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Gd-doped EuO: Temperature dependence of the 4*f*-photoelectron spin polarization

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The spin polarization of the 4*f* electrons photoemitted from ferromagnetic EuO + x-at.% Gd ($x = 0.1, 2.0, 4.3$) has been measured for temperatures $T \gtrsim 20$ K. During the photoemission process depolarization of the excited electrons takes place. At low temperatures, the depolarization is nearly constant. It is attributed to spin-flip scattering of the photoelectrons with not ordered Eu^{2+} moments existing at irreqularities of the surface. On approaching T_c, the depolarization increases. this is expected because near T_c the magnetization of the ideal, i.e., atomically smooth part of the surface deviates significantly from the one of the bulk, thereby giving rise to additional spin-reversal scattering.

The spin polarization of the 4*f* electrons photoemitted from EuO is considerably lower than what is expected from the bulk magnetization. In the bulk, at temperatures much below the Curie temperature T_C, all 4*f* spins are aligned parallel. However the spin polarization of the 4*f* photoelectrons never exceeds 80%, the exact value depending on the sample and at $T << T_C$, on the external magnetic field.[1] Various mechanisms have been involved to explain this peculiar feature.[1-3] From the earlier low-temperature data alone it was very difficult to make contact with the theory. Now, the polarization has been measured over a wide temperature range. The results indicate that the depolarization is caused by two different mechanisms: one which does not depend on temperature over the whole temperature range considered and one, becoming significant only for $T \gtrsim \frac{1}{2} T_C$, which does depend on temperature.

The main stimulus to investigate EuO by spin-polarized photoemission is due to the fact that the bulk magnetic properties of this ferromagnetic semiconductor are very simple in many respects.[4] This helps to trace back the photoelectron depolarization to a few possible causes, eliminating interpretational ambiguities which might arise for more complicated materials.

Figure 1 shows measurements of the 4*f*-photoelectron spin polarization (photo-ESP) $P(T)$ of variously doped EuO. The value x of the Gd^{3+} admixture refers to the batch composition and may differ significantly from the actually present amount. P was obtained at a photon energy of $h\nu = 5$ eV. To align the magnetic domains, an external field of 10 kG was applied. This field is considerably larger than the bulk saturation field of all samples studied. The crystals were cleaved and measured at a pressure of $p = 2 \times 10^{-10}$ Torr. A detailed account of the experimental setup is given in Ref. 5.

Also shown in Fig. 1 is the normalized bulk magnetization $M(T)/M(0)$, measured with a moving sample magnetometer. The magnetization measurements were done with the same crystals that were used for photoemission, in the same external magnetic field.

The EuO crystals showed a slight Eu^{2+} deficiency. Although each Eu^{2+} ion carries a magnetic moment of $7\mu_B$, the number of Bohr magnetons μ_B per Eu^{2+} ion found experimentally was $6.66\mu_B$ for $x = 01.$, $6.81\mu_B$ for $x = 2.0$, and $6.67\mu_B$ for $x = 4.3$. A nickel sample was used for calibration.

A schematic energy scheme of EuO is presented in Fig. 2. In the ground state $^8S_{7/2}$ the seven 4*f* electrons of the Eu^{2+} ion form a half-filled shell, the spins being aligned parallel. Energetically the $^8S_{7/2}$ state lies between the oxygen *p*-derived valence band and the *s*-*d* conduction band. The spin-orbit split ^7F_J final states observed after ejection of a 4*f* electron extend over a width of about 1 eV, as shown in Fig. 2. For the following discussion some properties of EuO are particularly important: It is a semiconducting Heisenberg ferromagnet of NaCl structure, the exchange constants between nearest neighbors and next-nearest neighbors being positive.[6] The average escape depth of the photoelectrons has been determined to be at least 100 Å at photon energies $h\nu < 5.2$ eV.[7] This implies that most photoelectrons are excited in the bulk region of the crystal.

In order to study the depolarization of the 4*f* photoelectrons it is necessary to determine at what stages of the photoemission process it can possibly occur. Excitation by electric dipole radiation conserves the spin z component. However, the final state need not be a pure spin state. This is the case if spin-orbit coupling mixes both spin components. Clearly, the polarization measured in the photoemission experiment is not the spin polarization of the ground state

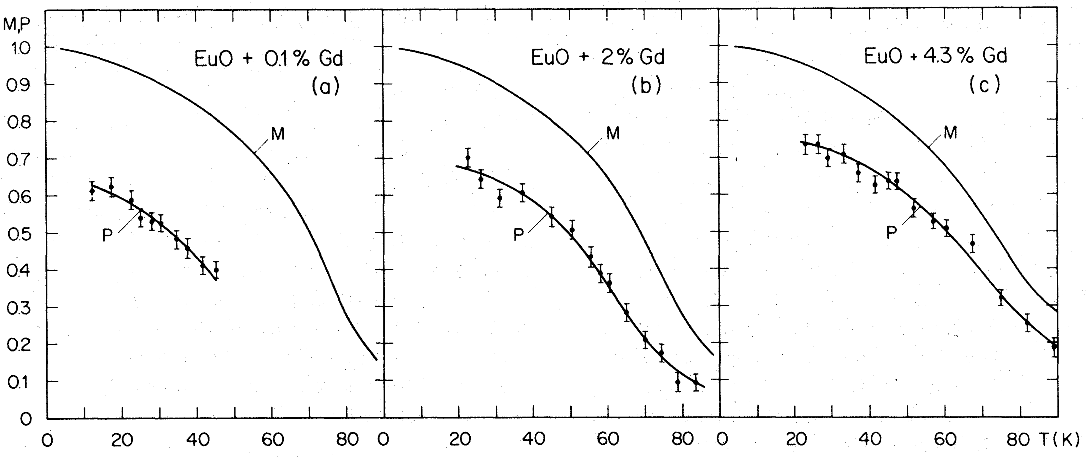

FIG. 1. Temperature dependence of the spin polarization P of the $4f$ photoelectrons emitted from EuO $+x$-at.% Gd in an external field of 10 kG. M is the normalized bulk magnetization $M(T)/M(0)$ of the same samples as used for the photoemission experiment, also measured in an external field of 10 kG.

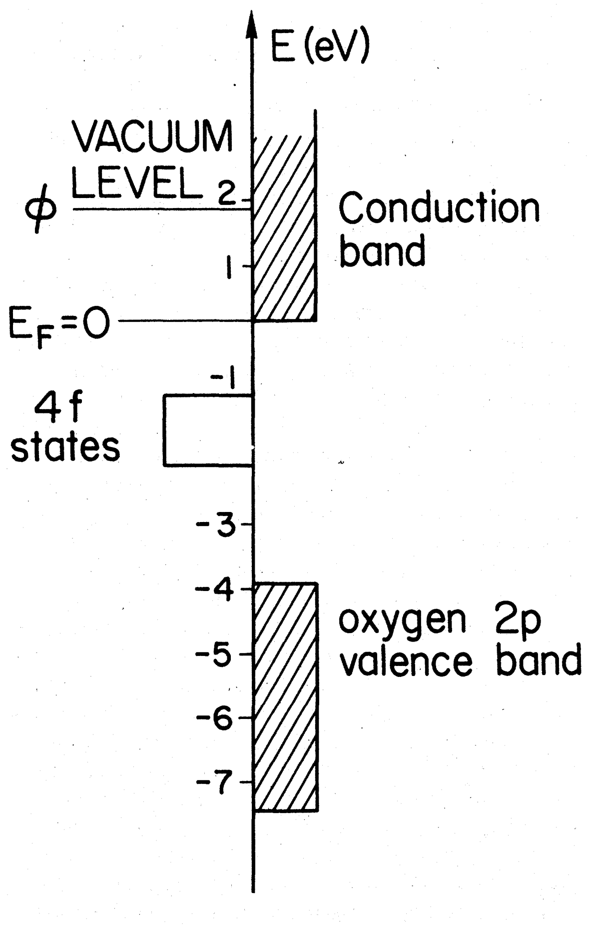

FIG. 2. Energy scheme of EuO, according to Ref. 7 for $T > T_C$. E_F: Fermi level.

but of the excited state. Fortunately, however, it turns out that by excitation with light of photon energy $h\nu = 5$ eV the $4f$ electrons are excited into the $5de_g$ conduction band where spin-orbit coupling is negligible.[8,9] Therefore this interaction cannot be responsible for the reduction of the ground-state polarization. Experimentally this conclusion is supported by Ref. 1 where it is shown that at low temperatures ($T \sim 10$ K) the photoelectron spin polarization depends strongly on the applied magnetic field. If the depolarization were due to spin-orbit interaction it should not depend on the external magnetic field, which is of the order 10 kG.

Next it must be clarified whether depolarization is produced during the transport of the hot electron to the surface. It has been proposed that bulk magnon scattering reduces the polarization, a process favored by the long escape depth. Experimentally it was shown that this possibility must be ruled out.[10] This follows also from a simple argument given below.

Yet another bulk depolarization process can be excluded for EuO: spin-flip scattering of excited $4f$ electrons with valence electrons. As there are no free valence-band states the Pauli principle requires that spin exchange must be accompanied by the excitation of a valence elelctron across the band gap. At 5 eV excitation energy of the primary $4f$ electron, however, such a process is energetically very improbable because the gap width is already 4 eV, see Fig. 2. Furthermore, even if a valence electron is excited, it has not sufficient energy to escape. Thus, the energy scheme of EuO has the remarkable property to act as a filter for secondary electrons: they do not appear in the photocurrent at photo energies $h\nu < 5$ eV.

The failure to find any bulk depolarization sources suggests to look for spin-exchange processes during the last stage of the emission process. This is when the photoelectron traverses the surface to escape into the vacuum. Therefore we conclude that the surface is the location where the depolarization takes place.

A considerable, mainly theoretical literature exists on the magnetic properties of ideal, i.e., atomically smooth surfaces of Heisenberg ferromagnets.[3] The conditions for the existence of various surface spin structures (magnetic surface reconstruction) have been explored. For the rare-earth chalcogenides the exchange constants are known to depend sensitively on the lattice spacing.[11] For EuO experimental evidence exists that the lattice parameters at the surface are identical to the bulk.[12] Therefore it is reasonable to use a theoretical model where the magnetic surface properties just arise from the breaking of the three-dimensional symmetry and a surface exchange J_s differing possibly from the bulk exchange J_b by $J_s = J_b(1-\delta)$. Such a model has been investigated within the mean-field approximation by Mills.[13]

For $T \lesssim T_c$, the surface magnetization $M_{\rm is}$ depends linearly on the temperature (the index "is" refers to ideal surface),

$$M_{\rm is} = 2.5\,\frac{1}{1+4\delta}\,\frac{T_C - T}{T_C}\ . \tag{1}$$

The factor 2.5 is correct only for a spin $S=\frac{7}{2}$ Heisenberg ferromagnet,[13] e.g., EuO. It is evident from Eq. (1) that even when the surface and bulk exchange are identical, i.e., $\delta = 0$, the surface magnetization differs markedly from the one of the bulk.

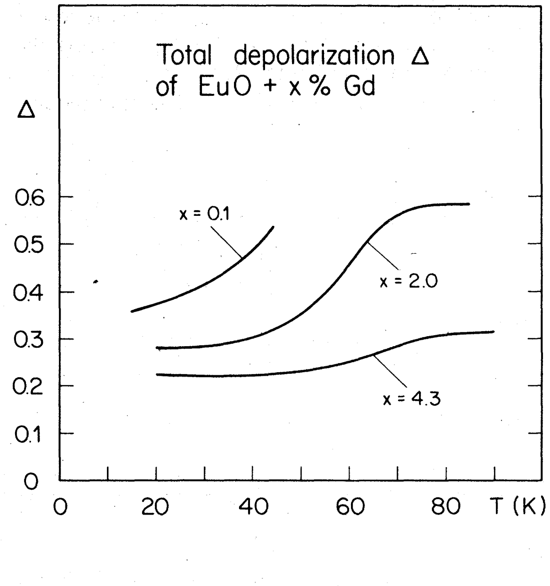

FIG. 3. Total depolarization $\Delta = (M - P)$ for EuO + x-at.% Gd.

In the following a simple expression is given for the depolarization of the photoelectrons upon crossing a surface magnetization layer. We assume that a hot electron has a constant probability to reverse its spin when it interacts with a $4f$ spin of opposite z component. No multiple scattering is considered. Denoting the number of up (down) spins in the surface by $n_s\uparrow$ ($n_s\downarrow$), the normalized surface magnetization becomes $M_{\rm is} = (n_s\uparrow - n_s\downarrow)/(n_s\uparrow + n_s\downarrow)$. The analogous quantity for the bulk spins is $M_b = (n_b\uparrow - n_b\downarrow)/(n_b\uparrow + n_b\downarrow)$: this is equal to the initial polarization of the photoelectrons just after excitation. The polarization $P_{\rm is}$ of the photoelectrons after traversing the surface magnetization layer is then easily found to be

$$M_b - P_{\rm is} = \alpha(M_b - M_{\rm is})\ , \tag{2}$$

where α is a constant determined mainly by the spin-flip scattering probability. It is clear from Eq. (2) that no depolarization occurs for $M_b = M_{\rm is}$, i.e., if the sample is homogeneously magnetized. This alone shows that bulk magnon scattering cannot depolarize

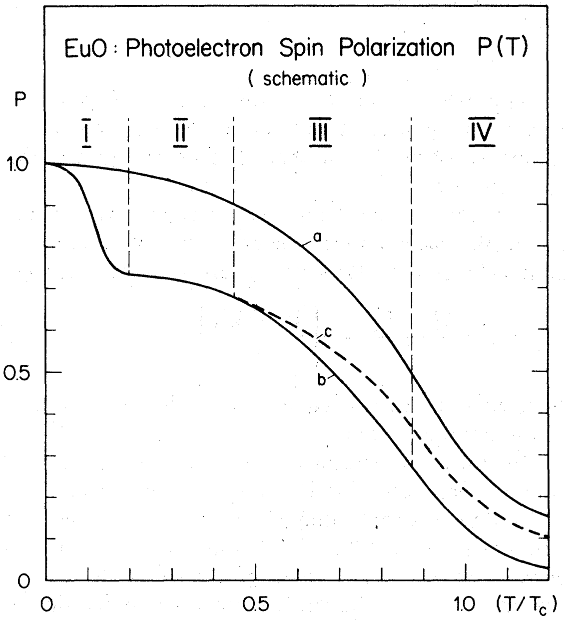

FIG. 4. Schematic representation of the depolarization in various temperature ranges I–IV. I: Experimentally inaccessible region where the effective field acting on the quasiparamagnetic moments is strong enough to produce alignment of the moments. II: Quasiparamagnetic moments are completely disordered: Depolarization T independent. III: Additional depolarization by the ideal surface becomes effective. IV: The external field causes a tailing of the M and P curves: the theoretical models valid for zero external field are no longer applicable.

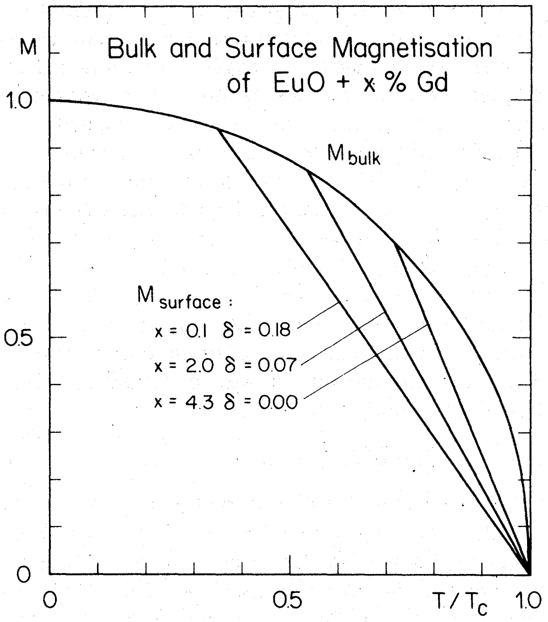

FIG. 5. Linear surface magnetization for Gd-doped EuO. Also shown is the mean-field magnetization curve for a bulk $X = \frac{7}{2}$ ferromagnet.

the photoelectrons in EuO: on the average the number of spins scattered in one direction is just compensated by the number of spins scattered in the opposite direction.

From Eq. (2) the photoelectron depolarization Δ_{is} due to the specific magnetic properties of an ideal, atomically smooth Heisenberg ferromagnet becomes

$$\Delta_{is} = \frac{M_b - P_{is}}{M_b} = \alpha\left(\frac{M_b - M_{is}}{M_b}\right) . \tag{3}$$

Note again that M_b is equal to the initial polarization of the photoelectrons.

The linear temperature dependence of the magnetization is valid only for $T \lesssim T_C$. For EuO, Takeda and Fukuyama calculated $M_s(T)$ over the whole temperature range $0 < T < T_C$,[14] unfortunately using incorrect values for the exchange constants. They find that at $T < 0.2T_C$ the surface layer is also practically saturated. Therefore, even taking into account the particular magnetic surface properties of a Heisenberg ferromagnet, the large depolarization at low temperatures remains unexplained.

Therefore another mechanism must be present which is responsible for the depolarization at low T. Sattler and Siegmann,[1] and Helman and Siegmann[2] attributed the low T depolarization to quasiparamagnetic surface moments which are largely decoupled from the bulk magnetization. The fact that the depolarization of Gd-doped EuO is fairly temperature independent at $T \ll T_C$ supports this view impressively, see Fig. 3. It is also quite natural that such quasiparamagnetic moments are present on a real surface. A cleavage plane of EuO is not completely smooth as can be easily verified with an electron microscope. There is a high density of anomalous lattice sites like edges, corners, steps where the magnetic moments are in an irregular environment. These moments, which we call irregular from now on are believed to be the origin of the temperature-independent depolarization.[15]

Assuming that the depolarization by the ideal surface magnetization, Δ_{is}, and by the irregular surface moments, Δ_{para}, is additive, the total depolarization Δ is the sum of two terms

$$\Delta = \Delta_{para} + \Delta_{is} . \tag{4}$$

Δ can be derived from the measurements shown in Fig. 1: we have $\Delta = (M_b - P)/M_b$, where P is the measured spin polarization.

At temperatures $T < 0.4T_C$, Δ is practically T independent. Then we have $\Delta = \Delta_{para}$. At higher T the term Δ_{is} becomes increasingly important. $\Delta(T)$ is shown in Fig. 3 for 3 dopant concentrations.

If it were possible to measure at much lower temperatures than 10–20 K, even the irregular surface magnetic moments would align in the external field and the depolarization would vanish. This is shown schematically in Fig. 4 where the depolarization mechanisms and the influence of the external field are shown for various T ranges.

A quantity of great interest which can be derived from Fig. 1 is the parameter δ relating the surface and bulk exchange. As Eq. (1) shows the only unknown parameter in the expression for the surface magnetization is δ. Extracting Δ_{para} from the low-T data, Δ_{is} is determined by $\Delta_{is} = \Delta - \Delta_{para}$. Using the values of Δ_{is} at two temperatures $T_1, T_2 \lesssim T_C$ and taking their ratio, the constant α of Eq. (3) is eliminated

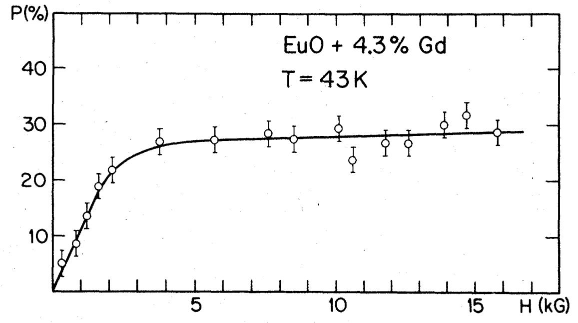

FIG. 6. Spin polarization of the $4f$ electrons emitted from $Eu_{0.98}Gd_{0.02}O$ at $T = 43$ K as function of the applied magnetic field.

and the resulting equation can be solved for δ. One obtains

$$\delta = 0.63\,\frac{\Delta_{\text{is}}(T_1)(T_C - T_2)/T_C - \Delta_{\text{is}}(T_2)(T_C - T_1)/T_C}{\Delta_{\text{is}}(T_1)M_b(T_2) - \Delta_{\text{is}}(T_2)M_b(T_1)}\ .$$

The T_C values for the samples with $x = 0.1, 2, 4.3$ were estimated from a Curie plot. They are 75, 78, and 80 K, respectively. For the evaluation of the δ values, the temperatures T_1 and T_2 should not be chosen too close to T_C; otherwise the influence of the external field on the measured magnetization becomes significant. For the sample $x = 4.3$, δ was calculated with the temperature pairs (65,70), (70,75), and (65,75), the numbers denoting degrees Kelvin. The result is $\delta = 0.00 \pm 0.03$. For $x = 2$, the temperatures are (55,60), (60,65), and (50,65) giving $\delta = 0.06 \pm 0.03$ and for $x = 0.1$ the temperatures (40,45), (35,40), and (35,45) give $\delta = 0.175 \pm 0.02$.

For these δ values the linear surface magnetization is shown in Fig. 5 together with the mean-field result for the bulk magnetization of a $S = \frac{7}{2}$ ferromagnet. It should be noted that δ is larger for the less doped samples, indicating that the surface exchange is stiffened (more ferromagnetic) by the conduction electrons introduced by doping.[16]

The measurements of Fig. 1 also show that the temperature-independent depolarization is stronger for the less doped samples. This suggests that there are surface sites which are quasiparamagnetic, i.e., irregular, for weakly doped samples become magnetically coupled to the bulk for heavily doped samples.

Finally, an additional experiment was made to verify the quasiparamagnetic character of the irregular surface moments. In their original paper,[1] Sattler and Siegmann observed that at low temperatures ($T \sim 10$ K), the spin polarization increased with increasing applied magnetic field even when the bulk of the sample was already saturated. Clearly, the external field aligns the irregular surface moments thereby reducing their depolarizing effect. The magnetic energy of the irregular moments is $E_M = Sg\mu_B H_{\text{eff}}$, where H_{eff} is some effective magnetic field acting on the quasiparamagnetic moments. At temperatures where $kT > E_M$, the alignment by the external field should be negligible. In fact, the measurement of the spin polarization as function of the applied magnetic field shows that P is practically independent of H at $T = 43$ K, see Fig. 6, for comparable magnetic fields as used in Ref. 1.

In conclusion we note that a plausible model for a real magnetic surface describes our spin-polarized photoemission experiments with EuO satisfactorily. However, it also shows that absolute values of the photoelectron spin polarization have generally no simple connection to the magnetization of the bulk sample.

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[15] Recently, disorder of the cleaved EuO (100) surface was reported by R. Felton, M. Prutton, J. A. D. Matthew, and W. Zinn (Fourth General Conference of the European Physical Society, York, England, 1978, unpublished). It is likely that such a disordered surface carries quasiparamagnetic moments of the type discussed. We are not sure how far these findings contradict those of Ref. 12.

[16] In $\text{Eu}_{1-x}\text{Gd}_x\text{O}$, the gadolinium is trivalent contrary to the europium which is divalent. For samples $x > 0.1$, the extra electron of Gd^{3+} is in a conduction-band state, enhancing the ferromagnetic exchange interaction. See, e.g., M. W. Shafer and T. R. McGuire, J. Appl. Phys. 39, 588 (1968).