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Exchange optics in Gd-doped EuO

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This paper is concerned with magneto-optical properties of EuO single crystals, doped with up to 5-at.% Gd. The optical absorption and the Faraday rotation have been measured above and below the magnetic-ordering temperatures and in various magnetic fields. In addition the reflectivity between 13 eV and 250 μm has been observed and the Curie temperature has been determined. The measurements permit the evaluation of the magnetic short- and long-range order. The exchange interaction between free electrons and $4f$ spins can be determined and is found to decrease with increasing doping. The analysis of the optical data permits the derivation of the carrier concentration, their mobility, and temperature dependence. The carrier concentration shows an exchange-induced ionization near T_C for nondegenerate samples and the mobility has a sharp minimum at T_C. The transport parameters also reflect the fact that the electron–$4f$-spin interaction decreases with increasing Gd concentration, probably owing to electrostatic-shielding effects.

I. INTRODUCTION

The europium chalcogenides, which all crystallize in the rocksalt structure, are an ideal system for the investigation of magnetic interactions. First, within the chalcogenide series we find all kinds of fundamental magnetic order. Second, these materials are nearly ideal Heisenberg magnets. Third, the undoped compounds are insulators or semiconductors. However, by suitable doping one can introduce free carriers and thus study the additional magnetic interactions.[1] Fourth, dopants can be incorporated in various ways and it is of considerable interest to distinguish between dopants with and without spin and between doping in the cation or anion lattice. In this paper we want to put emphasis on the exchange interactions in Gd-doped EuO as obtained by optical and magneto-optical investigations of this material.

Without going into the details of a band-structure calculation of EuO, we want to point out the essential features of an energy-level scheme on which all investigators agree.[1–3] The highest occupied valence band is formed by p^6 states of the oxygen. Above this band the localized and partially occupied $4f^7(^8S_{7/2})$ states of Eu^{2+} are situated and at still higher energies conduction bands with $5d$ and $6s$ symmetry are found. n-type doping introduces donor levels somewhat below the bottom of the conduction band. If Gd is chosen as the donor, and if Gd^{3+} substitutes for Eu^{2+}, the donor is a shallow level (~0.017 eV) with $4f^7 5d^1$ symmetry.[4] However, already here we want to remark that with the incorporation of Gd, a usually uncontrolled change in the anion lattice, such as the formation of vacancies, may go in parallel. Thermal ionization of shallow donors yields free conduction electrons and, at high concentrations of the dopant, impurity bands will form and the Fermi level will move into the conduction band.

II. OPTICAL ABSORPTION $K(\lambda, N)$

First, we want to describe the effect of doping on the optical absorption of EuO. In Fig. 1 we show the absorption coefficient $K(\lambda, N)$ for undoped, off-stoichiometric and Gd-doped EuO. The absorption edge corresponds to a $4f^7$-$4f^6(^7F_J)\,5d(t_{2g})$ transition. In the Gd-doped samples a free-carrier absorption at longer wavelengths than the edge is obvious. If EuO is prepared the usual way by melting together $Eu + Eu_2O_3$, the samples generally have

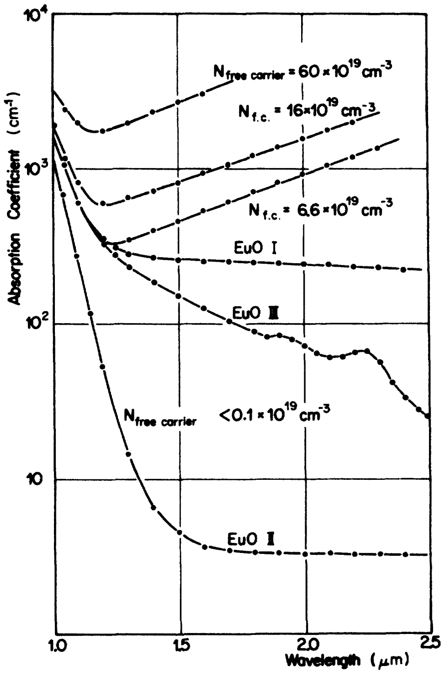

FIG. 1. Absorption coefficient of nearly stoichiometric, off-stoichiometric, and Gd-doped EuO crystals. The Gd-doped samples are characterized by their room-temperature free-carrier concentration.

Eu deficiencies and the deviation from stoichiometry manifests itself in a high residual absorption coefficient [EuO(I)]. Heating such a ground and polished EuO sample in Eu vapor results in a nearly stoichiometric material as verified by its excellent transparency in the infrared [EuO(II)]. Further heating in Eu vapor of the very same sample finally leads to a deficiency in oxygen, and the absorption coefficient displays two discrete humps at 0.65 and 0.55 eV [EuO(III)].

Exactly these latter samples make an insulator-metal transition below the Curie temperature. This transition is interpreted by Torrance *et al.*[5] as being due to the ionization of a "bound magnetic polaron." The doubly positively charged oxygen vacancy, acting like an *F* center, can trap two electrons with different binding energies. In the paramagnetic temperature range these electrons are bound both electrically and magnetically because the electrons, owing to their exchange interaction, polarize magnetically the next-neighbor Eu $4f^7$ spins during their orbit around the vacancy. Below T_C the magnetic part of the binding energy disappears more and more and the Coulombic part of the weaker bound electron is not large enough to localize the electron, thus leading to a metal-like conductivity. In the paramagnetic state the total binding energy, Coulombic and magnetic, of the oxygen vacancy results in a deep donor (~0.3 eV): at 300 K only a small part of these deep donors are ionized; therefore a free carrier absorption in these off-stoichiometric samples is not observed in the indicated wavelength region.

It has also been proposed[6] that the two humps observed in the ir absorption spectrum of samples containing oxygen deficiencies are due to an exchange resonance between the electron and the neighboring $4f^7$-spin system. In this resonance the electron is flipping its spin and it is the spin-orbit coupling which makes this optical transition allowed and splits the absorption into a doublet. Thus the oxygen vacancy is acting as a probe for the strength of the exchange interaction, because it is a measure of the energy difference between the spin-up and spin-down state of the electron when it is in an extended state and "sees" several Eu neighbors. This energy difference then is about 0.6 eV. The absorption edge in the paramagnetic state appears to be at longer wavelengths for Gd-doped samples than for pure samples, as best seen in Fig. 2. This is a general behavior of highly doped semiconductors where impurities and local lattice distortions tend to reduce the energy gap similar as in amorphous materials.[7]

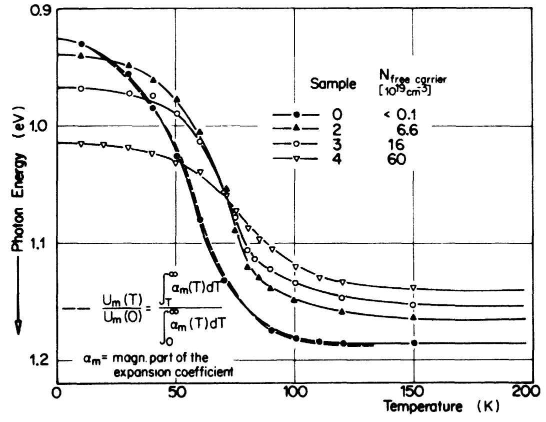

FIG. 2. Temperature shift of the absorption edge of undoped and Gd-doped EuO. Dashed curve represents the spin correlation function.

III. TEMPERATURE DEPENDENCE OF THE ABSORPTION EDGE $K(T, N)$

In Fig. 2 we show the shift of the absorption edge with temperature for undoped and Gd-doped EuO. For better comparison of the various doped samples the temperature dependence of an arbitrarily chosen but common absorption coefficient is plotted. For all samples we observe a red shift of the absorption edge upon cooling below about 150 K. We explain this in the following way: above the Curie temperature each state in the conduction band can be occupied by two electrons with opposite spin. Below T_C the spin degeneracy is lifted and the bands are split owing to the exchange interaction[8]

$$H_{ex} = -2\sum_n J_n(r-R_n)\vec{s}\cdot\vec{S}_n \quad (\sim 0.6 \text{ eV for pure EuO}),$$

where $\vec{s}$ is the spin of a conduction electron, $\vec{S}_n$ are the spins of neighboring Eu^{2+} ions, and $J_n(r-R_n)$ is the distance-dependent exchange constant between electron and ion spins. The energy gap between $4f^7$ (the highest occupied valence state) and the conduction band thus becomes reduced, resulting in a red shift of the absorption edge. As we see from the figure the total shift, when the magnetization $0 < M < M_s$, amounts to about 0.3 eV for the undoped sample and it is thus one-half the total exchange splitting between up- and down-spin conduction bands. Inclusion of second-order terms has shown that the temperature dependence of H_{ex} is proportional to the spin correlation function.[8] To demonstrate this we made a fit of a spin correlation function—taken from the magnetic part of the specific heat or the magnetostriction[1]—with the red shift of the absorption edge of a pure EuO (dashed line in Fig. 2).

EuO containing oxygen vacancies practically has the same Curie temperature as stoichiometric EuO and only a small free-carrier concentration at 300 K.[5,9] The exchange energy, therefore, will not be very different from an undoped sample. We then realize that the exchange energy determined from the exchange resonance of the bound magnetic polaron (~0.6 eV) and the one taken from the red shift of the absorption edge (~2×0.3 eV) agree.

Considering now that the total red shift of the absorption edge in Gd-doped EuO decreases with increasing carrier concentration (Fig. 2), we must conclude that the exchange energy becomes reduced in doped materials. The sample with the highest carrier concentration (sample 4) displays a red shift of 0.12 eV, less than half as much as for undoped EuO. We tentatively conclude that the exchange interaction energy of this doped sample is about one-half the one in pure EuO.

IV. REFLECTIVITY OF PURE AND Gd-DOPED EuO $R(\lambda, N)$

In order to extend our optical measurements also to higher doping levels, we had to go from transmission to reflection measurements. (Single-crystal specimens could not be ground thinner than about 10 μm.) The reflectivity of variously doped EuO single crystals at 300 K has been investigated over nearly five orders of magnitude of photon energy (13 eV–250 μm) and is shown in Fig. 3.[10] For $h\nu > 1$ eV we observe band to band transitions, a possible assignment of which has been performed elsewhere.[11] Between 10^{-1} and 5×10^{-1} eV we find reflectivity minima in the doped samples which are absent in undoped material. These minima are due to the plasma resonance of the free carriers. For $h\nu < 10^{-1}$ eV, and best observed in pure EuO, minima and maxima are found which can be attributed to longitudinal- and tranverse-phonon modes, generally known as the residual rays.[12] In addition we observe at the higher-doped samples (x represents the at.%-Gd concentration actually found in the samples and measured by micro-probe or x-ray fluorescence) two reflectivity peaks near 0.3 eV. There can be no doubt that in these highly doped samples, we unintentionally also incorporate oxygen vacancies.

Earlier we described the model of the bound magnetic polaron and the exchange resonance connected with the oxygen vacancy. If now we identify these doublets with the exchange resonance, the oxygen vacancy acting as the probe of the exchange energy, we realize that in the higher-doped samples the resonance energy is at 0.3 eV, i.e., one-half the value it had in the Gd-free compounds. We arrived at just the same conclusion in Sec. III concerning the red shift of the absorption edge, especially if we note that the Gd concentration of the $x = 1.26\%$ and sample 4 are similar. The fact that we do not observe this exchange resonance in weakly doped material only indicates that the concentration of oxygen vacancies is not very large. This is very important to realize and is experimentally verified, since our samples 0, 1, and 2 showed no metallic behavior below T_C. Another important feature of our samples is the fact that with increasing doping (at least for $x < 2\%$) we observe a steadily increasing carrier concentration and a concomitant increase in T_C (see Table I). This is definitely not the case with Gd-doped EuO, as reported by Samokhvalov *et al.*,[13] and must be due to other defects also incorporated into the material.

These additional defects are also obvious from the appearance of an extremely high reflectivity peak[14] (~30%) at about 0.6 eV which is only weakly indicated in our samples.

V. QUANTITATIVE COMPARISON OF EXCHANGE ENERGY AND INCREASE OF T_C

In previous sections we have shown that the exchange energy H_{ex} of Gd-doped EuO is decreasing with increasing doping level. However, one should remember that doping with Gd nevertheless increases the Curie temperature; e.g., for sample 4, T_C increases to 115 K as compared with 69 K for pure EuO. The highest reported T_C for Gd-doped EuO is 135 K for $x \sim 3.4$ at.%.[15] It therefore seems useful to briefly discuss the various exchange interactions.

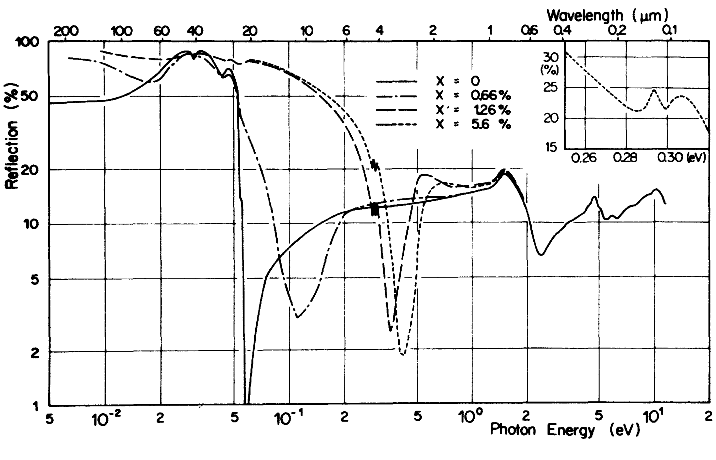

FIG. 3. Reflection coefficient of pure and Gd-doped EuO at 300 K. The insert shows the detailed structure of R of a 5.6-at.%-Gd-doped EuO near 0.3-eV photon energy.

TABLE I. Collection of magnetic, transport, and optical data of undoped and Gd-doped EuO. Verification of $k\Delta T_C \simeq 2(N/N_{Eu})\Delta E$ for Gd-doped EuO.

Sample	T_C (K)	$N_{free\ carrier}$ (10^{19} cm^{-3})	$k\Delta T_C$ (10^{-4} eV)	ΔE (eV)	$2(N/N_{Eu})\Delta E$ (10^{-4} eV)
0	69	$\ll 0.1$	≈ 0	0.260	≈ 0
1	80	3.8	9.5	0.236	6
2	80	6.6	9.5	0.224	10
3	83	16	12	0.188	20
4	115	60	40	0.124	50

For undoped EuO we write the spin Hamiltonian $H = -\sum_{nm} J_{nm} \vec{S}_n \cdot \vec{S}_m$, with $\vec{S}_n$ and $\vec{S}_m$ the $4f^7$ ion spins. This Hamiltonian leads to a Curie temperature of 69 K. In doped materials the observed increase of T_C necessitates an additional term in the exchange Hamiltonian. For this Kasuya and Yanase[2] proposed the idea of a giant spin molecule or spin cluster. Similarly, as in the trapped magnetic polaron, the impurity electron, owing to its strong interaction with the $4f^7$ spins, polarizes the neighbor Eu ions. For the additional exchange interaction, these authors propose the following term: $-2\sum_{in} J_{in} \vec{s}_i \cdot \vec{S}_n$, with $\vec{s}_i$ the spin of the impurity electron and S_n the spin of the ions. In the case of very high doping, an electron-electron interaction can be included, having the form $-4\sum_{ij} J_{ij} \vec{s}_i \cdot \vec{S}_j$. In the present discussion we will neglect this latter term. The increase in Curie temperature, therefore, mainly is given by

$$k\Delta T_C \simeq 2\sum_{in} J_{in} \vec{s}_i \cdot \vec{S}_n ,$$

where n is summed over the number of neighboring $4f$ spins and i is summed over the number of impurity electrons. Therefore, we can rewrite this expression approximately in the following form:

$$k\Delta T_C \simeq (N/N_{Eu}) \left(2\sum_{n} J_n \vec{s} \cdot \vec{S}_n \right) ,$$

where N/N_{Eu} is the concentration of impurity electrons.

In the larger parentheses of this equation we find the same term as used before to describe the exchange resonance or the red shift of the absorption edge and its magnitude is reduced with increased doping as shown before. Nevertheless the right-hand part of this equation increases upon doping, as will be shown quantitatively now. For this purpose we have to know the number of carriers in our samples and the Curie temperatures.

These quantities are summarized in Table I. All the values in the table have been determined by magneto-optical investigations which will be described later on. It is, however, essential that all the information is obtained on the very same sample to avoid errors due to concentration gradients of the dopant in different samples of the same nominal concentration. In addition our light-transmission measurements average over possible volume donor fluctuations, which is not the case in a photoemission experiment, where local fluctuations are measured as such. It can be seen from Table I that the above equation is more or less fulfilled comparing columns 4 and 6. It is, however, not our main intention to verify this equation, but to measure independently the entities entering into the equation. We observe that the agreement becomes better with higher impurity concentration. The reason is that we inserted the number of free carriers into the equation instead of the total number of impurity electrons. For high doping, these two concentrations coincide due to the degeneracy of the samples.

In a certain way we can interpret the last equation also as a consequence of energy conservation. In the model used to describe the red shift of the absorption edge, the bottom of the conduction band becomes lowered upon magnetic order. If there are electrons in the conduction band or in donors, the lowering of these states represents an increase in energy of the crystal (column 6). If all this energy becomes transformed into magnetic energy, we find a corresponding increase in T_C. However, we have to draw the conclusion that T_C is not increasing proportionally to the impurity concentration, as has been assumed up to now,[2] since the exchange interactions of the impurity electrons are decreasing with increasing concentration. We thus realize that $k\Delta T_C$ will not increase without limits, but rather exhibit a maximum for doping in the order of percent, as verified experimentally.

VI. MAGNETIZATION OF Gd-DOPED EuO

While the red shift of the absorption edge is proportional to the magnetic short-range interaction, the magnetization is proportional to the long-range order. Since the Faraday rotation for strong spin-orbit interaction is proportional to the magnetization, we measure the long-range order magneto-optically in an applied field of 6.7 kOe. In Fig. 4 we compare the magnetization of a sample having $N = 16 \times 10^{19}$ cm^{-3} with undoped EuO. For better comparison the saturation magnetization at 4.2 K and the Curie temperature has been normalized. We realize that in practically the whole temperature region the magnetization of the doped sample is below the one for the pure material, for $T/T_C = 1$ the difference is nearly a factor 1.5.

We must conslude that the doped material is harder to magnetize, which is also observed in a M-vs-H curve. This type of behavior is often found in amorphous ferromagnets where the magnetic ions are distributed statistically as compared

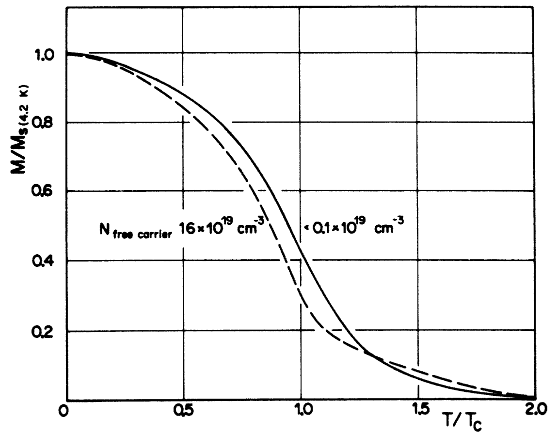

FIG. 4. Normalized magnetization of an undoped and Gd-doped EuO with 16×10^{19} electrons/cm^3. A magnetic field of $H=6.7$ kOe is applied.

with the corresponding crystalline material.[16] Also, we must conclude that the Gd dopant locally has a large fluctuation in concentration and that statistically Gd clusters form. Thus we can describe these highly doped materials as "amorphous ferromagnets."[17] It is not so much the crystal structure that becomes amorphous, but due to the large local distortions introduced by the Gd clusters and with doping levels close to degeneracy, the bottom of the conduction band becomes locally warped, as is the case for an amorphous glass. Thus these highly doped materials may be termed "electronically amorphous."[17]

On the other hand, it has been shown in EuS films doped with Gd,[18] and more recently with single crystals of the mixed system $Eu_{1-x}Gd_xS$,[19] that the Gd spin enters the material antiparallel with respect to the Eu spins. It is obvious that for the Gd concentrations we are discussing in this section, the saturation magnetization at 4 K can only be reduced on the order of 10^{-2} due to antiferromagnetic Gd clusters. This would be within the limits of error of the measurements. However, at intermediate temperatures, appreciable deviations from the magnetization curve of an ideal ferromagnet can be understood qualitatively.

VII. EVALUATION OF TRANSPORT PARAMETERS

In this section we want to describe the methods we used to obtain the parameters shown in Table I. The basic idea behind our method of measurement was to obtain all possible information on the very same sample and to avoid electrical contacts, since it is well known that one encounters severe contact problems with intermediately doped magnetic semiconductors, especially when performing a Hall measurement. Another fundamental problem in these doped ferromagnetic semiconductors is the determination of the Curie temperature in zero external magnetic field. It should be realized that an external magnetic field may have different effects on the electron and on the ion spin system, so the usual extrapolation methods to zero field fail when using a molecular-field approximation. Taking T_C from the maximum of a specific-heat curve also has only a nonconvincing accuracy, since the sharp λ anomaly in pure EuO is replaced by a more and more rounded peak upon doping,[17,20] which is just another indication that simple molecular-field theory is not applicable. We therefore have chosen the appearance of ferromagnetic domains in zero field as the sign of long-range ferromagnetic order. Owing to the Faraday rotation of individual ferromagnetic domains, linearly polarized light transmitting the sample becomes depolarized at T_C.

To determine the transport parameters, the carrier concentration N, their mobility μ, and the effective mass m^*, we have to perform three different, but correlated, types of experiments. We have chosen the free-carrier absorption, the Faraday rotation due to free carriers, and the plasma resonance of the free carriers. The Faraday rotation of bound electrons is used to evaluate the magnetization. The equations interconnecting the measurements are shown in Table II. In the first column we have the complete formulas when the damping term cannot be neglected against frequency. In the second column the well-known simplified equations are shown in the case $g \ll \omega$. In all these equations the parameters N, g, and m^* appear, where $g=e/(m^*\mu)$. Only when the damping factor g is frequency independent, simple Drude theory predicts a λ^2 law for the absorption coefficient K. This is expected to occur for very low frequencies ($h\nu \lesssim kT$) which is not the case in our experiment.[4,21] In the other cases g, and therefore μ, is a function of frequency, the dependence of which is found experimentally by observing the frequency dependence of the free-carrier absorption. If K vs λ is found to obey a power law[4] with a power α different

TABLE II. Drude's formulas.

	$g^2 \approx \omega^2$	$g^2 \ll \omega^2$
Absorption	$K=\frac{e^2}{\epsilon_0 cn}\frac{N}{m^*}\frac{g}{g^2+\omega^2}$	$K=\frac{e^2}{\epsilon_0 cn}\frac{N}{m^*}\frac{g}{\omega^2}$
Faraday Rotation	$\theta=\frac{e^3B}{2\epsilon_0 cn}\frac{N}{m^{*2}}\frac{g^2-\omega^2}{(g^2+\omega^2)^2}$	$\theta=\frac{e^3B}{2\epsilon_0 cn}\frac{N}{m^{*2}}\frac{1}{\omega^2}$
Optical constants near R_{min}	$n^2-k^2-n_c^2=\frac{-e^2}{\epsilon_0}\frac{N}{m^*}\frac{1}{g_p^2+\omega_p^2}$	$1-n_c^2=\frac{-e^2}{\epsilon_0}\frac{N}{m^*}\frac{1}{\omega_p^2}$

from 2, the difference can be attributed to $g \propto \lambda^{\alpha-2}$.[22] In general we made use of the equations in the left-hand column of Table II and solved them rigorously. The plasma-resonance experiments were performed at frequencies near ω_p which are less than the frequency range covered by K or θ. Therefore we have to use g_p instead of g, which can be obtained from an extrapolation using the known frequency dependence $g(\omega)$. This point has not been considered in Ref. 4 therefore N, μ, and m^* in this work is slightly different from Ref. 4. The plasma-resonance measurements could not yet be extended to lower temperatures, so we have kept the effective mass ($m^* = 0.35m$) obtained at 300 K temperature independent. With this provision we computed the temperature dependence of N and μ.

For a sample with 0.66-at.% Gd we show the temperature dependence of N in Fig. 5. Above about 150 K one observes a decreasing carrier concentration with decreasing temperature as typical for a nondegenerate semiconductor. The activation energy in this temperature interval is found to be $E_D = 0.017$ eV (shallow donor). Already appreciably above T_C, where magnetic short-range order commences, we observe an increase in N, somewhat below T_c N decreases again but now the activation energy is considerably reduced; the material, however, remains semiconducting (no observable effect of oxygen vacancies!). To explain, in principle, the increase in N near T_C we recall that the magnetic order splits the conduction band into spin-polarized subbands. An exchange splitting must also be expected for a donor level.[23] However, depending on the degree of coupling between donor and the conduction band, the splitting of the donor is always less than the one of the conduction band.[4] This results in an effective decrease of the activation energy of the donor near T_C, thus that

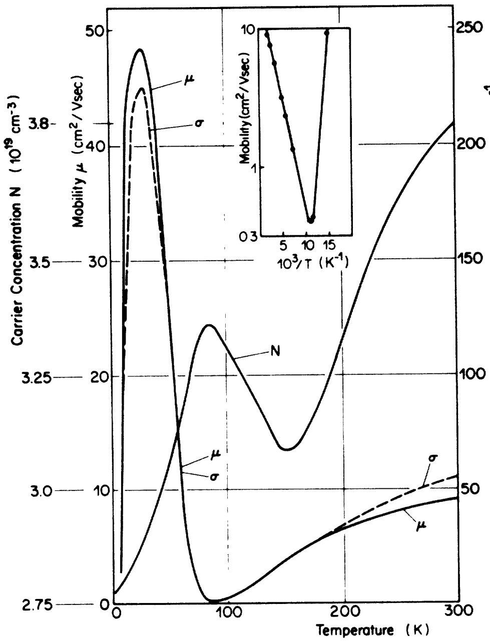

FIG. 5. Carrier concentration N, dc mobility μ, and dc conductivity σ of a Gd-doped EuO sample, containing 3.8×10^{19} electrons/cm^3 at 300 K.

$$\left|\frac{d[E_D(T)/kT]}{dT}\right| < 0 \qquad E_D(T) = E_{D300} - \left|\frac{(1-\gamma)\langle S_0 S_1\rangle \Delta E}{S^2}\right| ,$$

where E_{D300} is the donor activation energy at 300 K, γ is a measure of the donor–conduction-band coupling strength, $0 < \gamma \lesssim 1$, $[\langle S_0 S_1\rangle / S^2]\Delta E$ is the spin correlation function taken from the red shift of the absorption edge.[4] We therefore observe an exchange-induced ionization of the donor (see also Ref. 24 for Cr_2S_3).

Now, in our case the exchange splitting of the donor has to be taken as the exchange splitting of the conduction band minus twice the donor activation energy. Since the latter is only a negligible fraction of the former, it follows that the donor is coupled very hard onto its conduction band.[4] The Gd donor level is a $4f^7\,5d^1$ state; therefore, we must conclude that the lowest conduction band also has d symmetry.

Further support for this conclusion is obtained by comparing the pressure dependence of the optical-absorption edge[25] with the one of the electrical conductivity in lightly doped EuO.[26] The pressure coefficients of both the absorption and the conductivity are identically −4.4 meV/kbar. Since the excited state of the longest wavelength allowed optical transition is a $5d$ state and the free impurity electron is sitting in the lowest possible conduction band, equal pressure coefficients can only mean that the bands in question are of the same character: this is a d band, as indicated by the optical transition. An additional argument is derived from the comparison of the optical-absorption energy at the edge and the thermal activation energy of conductivity in p-doped EuO.[3] Both energies are identically 1.1 eV, and since thermal activation of electrons is not governed by selection rules it follows again that the lowest conduction band, at least in EuO, must possess d character. A last bit of information may be enough to settle this problem. In the model of the bound magnetic polaron in EuO,[5] quantitative agreement with the experiment can only be obtained by assuming the impurity electron to interact by means of a J_{fd} exchange and not a J_{sf} exchange. It thus seems to be well established, that at least in EuO the $6s$ conduction band is *not lower* in energy than the $5d$ band, as has been assumed by Kasuya *et al.*[2]

Considering again the carrier concentration $N(T)$ in Fig. 5, we want to stress the point that our Gd-doped samples do not exhibit a temperature-induced insulator-metal transition below 300 K. This observation is in sharp contrast with measurements of Samokhvalov *et al.*[27] in Gd-doped EuO, where an insulator-metal transition is claimed to occur. As mentioned already, these authors[13,14] apparently have incorporated in addition with Gd also a sizable amount of oxygen vacancies, which are the cause of the insulator-metal transition near T_C: With oxygen vacancies as the *only* defect, an insulator-metal transition is found,[5,9] with Gd doping *alone* (see above) an insulator-metal transition upon cooling is absent. This statement is confirmed by considering also $N(T)$ in EuO with different concentrations of electrons than shown in Fig. 5. With a much larger concentration of N, EuO is degenerate and metallic-like already at 300 K and N is nearly temperature independent. With a smaller concentration of N, the sample is semiconducting at 300 K, the swing in N near T_C is somewhat larger [slight increase in ΔE (see Fig. 2)], but the maximum in N below T_C never reaches values higher than N at 300 K (shallow donor). The absence of an insulator-metal transition in Gd-doped EuO follows also from the model of a shallow donor which is hard-coupled to the bottom of the conduction band, a model which has been derived and verified above.

However, doping with Gd in the percentage range, the formation of Gd clusters and the consequent lattice distortions will always result in the formation of electronic trapping levels other than Gd states.[18] Near these distortions Eu deficiencies, for example, may appear with the formation of a deep-trap Eu^{3+}. The number and kind of electronic states in the energy gap other than Gd and oxygen depend on the history of sample preparation and is generally not known. The measured number N is thus in no quantitative relation with x, the microprobe analysis of at.% Gd. There exist samples with, for example, the same Gd concentration but different N and consequently different T_C. We therefore have omitted x in Table I as not being relevant. The conclusion which must be drawn from Table I is the important relation between N, T_C, and ΔE, and not between x and T_C as has been assumed up to now (see, e.g., Ref. 1).

A further parameter in our analysis of transport data is the mobility μ. Of course, we primarily obtain an ac mobility, i.e., a scattering time at optical frequencies (see Fig. 3 in Ref. 4). However, since the frequency dependence of $g(\omega)$ and thus $\mu(\omega)$ is experimentally known, we can extrapolate towards the dc mobility, i.e., towards $h\nu \sim kT$, since this is the average electron energy in a dc experiment.[21] The temperature dependence of the dc mobility for a characteristic sample (EuO +0.66-at.% Gd) is also shown in Fig. 5. It is remarkable and reassuring that the absolute value of the dc mobility at 300 K and at the maximum near 20 K is in reasonable agreement with derivations of the mobility from Hall effect and conductivity on a degenerate sample at the same temperatures.[28] At T_C, μ displays a pointed minimum due to critical scattering on spin fluctuations[23] or magnetic trapping effects. In the paramagnetic temperature region the mobility is of the hopping type with an activation energy of 0.035 eV (see insert in Fig. 5). Similar measurements have been performed in EuTe doped with iodine.[29] Also, in this material the mobility is thermally activated in the paramagnetic region. The activation energy agrees exactly with the one determined independently by photoconductivity experiments in undoped samples,[30] thus giving us confidence into our method of evaluating μ. In EuO as well as in EuTe the activation energy for the mobility E_μ is larger than the one for the carriers E_N: $E_\mu > E_N$.

Kasuya and von Molnar,[31] in order to explain a hopping mobility, have proposed a hopping between occupied and empty impurity states. In this model E_μ must always be smaller than E_N. Our experiments rule out this possibility. We therefore propose that the activation energy for the hopping mobility is purely magnetic in origin and has nothing to do with a donor or impurity level. In Fig. 5 we also show the conductivity $\sigma = eN\mu$. The room-temperature value of σ has been checked by a conventional four-probe technique and was found to agree perfectly with the value derived optically. It is remarkable that the conductivity as well as the mobility has its minimum value at T_C and σ shows a steep increase below T_C, simulating a process proportional to the magnetization instead of the spin correlation function. Only the detailed and independent measurement of N and μ as performed in this article, reveals that this is not the case. (In Ref. 32 this point has not been considered; see also comments in Ref. 33.)

In Fig. 6 we show a comparison of the dc mobility of EuO taken from different authors, where the parameter is the degree of doping. In an undoped sample, the mobility, as derived from the photoconductivity,[34] has a minimum at T_C and an increase of five orders of magnitude below T_C. (The photoconductivity is proportional to $\beta\mu\tau$, where β is the quantum efficiency and τ is the lifetime of the excited carrier. It has been shown in several cases that $\beta\tau$ becomes constant below about 100 K, so that the photoconductivity is proportional to μ.[31]) A 0.66-at.%-Gd-doped sample as described in this paper shows an increase in μ of more than two orders of magnitude, and a 2-at.%-Gd-doped sample which is degenerate displays only a one-order-

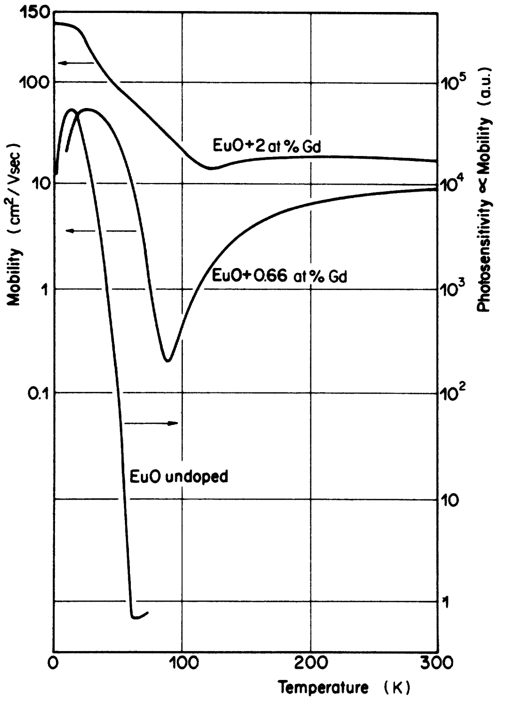

FIG. 6. Comparison of the temperature dependence of the dc mobility of undoped and Gd-doped EuO crystals. EuO + 2-at. % Gd after Ref. 28).

of-magnitude increase in μ below T_C. Haas[23] has shown that the spin-disorder scattering depends on H_{ex} as given in our first equation. The reduction of the dip of the mobility at T_C with increasing doping then is a manifestation of the decreasing H_{ex}, a conclusion which has been arrived at in other parts of this paper. Apparently electrostatic shielding and correlation effects between the conduction electrons are the cause of this effect.

VIII. CONCLUSION

The basic interest in doping the Eu chalcogenides has been the increase in T_C and the possibility to use these materials as magneto-optical memory devices. Gd has been chosen as a donor because it has the same $4f^7$-spin configuration as Eu. It now appears that heavy doping, and especially with Gd, introduces a lot more problems than were thought of at the beginning. The Gd spin has a tendency to enter the material antiparallel to the Eu spins, and it forms pairs or clusters of Gd. This in turn leads to local degeneracy and a coexistence of the metallic and semiconducting state. The material thus becomes "electronic amorphous" and as a consequence electrical and magnetic switching effects of the Ovshinsky type can be observed.[35] On the other hand, the additional magnetic coupling via impurity electrons results in a distribution of exchange constants and a smearing out of the magnetic order. One might say that the long-range magnetic order is gradually turned on by the short-range magnetic interactions.

One of the severe and not generally realized problems in doping these materials is the uncontrolled change in the stoichiometry of the samples. Such compensational effects are the reason that in the past sometimes doping up to 2% were reported with no appreciable change in the conductivity and in T_C. It is one of the main purposes of this paper to demonstrate that already with very weak doping and in the nondegenerate case one can have a steady increase in σ and a concommittant increase in T_C. Besides we have shown for the first time the magneto-optical behavior of Gd-doped EuO single crystals and the dependence of N and μ near T_C in still semiconducting samples, and we have demonstrated that with increasing doping the exchange interactions due to impurity electrons are decreasing.

In the meantime similar measurements have been performed for antiferromagnetic EuTe doped with iodine and first results have been published.[29] An extended report is in preparation.

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