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Exchange Interactions in the Samarium Monochalcogenides

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In the insulating state of the samarium monochalcogenides SmS, SmSe, and SmTe, the $\text{Sm}^{2+}(4f^6)$ ion has a nonmagnetic 7F_0 ground state exhibiting Van Vleck paramagnetism at low temperatures. From an analysis of the susceptibility, information about the Sm-Sm exchange interactions is obtained. The deduced variation of this exchange with lattice parameter is shown to be consistent with the pressure dependence of the susceptibilities. Electron paramagnetic resonance of Eu^{2+} , Gd^{3+} , and Mn^{2+} present as dilute impurities has also been observed. The resonance fields are subject to large shifts (nearly 50% for Mn^{2+} in SmS) due to the impurity-host lattice interaction; this enables one to deduce the Sm-impurity exchange interactions. It is found that the Eu-Sm and Sm-Sm interactions are nearly identical in each lattice and furthermore that they follow the same systematic trend as the Eu-Eu exchange in the corresponding europium chalcogenides. The magnitude however is much larger in the Sm lattice, directly reflecting the closer proximity of the conduction band. The Gd-Sm exchange interaction is roughly twice as large as that found for Eu-Sm in each host lattice. This increase in exchange in going from the larger Eu^{2+} ion to the smaller isoelectronic Gd^{3+} ion implies that the extra electron accompanying the Gd^{3+} ion plays an active role in the exchange process. The Mn-Sm interactions are found to be of opposite sign (antiferromagnetic) and approximately four times larger than those for Eu-Sm.

I. INTRODUCTION

Since the discovery¹ of high-temperature ferromagnetism in EuO , there has been considerable interest in the magnetic, transport, and optical properties of the europium chalcogenides.² Particular effort has been directed towards obtaining an understanding of the microscopic origins of the anomalously large Eu^{2+} - Eu^{2+} exchange in these compounds.³ It is now generally recognized that

the $5d$, $6s$ conduction states play an important intermediary role in the exchange interaction. However, because of the large number of possible high-order processes, it has proven extremely difficult to isolate the dominant mechanisms. It is therefore of interest to obtain additional empirical information on the magnetic interactions in similar systems.

In this paper we report a study of exchange interactions in the samarium monochalcogenides

SmS, SmSe, and SmTe. At atmospheric pressure the samarium ions are in the $4f^6$ configuration with a nonmagnetic 7F_0 ground state and 7F_1 first excited state.⁴ No reliable information is as yet available on the band structure⁵; however, optical measurements indicate that the $4f$ - $5d$ band gap in these materials is about 1 eV,⁴ approximately one-half the value for the corresponding Eu compounds.⁶ These samarium compounds are of interest not only because of their similarity to the europium chalcogenides but, rather more importantly, because of the recently discovered fact that they exhibit semiconductor-metal transitions as a function of pressure due to a $4f$ -electron delocalization.⁷ We shall not shed any light on the latter problem in this paper, however.

Information about the exchange may be readily obtained using two different techniques. First, the Van Vleck susceptibility at low temperatures is modified by the Sm-Sm interactions in a manner which may be simply described using molecular field theory. Hence, for a known $J=0 \rightarrow J=1$ splitting, the effective exchange field may be immediately deduced. Measurements of the susceptibilities of SmS, SmSe, and SmTe have already been reported,⁴ and in this paper we reanalyze these results using the exchange model. Second, as first pointed out by Hutchings and Wolf,⁸ for impurities in a paramagnetic lattice, the electron-spin-resonance (ESR) field is shifted from its value in a corresponding nonmagnetic host by an amount which is simply related to the impurity-host magnetic interaction. We have observed the electron-spin resonance of the S-state ions Eu^{2+} , Gd^{3+} , and Mn^{2+} in SmS, SmSe, and SmTe and in some intermediate alloys. In each case there are large g shifts which measure directly the samarium-impurity interactions. These exchange couplings in the samarium lattices will be compared with each other and with the Eu-Eu interactions in the corresponding europium compounds. ESR studies of Eu^{2+} in the three monochalcogenides of Sm and of Mn^{2+} in SmTe have been independently undertaken by Mehran *et al.*⁹

II. THEORY

The theory for the low-temperature magnetic properties of a Sm^{2+} lattice with a small number of S-state impurities may be readily deduced using standard techniques. We assume that the Sm ions are in the 7F_0 ground state with the first excited 7F_1 state at an energy Δ . We take as the perturbing Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{HZ}} + \mathcal{H}_{\text{HE}} + \mathcal{H}_{\text{IZ}} + \mathcal{H}_{\text{IH}}, \quad (1a)$$

$$\mathcal{H}_{\text{HZ}} = \sum_i \mu_B \vec{H} \cdot (\vec{L}_i + 2\vec{S}_i),$$

$$\mathcal{H}_{\text{HE}} = \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (1b)$$

$$\mathcal{H}_{\text{IZ}} = \sum_{i'} g_{i'} \mu_B \vec{H} \cdot \vec{S}_{i'}, \quad (1c)$$

$$\mathcal{H}_{\text{IH}} = \sum_{i',j} J_{i',j} \vec{S}_{i'} \cdot \vec{S}_j. \quad (1d)$$

Primed symbols refer to the impurity ions, and it is assumed that all coupling between the dilute impurity ions is negligible. The appropriate matrix elements between the 7F_0 and 7F_1 states are given by

$$\langle 1, 0 | L^z + 2S^z | 0, 0 \rangle = \langle 1, 0 | S^z | 0, 0 \rangle = 2. \quad (2)$$

We now treat each term of Eq. (1) in succession. The host-Zeeman term (1a) generates a moment characterized by the Van Vleck susceptibility at 0 K:

$$\chi_{\text{VV}} = (8N\mu_B^2/\Delta). \quad (3)$$

The samarium-samarium interaction terms (1b) may be treated in the molecular field approximation. The susceptibility Eq. (3) then becomes at 0 K

$$\chi_{\text{VV}} = 8N\mu_B^2/(\Delta + 8\sum_i Z_i J_i), \quad (4)$$

where Z_i is the number of samarium i th equivalent neighbors and J_i is the appropriate exchange interaction. In the rocksalt structure, $Z_1=12$, $Z_2=6$, and $Z_3=24$. Equation (4) predicts a phase transition for $8\sum_i Z_i J_i/\Delta \approx -1$. However, in the samarium chalcogenides this parameter is always small in magnitude so that no magnetic ordering occurs.

We now consider the impurity terms (1c) and (1d). This problem has been treated in some detail by Hutchings, Windsor, and Wolf¹⁰ for Eq. (1) without the host-lattice exchange term (1b). They show that the impurity ion i' will exhibit a spin resonance with a g value shifted from g'_i by an amount

$$\Delta g'_i = -(8/\Delta)\sum_j Z_j J'_j, \quad (5)$$

where J'_j is the exchange interaction between the impurity ion and its j th nearest Sm^{2+} neighbor. The corresponding $\Delta g'_i$ including the host interaction terms (1b) is rather more complicated. However, to a good approximation it may be expressed as

$$\Delta g'_i = -[8/(\Delta + 8\sum_i Z_i J_i)]\sum_j J'_j. \quad (6)$$

We shall use Eq. (6) in analyzing our data. The impurities will also contribute a Curie term to the susceptibility Eq. (4). However, these contributions may be readily separated out from the pure Sm-Sm host-lattice Van Vleck susceptibility. In summary, therefore, from the bulk susceptibility, one may find the Sm^{2+} - Sm^{2+} exchange sum $\sum_i Z_i J_i$ and from the impurity g shift one obtains $\sum_j Z_j J'_j$ for each impurity.

III. EXPERIMENT

Single crystals of the samarium monochalcogenides were prepared by prereacting fine turnings of

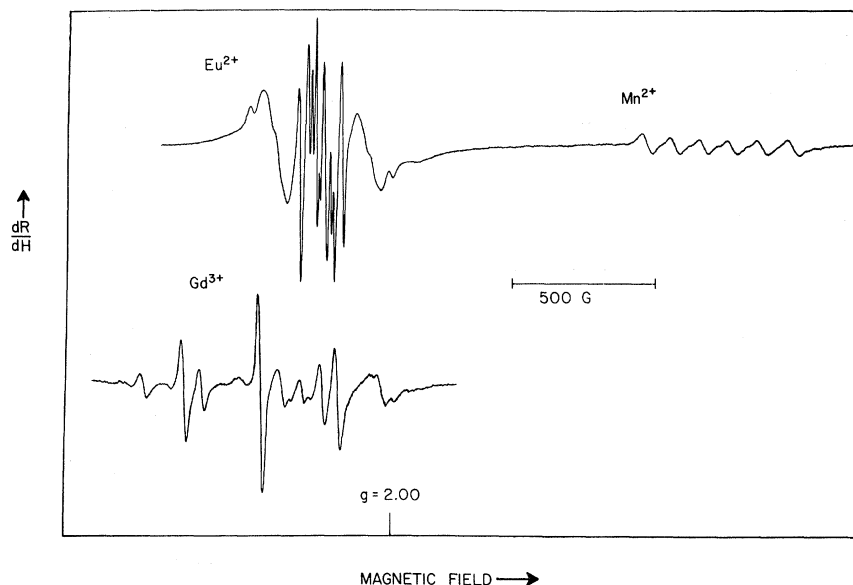


FIG. 1. ESR spectra of Eu^{2+} , Gd^{3+} , and Mn^{2+} in SmSe crystals showing the ferromagnetic shifts of the two rare-earth ions and the much stronger antiferromagnetic shift of Mn. The experiment was performed at 4.2 K in a 12.025-GHz cavity with the magnetic field along $\langle 100 \rangle$ to maximize fine-structure resolution.

samarium metal in the appropriate chalcogenide vapor followed by melting in sealed tantalum crucibles. The sulphides were quenched from just below the temperature of solidification in order to retain the rocksalt phase.¹¹ The tellurides were handled in dry nitrogen to avoid reaction with water vapor. The resultant polycrystalline boules contained large regions of easily cleaved single-crystal material. Many of the ESR experiments were performed on nominally pure materials which commonly proved to contain several tens of parts per million of Eu^{2+} and somewhat less Mn^{2+} . Intentionally doped samples were also prepared, particularly in the case of Gd^{3+} , by dilution of master alloys containing 1 at. % of the desired substituent. Reference samples of diamagnetic YbSe were also prepared in a nitrogen atmosphere.

The magnetic susceptibilities of the undoped SmS , SmSe , and SmTe were reported earlier by Bucher *et al.*⁴ and will be discussed below.

The ESR experiments were performed using conventional homodyne spectrometers operating at 12, 17, and 34 GHz. Cleaved single-crystal samples were examined principally at 1.4 and 4.2 K to minimize microwave losses arising from thermally

excited conduction electrons. The magnetic field was rotated in the $\{110\}$ plane of the samples to determine the crystalline field symmetry at the impurity ion sites. In general, fine-structure transitions, that is, transitions other than $\frac{1}{2} \leftrightarrow -\frac{1}{2}$, were quite broad, presumably because of residual strains of less than cubic symmetry.

Divalent europium ($4f^7$, $S = \frac{7}{2}$) was readily identifiable as a universal impurity via its characteristic hyperfine structure arising from Eu^{151} and Eu^{153} . A typical Eu^{2+} spectrum is shown in Fig. 1 with sharp $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions but very broad fine structure. The fine-structure transitions showed anisotropy consistent with cubic site symmetry in all crystals studied. As seen in Table I, the magnitude of the parameter A^{151} is quite comparable to that observed in the diamagnetic rocksalt compound SrO . The observed weak reduction in the magnitude of A^{151} on going from sulphide to telluride is consistent with increasing convalency in the heavier chalcogenides. Crude estimates of the fourth-order crystal field parameter show a marked decrease from sulphide to telluride.

The g values are seen to change very strongly in proceeding through the series, the deviation from

TABLE I. Spin-Hamiltonian parameters for Eu^{2+} , Gd^{3+} , and Mn^{2+} in samarium monochalcogenides.

	Eu^{2+}			Gd^{3+}		Mn^{2+}	
	g	$ A^{151} \times 10^4 \text{ cm}^{-1}$	$ b_4 \times 10^4 \text{ cm}^{-1}$	g	$ b_4 \times 10^4 \text{ cm}^{-1}$	g	$ A^{55} \times 10^4 \text{ cm}^{-1}$
SmS	2.230 ± 0.005	30.5 ± 0.1	20 ± 2	2.43 ± 0.01	15 ± 3	1.05 ± 0.01	76.9 ± 0.2
SmSe	2.101 ± 0.003	29.6 ± 0.5	12 ± 1	2.22 ± 0.01	23 ± 1	1.567 ± 0.005	74.3 ± 0.2
SmTe	2.020 ± 0.003	28.6 ± 0.5	10 ± 1	2.10 ± 0.01	37 ± 2	1.904 ± 0.005	68.6 ± 0.2
YbSe						2.006 ± 0.005	74.6 ± 0.2
SrO^a	1.9914	29.7	$\sim < 1$	1.9912	~ 6	2.001	78.1

^aA. J. Shuskus, *J. Chem. Phys.* **41**, 1885 (1964).

the value 1.99 commonly observed in a wide variety of diamagnetic hosts increasing from 0.03 in the telluride, to 0.11 in the selenide, to 0.24 in the sulphide. While these shifts are at first sight very large compared to exchange-induced shifts in other Van Vleck paramagnetic crystals,¹⁰ their magnitudes are not inconsistent with the exchange couplings in the rare-earth chalcogenides, as will be discussed below. Shifts intermediate between those listed in Table I were found in $\text{SmS}_x\text{Se}_{1-x}$ mixed crystals, where even the hyperfine structure was unresolved due to a spread of g values presumably arising from compositional fluctuations. The deduced exchange couplings are shown in Fig. 2. Our values of the g shifts and other spin-Hamiltonian parameters for Eu are in rough agreement with those reported by Mehran *et al.*⁹ Experience indicates that these numbers vary somewhat from sample to sample presumably due to varying degrees of strain and stoichiometry, whence rather generous confidence limits must be set.

Trivalent gadolinium, isoelectronic with Eu^{2+} , was almost unobservable as a natural contaminant, but was readily introduced into all three lattices by doping. Nominal concentrations of 0.01 and 0.1% were examined; the spin-Hamiltonian parameters were found to be independent of concentration in this range. No hyperfine identification was possible because of the weak nuclear moments and modest abundances of Gd^{155} and Gd^{157} . It was generally possible to resolve the fine-structure pattern of a spin $S = \frac{7}{2}$ in cubic symmetry however, though considerable additional structure was also observed in many cases. A better-than-average spectrum is shown in Fig. 1. The magnitude of the dominant fourth-order crystal field parameter increases markedly on proceeding from the sulphide to the telluride (Table I).

Just as in the case of Eu^{2+} , the g value proves to be strikingly sensitive to the host lattice, the deviation from the usual value, 1.99, increasing from 0.11 in the telluride, to 0.23 in the selenide, to 0.44 in the sulphide.

The observation of ESR signals arising from Gd^{3+} ions in sites of lower than cubic symmetry, as well as the absence of appreciable electrical conductivity at liquid-helium temperatures in samples containing as much as ~0.1% Gd brings up the question of charge compensation. It is commonplace to attribute low-symmetry spectra to those ions whose compensating electron localizes within a few lattice constants. It would also be usual to assume that the ions exhibiting full substitutional site symmetry are uninfluenced by any nearby compensation. However, as will be discussed in the next section, the fact that the exchange-induced g shifts are roughly twice as large for cubically situated Gd^{3+} as for Eu^{2+} in a given host lattice suggests that the

"extra" electron is, in fact, nearby and distributed in a highly symmetric fashion, for example, occupying an orbital principally situated on the 12 nearest-neighbor Sm sites. The opposite variations of the magnitudes of the fourth-order crystal field splittings versus lattice parameter for Eu^{2+} and Gd^{3+} in the three host crystals may also be evidence for anomalous electronic structure in the vicinity of the latter.

Divalent manganese ($3d^5$, $S = \frac{5}{2}$) was readily observed as a natural contaminant in SmTe, less so in SmSe, and almost not all in SmS. Hyperfine identification due to the unique Mn^{55} nucleus (Fig. 1) proved consistent with that of Mn^{2+} in SrO and in the diamagnetic rare-earth selenide YbSe (Table I). Covalent reduction of A^{55} from sulphide to telluride is well known for this $3d^5$ ion.¹² No resolved fine structure was observed in the case of manganese, though a weak broad "pedestal" was detectable at high gain. Very large g shifts of opposite sign compared to Eu^{2+} and Gd^{3+} are observed, amounting to reduction of the applied field by almost exactly a factor of 2 in the case of Mn^{2+} in SmS.

IV. ANALYSIS AND DISCUSSION

We consider first the susceptibility measurements of Bucher *et al.*⁴ mentioned in the previous section. In each case, the susceptibility shows the

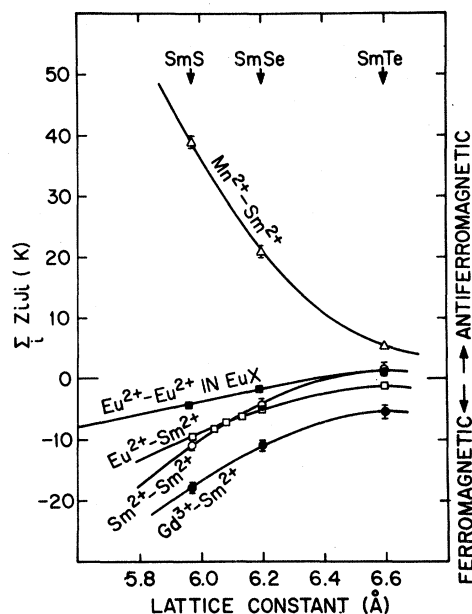


FIG. 2. Exchange sums for the host-host and host-impurity exchange interactions in the samarium monochalcogenides. The figure also includes the Eu^{2+} - Eu^{2+} exchange interactions in the corresponding europium monochalcogenides. The solid lines are guides to the eye.

TABLE II. 4.2-K Van Vleck susceptibilities and derived exchange sums in SmX.

	χ_{VV} (cm ³ /mole)	$\sum_i Z_i J_i$ (K)
SmS	9.15×10^{-3}	-11.0 ± 1.0
SmSe	7.85×10^{-3}	-4.2 ± 1.0
SmTe	7.00×10^{-3}	$+1.6 \pm 1.0$

characteristic Van Vleck form with a small impurity contribution at the lowest temperatures. The 4.2-K values of the susceptibility with the impurity effects subtracted off are listed in Table II. The principal difficulty in the interpretation of these results in terms of Eq. (4) is our lack of knowledge of the precise value of the spin-orbit splitting Δ . Indeed, Bucher *et al.* have interpreted their results in terms of an unusually strong lattice dependence of the spin-orbit coupling itself. However, this seems quite unlikely in light of the total insensitivity of the spin-orbit coupling of rare-earth ions to the local environment in the myriad of other crystals.¹² As we shall see, the variation of χ_{VV} as listed in Table II may be much more reasonably understood on the basis of an exchange mechanism.

The free-ion value of Δ for Sm²⁺ is 421 K.¹³ In a crystalline environment we might expect this to be reduced by 1 to 2%. Measurements are available for Δ in a variety of lattices; the most appropriate measurements for our purposes are those of Bron and Heller¹⁴ in the rocksalt compounds KCl, KBr, and RbCl, where Δ is 414.5, 415.7, and 413.8 K, respectively. We therefore take $\Delta = 415 \pm 6$ K for the samarium chalcogenides; this corresponds to a Van Vleck susceptibility of $7.22 \pm 0.10 \times 10^{-3}$ /mole. The Sm-Sm exchange may then be immediately deduced using Eq. (4). The results are tabulated in Table II and shown as a function of lattice constant in Fig. 2.

The $\sum_i Z_i J_i$ -vs- R dependence shown in Fig. 2 has some rather interesting consequences for the pressure dependence of the susceptibility. Maple and Wohlleben¹⁵ have measured $d\chi/dP$ vs P at room temperature in SmS, SmSe, and SmTe. They find that in each case the susceptibility initially increases with increasing pressure at the rates given in Table III. It is tempting to interpret this initial rise in terms of the distance dependence of the exchange. If we assume that this is the sole mechanism contributing to $d\chi/dP$, then in the molecular field approximation

$$\frac{d\chi}{dP} = -\frac{\chi^2}{N\mu_B^2} \frac{d\sum_i Z_i J_i}{dP}. \quad (7)$$

Here χ is already known in each case and $d\sum_i Z_i J_i/dP$ may be deduced from Fig. 2 and the compress-

sibility data of Jayaraman and co-workers.^{7,16} Substitution of these values into Eq. (7) yields the calculated values listed in Table III. The agreement between this simple theory and the measured values can only be described as remarkable. Indeed, it is probably misleadingly precise, since some Sm²⁺ ions are lost from the $4f^6$ configuration as pressure is applied. Nevertheless, it seems clear that we have identified the main mechanism contributing to $d\chi/dP$.

Using the results tabulated in Table II together with Eq. (6) we may now interpret the Eu²⁺, Gd³⁺, and Mn²⁺ g -shift measurements. The resultant impurity-host exchange sums are listed in Table IV and are displayed as a function of lattice constant in Fig. 2. We have also tabulated in Table V the corresponding values for the Eu²⁺-Eu²⁺ interactions in the europium chalcogenides. The final results, as displayed in Fig. 2, are quite striking. First, we note that in the sulphide and selenide the Eu-Sm and the Sm-Sm exchange interactions are identical to within the experimental error. In the telluride these interactions are both small and of similar magnitude but with opposite signs. The trend with lattice constant for these interactions is the same as that for the Eu-Eu interactions in the europium chalcogenides with a difference of approximately 3 in absolute magnitude. It seems clear that the microscopic mechanisms are the same in both systems and that the difference is simply one of scale.

At the present time it is believed that the nearest-neighbor exchange J_1 arises from direct cation-cation interactions, whereas the next-nearest-neighbor exchange J_2 involves some superexchange process via the intervening chalcogen. The increase in the ferromagnetic component of $\sum_i Z_i J_i$ in going from the europium to samarium compounds is consistent with an exchange mechanism involving hybridization with the $5d$ bands, since the $5d$ states are much lower in the latter systems. A more precise identification of the cation-cation mechanism is not possible until reliable values for the appropriate matrix elements become available. Indeed, it seems likely that polarization of the filled $5s^2 5p^6$ states on the rare earth plays an important role. However, even in the europium chalcogenides

TABLE III. Pressure dependence of the room-temperature SmX susceptibilities.

	$\frac{d\chi}{dP}$ (10 ⁻⁶ cm ³ /mole kbar)	
	observed	calculated
SmS	78 ± 7	75 ± 15
SmSe	17	14 ± 4
SmTe	2.2	0 ± 3

TABLE IV. Eu-Sm, Gd-Sm, and Mn-Sm exchange sums in the samarium monochalcogenides.

	a (Å)	Eu ²⁺ -Sm ²⁺	$\sum_i Z_i J_i'$ (K) Gd ³⁺ -Sm ²⁺	Mn ²⁺ -Sm ³⁺
SmS	5.97	-9.6 ± 0.4	-18.0 ± 0.8	39 ± 1
SmSe	6.20	-5.2 ± 0.3	-11.0 ± 1.0	21 ± 1
SmTe	6.60	-1.3 ± 0.3	-5.4 ± 1.1	5.3 ± 0.5

no calculations which explicitly take these effects into account have yet been reported. We note that Mehran *et al.*⁹ in their study of the ESR of Eu²⁺ ions in these systems have pointed out that, as expected, the g shifts are correlated with the activation energies of the $4f$ electrons of Sm²⁺ in the host material. The most important effect, however, is probably the distance dependence of the transfer integrals themselves.

The gadolinium g shifts for the ions with full cubic symmetry lead to the exchange sums listed in Table IV and shown in Fig. 2. The trend with host-lattice parameter is again similar to the case of the Eu-Sm exchange but with a factor-of-2 increase in magnitude. Initially this would seem difficult to understand on the basis of a direct cation-cation interaction involving hybridization with the $5d$ band, since the Gd³⁺ ion is significantly more compact than the isoelectronic Eu²⁺ ion. This size effect should lead to a considerable reduction in the appropriate transfer integrals. We suggest instead the Gd³⁺-Sm²⁺ exchange proceeds via a real rather than virtual $4f$ - $5d$ process involving the extra electron contributed by the Gd³⁺ ion. That is, the extra electron is localized around the Gd³⁺ ion in a cubically symmetric orbital and contributes directly to the Gd³⁺-Sm²⁺ exchange without exhibiting any direct magnetic effects itself. This picture of a localized extra electron is consistent both with the concentration independence of the Gd³⁺ g shifts and the failure of Gd³⁺ doping to significantly decrease the high electrical resistivity of these materials, at least at low temperatures.

Note added in proof. There are, however, some consequent difficulties in understanding our observation of sharp fine-structure lines [see P. Eisenberger and P. S. Pershan, Phys. Rev. **167**, 292 (1968)]; thus the detailed microscopic description of the Gd³⁺ ion in these systems must still be regarded as somewhat of an open question.

It is interesting to note that in the corresponding metallic gadolinium monochalcogenides GdS, GdSe, and GdTe the exchange sums are $\sum_i Z_i J_i = 19$, 17, and 16 K, respectively.¹⁷ Thus in the concentrated materials the exchange is antiferromagnetic and nearly independent of the anion and lattice constants. Clearly, the exchange in the two situations is of fundamentally different origin. As discussed

above, the Gd³⁺-Sm²⁺ exchange may involve a polarization of the bound extra electron which affects mainly the nearest-neighbor exchange, whereas the Gd³⁺-Gd³⁺ exchange in the gadolinium chalcogenides is the usual long-range RKKY process mediated by itinerant electrons.

With reference to the metallic state, one should also note that appreciable g shifts are observed in the ESR of localized magnetic moments in metals¹⁸ and are attributed to exchange coupling with band electrons. A particularly strong shift is found for Gd in palladium metal ($g=1.826$)¹⁹ due to the enhanced band susceptibility of the host. In general, the g shifts increase in magnitude with increasing d -like character of the conduction electrons. Therefore, it should be interesting to study the influence of conduction electrons on the various exchange couplings in the samarium monochalcogenides by performing experiments at higher temperatures and/or pressures.

The results for the Mn²⁺-Sm²⁺ exchange interactions are also listed in Table IV and displayed in Fig. 2. In this case the exchange is even larger but *antiferromagnetic*. It also shows a rapid dependence on lattice constant, again suggesting a dominant direct cation-cation interaction. We note that the Mn²⁺ hyperfine coupling constant decreases in going from the sulphide to the telluride, indicating increasing convalency. We would therefore expect any superexchange contributions to at least remain constant across the series. Indeed, in the corresponding rocksalt compounds MnO, α MnS, and α MnSe, it appears that $\sum_i Z_i J_i$ is nearly constant.²⁰

Finally, throughout this paper we have used the Hamiltonian Eq. (1) which assumes that the exchange is isotropic between the real spins, thus omitting any orbital dependence of the exchange for the Sm²⁺ ions.²¹ The good agreement between the Sm-Sm and Sm-Eu exchange sums would seem to confirm this approximation. Similar results were obtained by Birgeneau, Hutchings, and Wolf²² for the isoelectronic case of Gd³⁺ in EuCl₃. It is clear that these g -shift effects offer a powerful micro-

TABLE V. Eu-Eu exchange interactions in the europium chalcogenides.

	R (Å)	J_1 (K)	J_2 (K)	$12J_1 + 6J_2$ (K)
EuO ^a	5.15	-1.21 ± 0.01	-0.31 ± 0.02	-16.4 ± 0.2
EuS ^a	5.96	-0.47 ± 0.03	0.20 ± 0.02	-4.4 ± 0.4
EuSe ^b	6.19	-0.3	0.3	-1.7
EuTe ^b	6.60	-0.06	0.3 ± 0.05	+1.1

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scopic probe of the host-lattice electronic system. Experiments are now under way to study the temperature and pressure dependence of the Eu^{2+} and Gd^{3+} resonances in SmS, hopefully through the semiconductor-metal transition in order to obtain information about the nature of the metallic state.

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Quantum-Mechanical Treatment of the Abnormal Stopping Power for Channeling

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A quantum-mechanical method for the calculation of the abnormal stopping power of ion channeling is proposed. It is concluded that the abnormal stopping power is not proportional to the local electron density. Numerical calculations are performed for 3-MeV He ions in the Au crystal.

I. INTRODUCTION

The trajectory of ions channeled between crystal planes is governed by their interaction with the interatomic potentials of the atoms making up the plane, and the energy loss of channeled ions depends upon the detailed stopping power (local stopping power) it has encountered along its path.

The energy-loss spectra produced in beams of energetic He and I ions transmitted through thin gold monocrystals in directions lying very nearly in low-index crystallographic planes have been reported recently.¹⁻³ Robinson⁴ made a quantitative comparison of his anharmonic-oscillation model with the experiment of Datz *et al.*³ and concluded that the channeling stopping power $S^{pl}(\xi)$ is rep-