

washed out in the region where present experimental data were taken.

It is worth emphasizing the importance of the role played by the constant magnetic field  $H_0$ . Without it, the power transferred to the electromagnetic field is reduced by a factor  $Q^{-2}$ . The application of  $H_0$  alters the spatial distribution of the ac Josephson current density and allows it to couple to a mode having an inductive field extending into the penetration layer. This inductance can "resonate out" the capacitance of the junction.

It should be possible to construct junctions with  $Q$ 's sufficiently large that  $v_0/V_0 \approx 1$ . Under these conditions the power transferred to the field will be of the order of microwatts. In this case, our linear approximation of the drive in Eq. (7) fails and the system of Eqs. (1), (2), and (7) must be reinvestigated.

Finally, we mention that structure in addition to the main peak has been observed in a few samples. This structure is presently being investigated as well as the general effect of junction size and geometry.

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<sup>1</sup>Our junctions usually consisted of crossed perpendicular Pb strips 20 mm long, 0.25 mm wide, and between 2000 and 3000 Å thick. The oxide barrier

layers were thermally grown in pure dried oxygen, typical junction resistances being between 0.5 and 10 ohms. The Josephson dc currents were between 0.1 and 0.6 of their maximum theoretical values and the energy gaps for our Pb films were  $(2.67 \pm 0.04) \times 10^{-3}$  eV.

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<sup>5</sup>Low temperatures are needed to reduce the usual single-particle tunneling current to small values relative to the discontinuous current jump at  $eV = 2\Delta$  since the ratio of the height of the peak to this jump is  $\sim 1/5000$ .

<sup>6</sup>This data was obtained with the earth's field canceled to within 0.05 gauss.

<sup>7</sup>B. D. Josephson, Rev. Mod. Phys. **36**, 216 (1964).

<sup>8</sup>The integral of  $E_x$  in the superconductors gives a contribution of order  $(\lambda/\lambda_0)^2$  smaller than the integral of  $E_x$  in the oxide. Here  $\lambda_0$  is the wavelength of the junction mode which is typically  $10^{-1}$  cm to  $10^{-2}$  cm and  $\lambda$  is the penetration depth which, for temperatures well below the transition temperature, is of order  $10^{-5}$  cm.

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<sup>14</sup>The peak current therefore varies as the fourth power of the tunneling matrix element.

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## EFFECT OF ELECTRON CONCENTRATION ON MAGNETIC EXCHANGE INTERACTIONS IN RARE EARTH CHALCOGENIDES

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The magnetic moments of the lanthanides are localized in the 4f electron shells and the ferromagnetic or antiferromagnetic interactions observed in the lanthanide metals<sup>1</sup> and their metallic alloys<sup>2</sup> have been interpreted by the Ruderman-Kittel-Yosida-type indirect exchange<sup>3</sup> resulting from the polarization of the conduction electrons. We have examined in semiconducting lanthanide compounds the relationship between magnetic transition temperature and electrical properties which can be implied from the theory

of indirect exchange via conduction electrons. We reported previously experimental evidence for such correlation in the bcc  $\text{Th}_3\text{P}_4$  compounds  $\text{Gd}_2\text{Se}_3$  and  $\text{Gd}_2\text{S}_3$ .<sup>4</sup> In these compounds doping with excess Gd or Y up to 0.1 atom per molecule increased the electrical conductivity by orders of magnitude and changed the magnetic properties of  $\text{Gd}_2\text{Se}_3$  continuously from antiferromagnetic ( $T_N = 5^\circ\text{K}$ ) to ferromagnetic ( $T_C = 80^\circ\text{K}$ ) without variation in crystal structure.

The magnetic exchange interactions in NaCl-

type semiconducting chalcogenides of divalent Eu,<sup>5</sup> however, appear to be insensitive to accidental chemical impurities which affect the electrical conductivity. Samples prepared under various conditions show consistent values of the paramagnetic Curie temperature  $\theta$  but order-of-magnitude variation in electrical conductivity. It has been suggested that the 1:1 Eu chalcogenides are nearly ideal examples of Heisenberg ferromagnets and antiferromagnets with first- and second-neighbor exchange interactions<sup>6</sup>; this suggestion has been supported by measurements of the specific heat,<sup>7</sup> neutron diffraction,<sup>8</sup> nuclear magnetic resonance,<sup>9</sup> and electron paramagnetic resonance studies of dilute Eu<sup>2+</sup> pairs in CaO and SrO.<sup>10</sup>

In this Letter we report that partial replacement of the divalent Eu ions by trivalent lanthanides such as Gd, Tb, Dy, Lu, La, and Y increases the paramagnetic Curie temperature of the europium chalcogenides sharply in the low concentration range, where the material is still semiconducting. The Curie-temperature variation in metallic samples with higher trivalent ion concentrations agrees with the assumption of indirect exchange interaction via conduction electrons in the  $5d$  energy level. As an example we report here the magnetic and electric behavior of pseudobinary solid solutions between the semiconducting rocksalt compound EuSe and the metallic rocksalt compounds GdSe and LaSe. More details will be published later.<sup>11</sup>

EuSe is ferromagnetic below  $T_C \sim 7^\circ\text{K}$  and has a paramagnetic Curie temperature  $\theta = 9^\circ\text{K}$ . Single crystals of millimeter thickness are found to be optically transparent in the wavelength range above  $6700 \text{ \AA}$ . The  $(h\nu)^{1/2}$  dependence of the absorption indicates direct electron transition for energies larger than  $h\nu = 1.85 \text{ eV}$ . The electrical resistivity at room temperature is  $\rho = 1.70 \times 10^8 \text{ \Omega cm}$ , slightly higher than the value reported by Busch *et al.*<sup>12</sup>

GdSe is antiferromagnetic below a Néel temperature  $T_N \sim 50^\circ\text{K}$  (as defined by peaks in the electrical resistivity and magnetic susceptibility) and has a paramagnetic Curie temperature  $\theta = -60^\circ\text{K}$ . (Iandelli<sup>13</sup> reports  $\theta = -28.5^\circ\text{K}$ .) This NaCl-type compound has a golden color and an electrical resistivity of  $1.3 \times 10^{-4} \text{ \Omega cm}$  at room temperature (Miller, Matson, and Himes<sup>14</sup> report  $0.72 \times 10^{-4} \text{ \Omega cm}$ ) with a metallic temperature coefficient  $\partial\rho/\partial T = 13 \times 10^{-8} \text{ \Omega cm/deg}$  compared to  $7.5 \times 10^{-8} \text{ \Omega cm/deg}$  for Gd metal. Since the paramagnetic moment corresponds to that of

trivalent Gd ions, GdSe belongs to the group of metallic NaCl compounds with unbalanced valence, such as CeS, ThS, US, etc., for which Eastman *et al.*<sup>15</sup> proposed that the extra electrons are involved as free  $d$  electrons in the metallic bond connecting the metal ions. The five  $d$  orbitals of the lanthanide or actinide ions split in the octahedral coordination of the NaCl lattice. The threefold degenerate  $t_{2g}$  branch, which has the lower energy,<sup>16</sup> can overlap enough with the twelve next-nearest metal ions to provide a metallic bond. This metallic character of the electrons in the  $d$  orbitals superimposes on the ionic bond and its contribution to the total binding energy is indicated by the higher densities of the NaCl-type chalcogenides of lanthanides or actinides having a valence larger than 2.

In the solid solution system between the semiconducting EuSe and the metallic GdSe it is possible to study the relationship of magnetic interactions and electrical conductivity, as the conductivity varies twelve orders of magnitude, from an insulator to a metal in the same crystal structure. Figure 1(a) shows the paramagnetic Curie temperature  $\theta$ , representing the sum of all exchange interactions, and the cell dimensions of the NaCl structure as a function of  $x$ , the atomic fraction of trivalent Gd ions in  $(\text{Eu}_{1-x}\text{Gd}_x)\text{Se}$ . The steep increase of the magnetic interaction with the addition of small amounts of Gd ions is surprising.<sup>17</sup> With increasing Gd concentration  $\theta$  reaches a maximum, where its

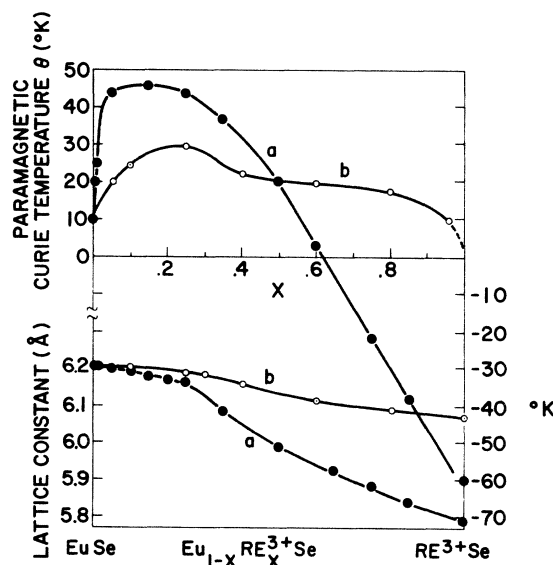


FIG. 1. Variation of the  $\theta$  value and lattice constant of EuSe with  $\text{RE}^{3+}$  substitution: (a)  $\text{Eu}_{1-x}\text{Gd}_x\text{Se}$ , (b)  $\text{Eu}_{1-x}\text{La}_x\text{Se}$ .

value is about five times greater than in pure EuSe, and then changes continuously to negative values corresponding to the antiferromagnetic state of the pure compound GdSe.

Since the abscissa of Fig. 1 can be interpreted as the number of extra electrons per magnetic lanthanide ion, varying between 0 and 1, it suggests that the observed  $\theta$  variation is the response of the Ruderman-Kittel-Yosida interaction to the variation of the conduction electron population in the  $5d$  orbitals. Figure 2 is a plot of de Gennes's relationship between  $\theta$  and the number of free conduction electrons per atom, as calculated by Mattis, Anthony, and Horowitz<sup>18</sup> in a bcc and fcc lattice. The abscissa shows the number of free conduction electrons per magnetic ion instead of the Fermi momentum  $k_F$ . The oscillatory succession of positive and negative regions with increasing electron population in the conduction band is a characteristic consequence of indirect exchange via conduction electrons having a Fermi distribution. The value  $\theta = 300^\circ\text{K}$  of hexagonal Gd metal with 2.1 free electrons<sup>19</sup> might be used as a guide for a rough calibration of the arbitrary  $\theta$  units for the fcc structure. For small electron concentrations the indirect exchange theory predicts ferromagnetic interaction for bcc and fcc lattices.  $\theta$  goes through zero at a conduction electron population of  $\frac{1}{4}$  electron per magnetic ion. Due to the three-fold degeneracy of the  $t_{2g}$  branch of the  $5d$  band in NaCl compounds, the sign change of  $\theta$  should occur for 0.75 free electron in the  $5d$  band, in fairly good agreement with the observations given

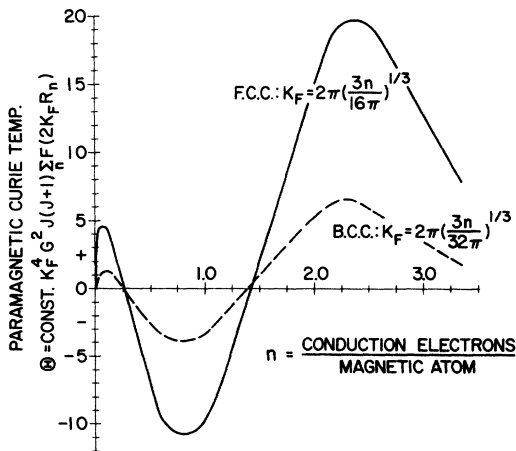


FIG. 2. Variation of the  $\theta$  value with the free electron concentration as given by de Gennes ( $k_F$  = Fermi momentum,  $G$  =  $s$ - $f$  exchange integral,  $J$  =  $4f$  magnetic moment,  $R_n$  = distance between magnetic ions,  $F(2k_F R)$  = Ruderman-Kittel function).

in Fig. 1. The relation between  $\theta$  values and conduction electron concentration, suggested by this agreement, can be supported by the investigation of solid solutions of EuSe with the metallic NaCl compound LaSe. La has the same valence as Gd, but no  $4f$  electrons and therefore no magnetic moment. The  $\theta$  variation with La concentration  $x$  in  $(\text{Eu}_{1-x}\text{La}_x)\text{Se}$  is shown in Fig. 1(b) and demonstrates that the number of extra electrons is the critical parameter for the magnetic interaction. Quantitative differences between the curves in Figs. 1(a) and 1(b) are due to the influence of the spin dilution on  $\theta$  in the latter case. In particular, the ferromagnetic alignment of very dilute Eu spins corresponds to the prediction of the indirect exchange theory for dilute spins statistically distributed among the lattice sites.

The use of the Ruderman-Kittel-Yosida theory is legitimate only if the Fermi energy of the conduction electrons is larger than the exchange interaction with the  $4f$  spins, i. e., a few tenths of an eV. The free electron concentration in the  $(\text{Eu}_{1-x}\text{Gd}_x)\text{Se}$  system, as derived from electrical resistivity and Hall effect measurements, does not increase proportionally to the Gd concentration  $x$ . For the composition  $x=0.5$ , as an example, we measured at room temperature the electrical resistivity  $\rho = 5.9 \times 10^{-4} \Omega \text{ cm}$ , which corresponds to a free electron concentration of  $n = 5.4 \times 10^{21} \text{ cm}^{-3}$  (or 0.3-0.4 electron/magnetic ion) with a Hall mobility of  $2 \text{ cm}^2/\text{V-sec}$ . At a concentration of  $x=0.01$ , however, the electrical resistivity at room temperature is  $18 \Omega \text{ cm}$  corresponding to only about  $10^{16}$  electrons/ $\text{cm}^3$ , assuming a Hall mobility less than  $1 \text{ cm}^2/\text{V sec}$ . Optical and electrical measurements characterize the composition  $(\text{Eu}_{0.99}\text{Gd}_{0.01})\text{Se}$  as a semiconductor with a band gap of 1.87 eV. The band gap increase compared to pure EuSe may be explained by the elevation of the Fermi level above the bottom of the conduction band due to the  $10^{16}$  conduction electrons of the trivalent Gd. The additional appearance of a continuous light absorption observed up to  $2400 \text{ \AA}$  is the optical manifestation of these conduction electrons, and the  $\lambda^{3.5}$  dependence of the absorption is characteristic of impurities with Coulombic perturbing potential as scattering centers.<sup>20</sup> If one also considers the nonlinear variation of the cell parameter of the NaCl structure with Gd or La concentration  $x$  in Fig. 1 the following conclusion is suggested: The metal ion distance in EuSe is too large for overlap of  $5d$ - $t_{2g}$  orbitals,

and therefore, the extra electron of the trivalent Gd or La cannot establish a metallic bond at small concentrations  $x$ . The  $5d$  wave functions of the divalent and trivalent lanthanide ions, however, must somehow interact sufficiently in a semiconductor so that the extra electrons can produce a magnetic exchange interaction which is a sensitive function of the concentration  $x$ .<sup>21</sup> The value of the ferromagnetic saturation moment at  $T=0^\circ\text{K}$  shows that this unexplained interaction couples all lanthanide ion spins independently of the valence. Only after the concentration  $x$  falls in the range between 0.2 and 0.4 does the metallic bond develop, and the cell dimensions shrink due to the metallic contribution to the crystal energy. The released extra electrons are now free enough to make an exchange interaction in the sense of the Ruderman-Kittel-Yosida theory.

The effect of other trivalent lanthanides such as Tb, Dy, Lu, and also Y on the paramagnetic Curie temperature of EuSe and EuS is found to be qualitatively the same as described here. Traces of lighter elements such as trivalent transition metals, however, appear to increase the electrical conductivity without variation of the Curie temperature, possibly because the energy levels of the donor centers are too low to increase the electron population in the  $5d$  orbitals of the Eu ions.

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