J\vec{S}_{\mathrm{Eu}}\cdot\vec{S}_{\mathrm{Sm}}$. Hutchings, Windsor, and Wolf[9] have shown that such an interaction produces a $g$ shift $\Delta g \propto J/\Delta$. There is then, however, the question of the origin of the exchange interaction $J$ and its dependence on the nature of the host materials.

In order to gain insight into the origin of the exchange interactions, we shall describe how the problem was approached using Fermi annihilation and creation operators in a second-quantized formulation,[12] which automatically takes care of the exclusion principle. The results were first derived for an isolated Eu$^{2+}$-Sm$^{2+}$ pair and then were extrapolated to the case of Eu$^{2+}$ in the samarium monochalcogenides. The model uses an approximate ground state for a Eu$^{2+}$-Sm$^{2+}$ pair in which the Eu$^{2+}$ is in the ${}^8S_{7/2}$ state and Sm$^{2+}$ is in ${}^7F_0$. This state is obtained by operating on a suitable "vacuum state" with operators which create and annihilate electrons in either Eu$^{2+}$ or Sm$^{2+}$ $4f$ orbits. By this technique the usual problem in magnetic exchange, of separating electrons into those which are on one atom and those which are on another, is avoided. The ground state is antisymmetric with respect to interchange of any pair of electrons. Similar antisymmetric states are used to describe the excited state in which the Eu$^{2+}$ ion remains in ${}^8S_{7/2}$ but the Sm$^{2+}$ ion is in ${}^7F_1$. It is found that the first-order processes which mix the ground and the excited states completely cancel one another, and it is necessary to consider higher-order processes. Among the strongest of these are second-order processes for which the intermediate states are the $5d$-like orbitals (bonding and antibonding). It is found that if two $4f$ electrons, one from each of Sm$^{2+}$ and Eu$^{2+}$ $4f$ orbits, are promoted into the

TABLE I. The experimental EPR parameters.

| | $g$(4.2°K) | $g$(77°K) | $b_4$ (G) | $A$ (G) | $E_i$ (eV)[a] | $\Delta$ (meV)[b] |
|---|---|---|---|---|---|---|
| SmS(Eu$^{2+}$) | 2.241 ± 0.001 | 2.226 ± 0.002 | 17 ± 2 | 29 ± 2 (Eu$^{151}$) | 0.79 | 29 |
| SmSe(Eu$^{2+}$) | 2.132 ± 0.001 | 2.124 ± 0.002 | 11 ± 2 | 30.8 ± 0.3 (Eu$^{151}$)<br>13.6 ± 0.3 (Eu$^{153}$) | 0.93 | 34 |
| SmTe(Eu$^{2+}$) | 2.016 ± 0.001 | 2.019 ± 0.002 | 6 ± 2 | 30.7 ± 0.3 (Eu$^{151}$)<br>13.8 ± 0.3 (Eu$^{153}$) | 1.18 | 38 |
| SmTe(Mn$^{2+}$) | 1.885 ± 0.001 | | | 78 ± 3 | 1.18 | 38 |

[a] Ref. 11.

[b] Ref. 5.

same $5d$ orbital, the sign of the admixture of $J=1$ into $J=0$ is that which corresponds to antiferromagnetic exchange between spins, whereas if they go into different orbitals the corresponding admixture can correspond to a ferromagnetic exchange. The shift in the $g$ value to $Eu^{2+}$ that results from the processes is given by

$$\Delta g = \Delta g(\text{ferromagnetic}) + \Delta g(\text{antiferromagnetic}), \qquad (1)$$

where

$$\Delta g(\text{ferromagnetic}) \propto [(2e_i + W)(2e_i + W - \Delta)]^{-1} \qquad (2)$$

and

$$\Delta g(\text{antiferromagnetic}) \propto [e_i(2e_i - \Delta)]^{-1}. \qquad (3)$$

In Eqs. (1)–(3), $e_i$ is the energy difference between the $4f$ and the bonding $d$ orbitals, and $W$ is the energy difference between the bonding and antibonding $d$ orbitals. If we extend these arguments to the case of a $Eu^{2+}$ ion in a samarium chalcogenide lattice, $e_i$ corresponds to the energy between the $4f$ level and the bottom of the lower of the $5d$ sub-bands,[13] and $W$ corresponds to the width of this sub-band. If we assume a symmetric $d$ sub-band,

$$e_i = E_i - \tfrac{1}{2}W \qquad (4)$$

and Eq. (2) simplifies to

$$\Delta g(\text{ferromagnetic}) \propto [E_i(2E_i - \Delta)]^{-1}. \qquad (5)$$

Experimentally the signs of the $g$ shifts for $Eu^{2+}$ in the three samarium chalcogenides indicate that the interactions are ferromagnetic. The decrease in the ferromagnetic $g$ shift with increasing $f$-$d$ excitation energy, $E_i$, predicted by Eq. (5) and the observations in Table I are qualitatively in agreement. The use of the strongest ferromagnetic interaction [Eq. (5)] for comparison with experiment ignores weaker antiferromagnetic and ferromagnetic interactions and no better than qualitative agreement is to be expected. In fact, great care must be exercised in extension of the theory which was derived for an isolated $Eu^{2+}$-$Sm^{2+}$ pair to the case of $Eu^{2+}$ in a samarium chalcogenide host. While the interaction in the crystal between $Eu^{2+}$ and its twelve nearest $Sm^{2+}$ neighbors might be expected to be similar to that of an isolated $Eu^{2+}$-$Sm^{2+}$ pair, the interaction between $Eu^{2+}$ and its six next nearest $Sm^{2+}$ neighbors may involve different mechanisms (for example, the intermediate chalcogenide ions). There is no reason to suppose that the interaction with next nearest neighbors even has the same sign as that with nearest neighbors. For $Eu^{2+}$-$Eu^{2+}$ exchange in EuS, EuSe, and EuTe it has been postulated[14] that the nearest-neighbor interaction is ferromagnetic while that with next nearest neighbors is antiferromagnetic. The small $g$ shift observed for $Eu^{2+}$ in SmTe (Table I) may therefore be due to a reduction in the ferromagnetic contribution with the increase in $E_i$ so that it is comparable in magnitude to the antiferromagnetic contribution from next nearest neighbors.

A problem closely related to the exchange interaction of $Eu^{2+}$-$Sm^{2+}$ at isolated $Eu^{2+}$ impurity sited in the samarium chalcogenides is the question of $Sm^{2+}$-$Sm^{2+}$ exchange in the host crystals themselves. Bucher, Narayanamurti, and Jayaraman[5] in their treatment of the susceptibility of the samarium chalcogenides assumed the $Sm^{2+}$-$Sm^{2+}$ exchange to be small. The Van Vleck susceptibility of the ground state of $Sm^{2+}$ ($^7F_0$) at absolute zero is then given by $\chi = 8N\beta^2/\Delta$, where $N$ is the number of ions per unit volume and $\beta$ the Bohr magneton. Bucher, Narayanamurti, and Jayaraman[5] ascribed the variation in the susceptibility of SmS, SmSe, and SmTe to variations in $\Delta$ which they assumed arose from promotion of $4f$ electrons to the $5d$ band. We however have noted in our treatment of $Eu^{2+}$-$Sm^{2+}$ pairs that this promotion is an important element in the exchange interaction, although in our theory the promotion is virtual. Though it may be difficult to extend such considerations rigorously to the entire $Sm^{2+}$ sublattice in these samarium chalcogenides, we can discuss the simpler model of isolated $Sm^{2+}$-$Sm^{2+}$ pairs. A $Sm^{2+}$-$Sm^{2+}$ pair has a sixfold degenerate level in which one ion is in the $J=0$. This level is split by an exchange interaction between the spins, and there is then a change in the Van Vleck susceptibility. If such considerations on a $Sm^{2+}$ pair can be extrapolated to the whole $Sm^{2+}$ sublattice, then the complete explanation of the susceptibilities observed by Bucher, Narayanamurti, and Jayaraman[5] may in part involve variations in the $Sm^{2+}$ exchange interaction from host to host.

The detailed theory will be given more fully elsewhere.

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# Cathodoluminescence of Magnetite*

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The cathodoluminescence spectrum of magnetite indicates optical transitions which correspond to energy separations of 2.6 and 3.2 eV. These luminescence data, coupled to the available optical absorption and soft x-ray data, lead to the first proposed semiquantitative band model for this material.

In the study of the electronic structure of the transition-metal oxides, the spectroscopic methods used thus far have been optical transmission and reflectance[1-5] and soft x-ray measurements.[6-8] The lack of large and thin crystals makes optical measurements very difficult[2] and does not permit easy distinction between band-to-band transitions and other absorption processes. X-ray data are not always easy to interpret and no resolution of better than 0.3–0.5 eV has been reported so far. In this Letter we propose a third method: the study of cathodoluminescence. This method has advantages in the above respects and is complementary to optical absorption studies. Further, we shall show how the combined data from all the above-mentioned methods can lead to a quite reliable picture of the band separations in these materials. We report here the first luminescence observation in transition-metal oxides and suggest the first semiquantitative band structure of magnetite ($Fe_3O_4$).

For the cathodoluminescence study of $Fe_3O_4$ we have used the natural magnetite single crystals from which slices were cut for our previous optical measurements.[1] The specimens were fastened to the cold finger of a Dewar equipped with a kinescope-type electron gun and a NaCl window transparent over the range of interest. Excitation was provided by an electron beam having a current density of about 1 A/cm$^2$ at 20 keV. The beam was pulsed for 0.5 μsec every 200 μsec. The infrared region was studied with a Perkin-Elmer 112 spectrometer equipped with a NaCl prism and a thermocouple detector. For the visible luminescence a quartz prism was used and the detector consisted of an RCA 8575 photomultiplier.

The resulting emission spectrum at two temperatures is shown in Fig. 1. Clearly, there is an emission peak at photon energy $h\nu = 2.6$ eV and a shoulder which is attributable to another peak at about 3.2 eV. The difference in intensities at the two temperatures is probably due to the usual increase in nonradiative processes with increasing temperature. The nonradiative recombination may be enhanced in the present case as the sample passes through the "semiconductor-to-metal" transition when heated from 77 to 300°K. The possible smearing of the 3.2-eV shoulder at 300°K will be discussed below. No other luminescence has been observed in the spectral range $0.1 \leq h\nu \leq 4$ eV. We shall first