

## ON THE FERROMAGNETISM OF EuO AND EuS

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## ABSTRACT

The indirect magnetic interaction in semiconductors is used to evaluate the exchange parameters for EuO and EuS respectively.

One obtains  $J_{\text{eff}}(\text{EuO}) \approx (0.06 \pm 0.02)\text{eV}$  and  $J_{\text{eff}}(\text{EuS}) \approx (0.08 \pm 0.04)\text{eV}$  in reasonable agreement with those usual in the literature for rare-earth systems.

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## I. INTRODUCTION

It is well known that EuO and EuS are ferromagnetic compounds (1)(2). Although it is well established that the Heisenberg Hamiltonian applies, the origin of exchange is a matter of dispute - see ref. (1) for earlier work in this field and (3), (4), (5) and (6).

The Bloembergen-Rowland indirect interaction (7) between localized magnetic moments in insulators has been invoked in order to explain the occurrence of ferromagnetism in these compounds (8), (9).

However it is now clear that EuO and EuS are intrinsic semiconductors (1), (2), (3), (10) and (11) so that computations based on the Bloembergen-Rowland interaction can only give rough estimates of the exchange parameters.

We have recently studied the indirect magnetic interaction in semiconductors (12). It is the purpose of this paper, to recall briefly this mechanism and to use it in the interpretation of the magnetic properties of EuO and EuS.

We will show that in spite of the somewhat drastic approximations involved, the exchange parameters estimated in this way are in good agreement with those obtained in rare earth systems by several workers on this field (1), (3), (13), (14) and (15).

## II. INDIRECT INTERACTION IN SEMICONDUCTORS

The indirect magnetic interaction  $E_{ij}$ , for spherical energy surfaces, between two localized spins  $\vec{S}_i$  and  $\vec{S}_j$  at lattice positions  $\vec{R}_i$  and  $\vec{R}_j$  is given by (12),

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$$E_{ij} = A_{ij} \vec{S}_i \cdot \vec{S}_j \quad (1)$$

$$A_{ij} = C_1 \phi(q, y', \gamma^2) \quad (2)$$

$$C_1 = \frac{2 \Omega^2 \Gamma_S^2 k_T^4 m_e}{(2\pi)^3 h^2 \alpha'}$$

$k_T = 2 (3/4\pi\Omega)^{1/3} = \frac{2\pi}{a_0} \left(\frac{3}{\pi}\right)^{1/3}$  is the Brillouin zone radius,  $a_0$  the lattice parameter, and  $\Omega$  is the atomic volume of the diamagnetic lattice.

$$\phi(q, y', \gamma^2) = \frac{1}{q^2} \int_0^1 dx \, x \sin(qx) e^{-q(y' + \gamma^2 x^2)^{1/2}}$$

$$y' = \frac{E_g}{\alpha' E_T} \quad \text{and} \quad \gamma^2 = \frac{\alpha}{\alpha'} \quad \text{and} \quad E_T = \frac{\hbar^2 k_T^2}{2 m c} \quad (3)$$

$$q = k_T R \quad \text{where} \quad R = |\vec{R}_j - \vec{R}_i|$$

$E_g$  is the energy gap, and  $\alpha$  and  $\alpha'$  are the effective masses defined by

$$E(k) = \alpha \frac{\hbar^2 k^2}{2m_e} \quad \text{for the valence band}$$

$$E(k') = \alpha' \frac{\hbar^2 k'^2}{2m_e} \quad \text{for the conduction band}$$

$\Gamma_S$  is a measure of the exchange interaction between the localized spin  $\vec{S}_i$  and the diamagnetic ions as defined in (12) and (16).

In a Bloembergen-Rowland insulator (sharp valence band) one has  $y'$  finite and  $\gamma^2 \rightarrow 0$ . In this case eq. (2) gives the result

$$\phi(q, y') = F(q) e^{-q\sqrt{y'}} \quad (4)$$

where  $F(x) = \frac{x \cos x - \sin x}{x^4}$  is the Ruderman-Kittel function.

For a typical intrinsic semiconductor  $\gamma^2$  may be  $0.1 \leq \gamma^2 \leq 1.0$ . The important point to be retained is that in general the indirect interaction in semiconductors is stronger than in insulators. Furthermore  $\phi(q, y', \gamma^2)$  as a function of  $q$ , is oscillatory. This is a very interesting result for it shows that this interaction may give rise to many magnetically stable configurations.

### III. QUALITATIVE COMMENTS ON THE MAGNETIC PROPERTIES OF Eu CHALCOGENIDES

As usual we shall consider  $\text{Eu}^{++}$  to be in a  $8_S$  state. We shall also assume that the 4f-shell is localized. In general, this is also a fair approximation (1), (2) and (3).

The Eu chalcogenides ( $\text{EuO}$ ,  $\text{EuS}$ ,  $\text{EuSe}$  and  $\text{EuTe}$ ) crystallize in a f.c.c. structure. Their Curie-Weiss temperatures are respectively  $76^\circ\text{K}$ ,  $19^\circ\text{K}$ ,  $9^\circ\text{K}$ ,  $-6^\circ\text{K}$ , approximately (1).

According to Anderson (17), (18) in insulators we have three magnetic interactions: kinetic exchange (also called "superexchange" in the literature) which dominates in the magnetic insulating compounds of the 3d series (for instance MnO) and which is antiferromagnetic; direct or potential exchange (also called "classical" Heisenberg exchange) and which is an order of magnitude smaller and the Bloembergen-Rowland interaction. Kinetic exchange increases with increasing covalency.

For insulating or semiconducting compounds of the 4f series direct exchange may be neglected due to the fact that the overlap of the 4f shells is negligible.

For compounds with a very low degree of covalency, like for instance EuO, the indirect magnetic interaction largely dominates.

With increasing covalency, on going from EuTe, the effect of Kinetic exchange becomes gradually more pronounced. We shall assume that kinetic exchange is negligible for EuO and EuS. This may be a fair approximation, specially for EuO. For EuSe, Kinetic exchange may be of the same order of magnitude as the indirect interaction thus making the compound metamagnetic (1), (9). Finally for EuTe Kinetic exchange overcomes the indirect exchange and the compound is antiferromagnetic.

Besides the qualitative agreement with the magnetic properties of Eu-chalcogenides, this model seems to be necessary in order to understand the variation of the Mössbauer parameters along the series (20).

#### IV. CALCULATION OF THE INDIRECT INTERACTION FOR EuO AND EuS

From refs. (1) and (21) one obtains the magnetic interaction

between the first neighbours  $A_{01}$  and second neighbours  $A_{02}$ , and the relation  $P = A_{02}/A_{01}$ .

For EuO  $P \approx 0.0923$  and for EuS  $P \approx 0.4$ . The errors involved in these measurements are of the order of 25%.

Now,

$$E_{\text{mag}} = \sum_{i \neq j} A_{ij} \vec{S}_i \cdot \vec{S}_j = 12 S^2 A_{01} + 6 S^2 A_{02} \quad (5)$$

for 12 first neighbours and 6 second neighbours. For  $\text{Eu}^{++}$ ,  $S = 7/2$ .

In the Weiss approximation

$$\theta_{\text{para}} = \frac{E_{\text{mag}}}{1.1666 k_B} \quad (6)$$

Using eqs. (1), (2), (3), (5) and (6) one obtains easily

$$\theta_{\text{para}} = C_2 \frac{\Gamma_S^2}{\alpha^3} a_0^2 \phi(q_{0i}) \left| 1 + \frac{1}{2} P \right| \quad (7)$$

where  $C_2 = 0.56 \times 10^6$ .

Now it is important to note that the proper calculation of the interactions involves essentially two steps: firstly one has to estimate the superexchange - this requires the knowledge of the band structure, specially the positions of the  $f_{\uparrow}$  and  $f_{\downarrow}$  states and the matrix elements of the Coulomb interactions (17)(18). There is no general agreement about these matters in the literature (1), (3), (5), (10), (11). This makes this computation

almost impossible at present, so we shall neglect this contribution. The second step is the calculation of the indirect interaction. This involves an integration over  $k$ , which implies some knowledge of the effective masses, the bandwidths and the energy gaps (12).

By using the results of ref. (12) one can easily obtain  $p$  as a function of  $\gamma^2$  for different values of  $y$ . From this pairs  $(\gamma^2, y)$  one calculates the ratios between the indirect interaction in semiconductors and the Bloembergen-Rowland interaction, that is  $\phi(y, \gamma^2)/\phi_{BR} = R\phi$  which are plotted as a function of  $y' = \gamma^2 y$  in fig. 1 for  $P(\text{EuO}) = 0.09$  and in fig. 2 for  $P(\text{EuS}) = 0.4$ . It should be noted that these ratios are not very sensitive to the experimental errors in  $P(\text{EuO})$  and  $P(\text{EuS})$ .

It can be easily seen that for large values of  $y'$  these ratios approach 1 asymptotically, as expected. However it is important to note that for small values of  $y'$  the indirect interaction is at least 2 or 3 times larger than the Bloembergen-Rowland interaction. This shows that the exchange calculated in a semiconductor can be 2 or 3 times smaller than the exchange calculated by the Bloembergen-Rowland interaction. Fig. 1 and 2 enable us to evaluate the exchange for EuO and EuS for a given  $y' = \frac{E_g}{\alpha' E_T}$  obtained from the band structures.

We shall now qualitatively estimate the exchange parameter of EuO and EuS by using, tentatively the estimated results for  $\alpha'$  obtained in the Bloembergen-Rowland approximation (9) that is  $\alpha'(\text{EuO}) \approx 0.4$  and  $\alpha'(\text{EuS}) \approx 0.3$ . It should be remarked that  $\alpha'(\text{EuO}) > \alpha'(\text{EuS})$  as expected, given that the energy gap in the oxide is smaller than in the sulphide (22).

Using also the experimental values for the energy gaps one obtains:

$$y'(Eu0) \approx 0.5$$

$$y'(Eu0) \approx 1.5$$

These are, of course, rough estimates, due to the fact that we are using an indirect interaction (12) which tends to average out the effective masses and gaps.

We shall make  $2 \Gamma_s = J_{\text{eff}}$  in order to compare our results with those in the literature. Using the results of fig. 1 and 2 one obtains:

$$J_{\text{eff}}(Eu0) \quad (0.06 \pm 0.02) \text{eV}$$

$$J_{\text{eff}}(EuS) \quad (0.08 \pm 0.04) \text{eV}$$

It should be interesting to know if  $J_{\text{eff}}(Eu0)$  is larger or smaller than  $J_{\text{eff}}(EuS)$ . As far as we can infer from this calculation  $J_{\text{eff}}(Eu0)$  may be of the same order of magnitude as  $J_{\text{eff}}(EuS)$ . It is important to point that their values are in the regions from 0.05eV to 0.1eV. This is typically the range of values for the exchange interaction in rare earth systems (13), (14), (15).

It should be emphasized that these are rough estimates of the exchanges. The errors involved come firstly from the neglect of Anderson's superexchange (or kinetic exchange) (the difficulties involved were discussed above). This is specially important in EuS. Secondly the calculation of the indirect interaction as mentioned before, involves many drastic approximations.

However it can be surely concluded that the indirect magnetic



interaction in semiconductors plays a significant role in the interpretation of the magnetic properties of Eu chalcogenides.

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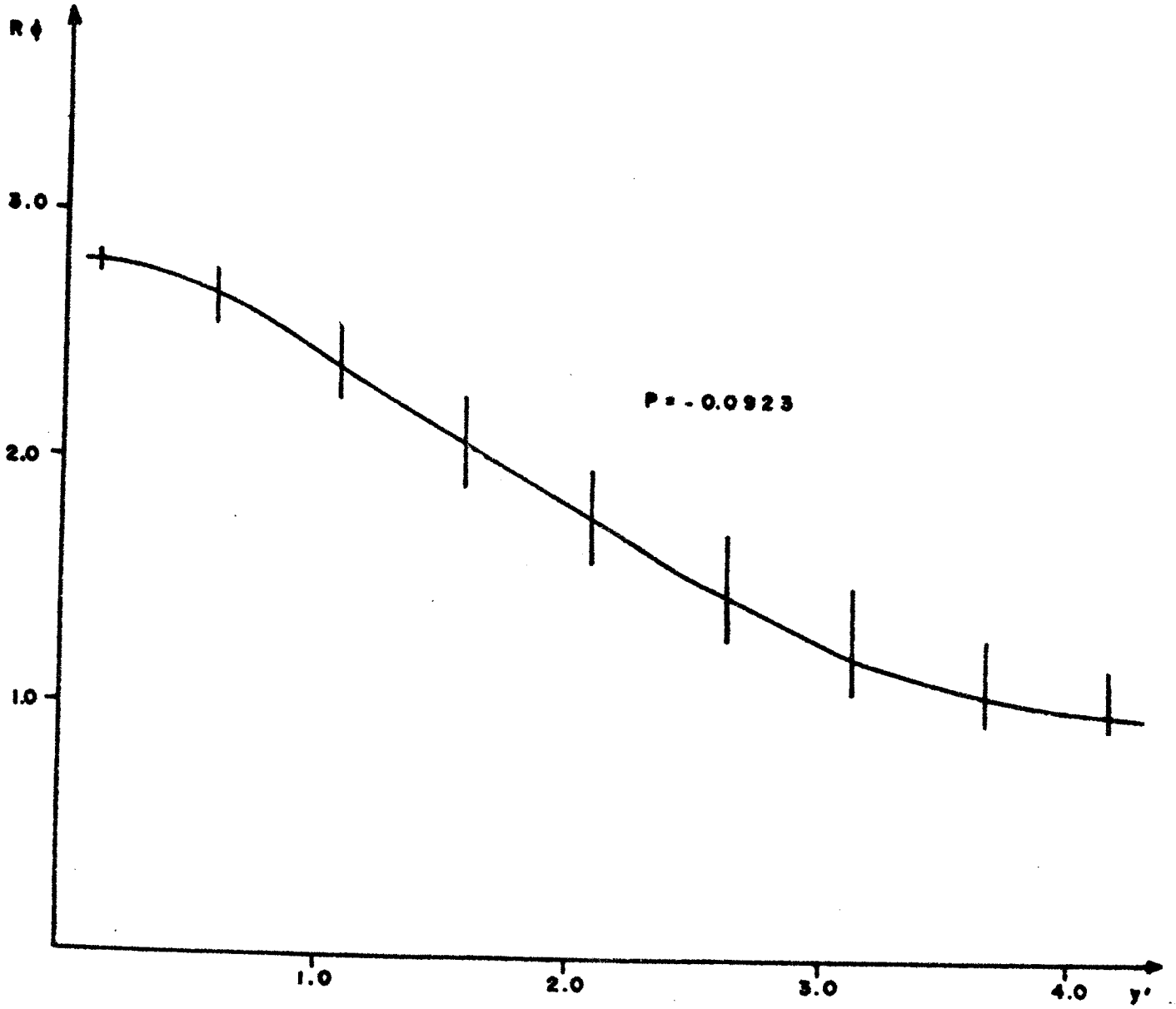


FIG. 1

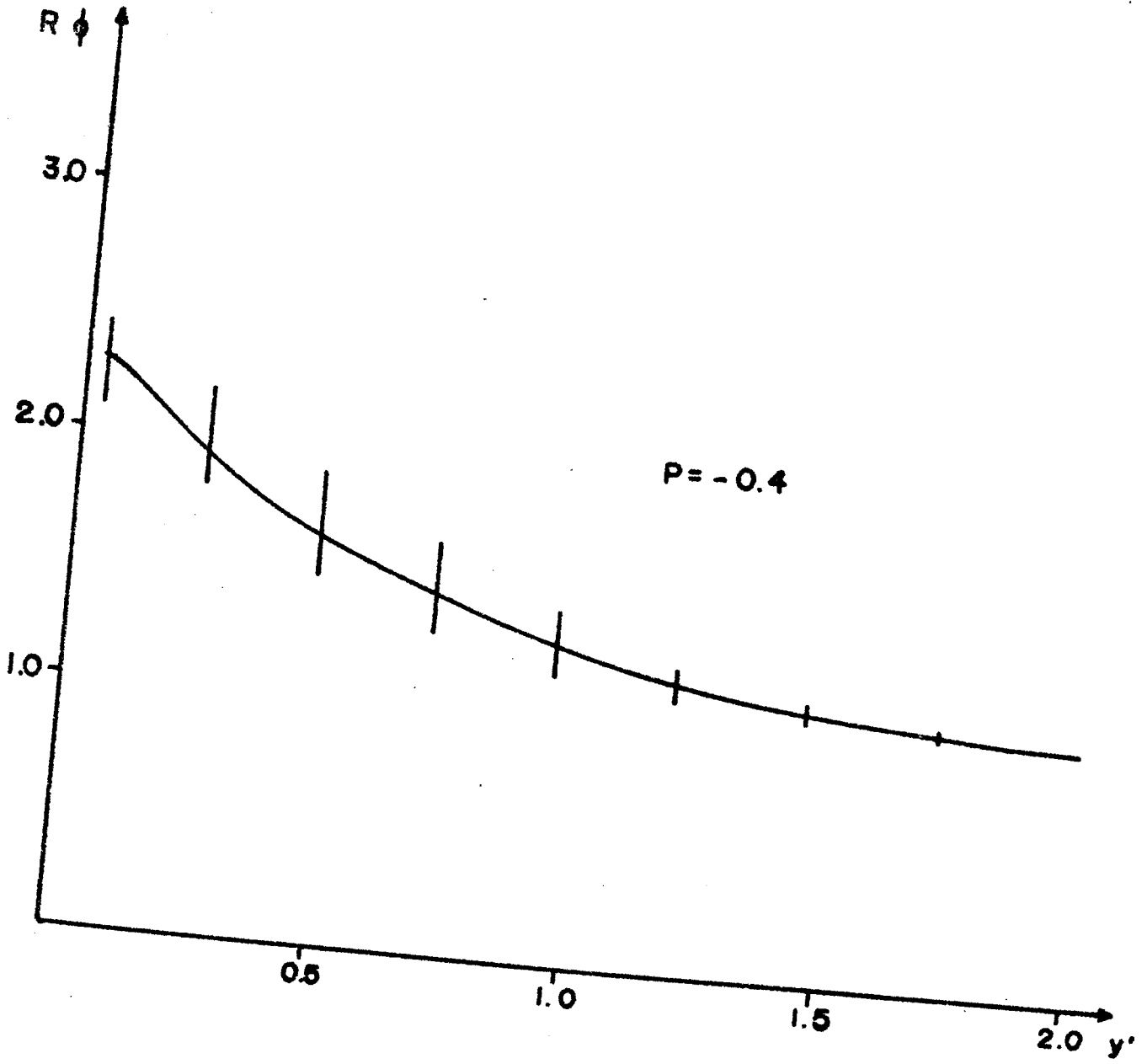


FIG- 2