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Nuclear Polarization in EuS and Eu†

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Transmission experiments have been carried out with polarized, monochromatic neutrons and polarized Eu^{151} nuclei using samples of EuS and Eu metal. It is found that the hyperfine field in both cases is negative.

There have recently been a number of measurements of the field acting on the europium nucleus in an Eu^{2+} ion in various surroundings. In particular, the magnitude of the splitting in EuS[1,2] and Eu metal[3] has been measured, but as far as the authors can determine, the sign of the field is only known for Eu^{2+} in dilute paramagnetic systems.[4] The field direction in europium metal is particularly interesting because of the possibility of conduction electron effects. We have determined this field to be negative by studying the transmission of polarized neutrons through polarized Eu nuclei in Eu metal and EuS. Although it is difficult to produce an appreciable polarization in the metal since it is antiferromagnetic we were able to produce large polarizations in ferromagnetic EuS and directly determine that the field is negative. The sign in the metal followed by comparing the sign of the polarized neutron transmission in the two samples.

DESCRIPTION OF EXPERIMENT

The theory behind the neutron "transmission effect" has been adequately discussed elsewhere.[5] Monochromatic, polarized slow neutrons from a crystal spectrometer are passed through a nuclear sample which is contained in a demagnetization cryostat on the spectrometer arm. The nuclear polarization may be varied within limits set by the highest available external field (17.5 kOe) and the lowest practically attainable temperature (0.05°K). We measure the transmission of the sample for neutrons polarized parallel (τ_p) and antiparallel (τ_a) to the external field. The transmission effect is defined as

$$\mathcal{E} = (\tau_p - \tau_a)/(\tau_p + \tau_a). \tag{1}$$

For a single resonance, or a set of overlapping resonances of the same spin state, this may be shown to be given by[5,6]

$$\mathcal{E} = -f_n^0 \frac{(1+\phi)}{2} h(1-Dt) \times \frac{\int_0^\infty \mathcal{R}(E-E') e^{-Nt\sigma} \sinh Nt\sigma\rho f_N dE'}{\int_0^\infty \mathcal{R}(E-E') e^{-Nt\sigma} \cosh Nt\sigma\rho f^N dE'}. \tag{2}$$

Generalizations to resonances in different isotopes or of different spin states have been given.[7] In Eq. (2), f_n^0 is the initial beam polarization, ϕ is the efficiency with which the beam polarization may be flipped, and h a correction for higher order reflections in the beam, as given by Schermer.[8] $\mathcal{R}$ is the spectrometer energy resolution function, N is the number of nuclei/cm^3, t the sample thickness and σ the total cross section. ρ, the statistical weight factor, is $I/(I+1)$ or -1, depending on whether the spin of the resonance is $J=I+\frac{1}{2}$ or $I-\frac{1}{2}$; f_N is the nuclear polarization and D is the reciprocal mean free path for beam depolarization in the sample due to magnetic processes. The depolarization parameter D is measured by analyzing the beam polarization with sample in f_n and sample out f_n^0. The ratio $f_n/f_n^0 = e^{-2Dt}$. The higher order correction was eliminated by using beam filters. Thus all the EuS results were obtained at a neutron energy of 0.364 eV using a 0.005-in. indium filter, which has a resonance at 1.456 eV. Since the sample transmission with double this thickness of indium was unchanged, we concluded that the remaining higher order contamination was negligible.

All other quantities appearing in (2) except ρ are either already known or were measured in the course of the experiment. In particular, the low energy cross section was measured by Landon and Sailor.[9] There are three resonances in Eu^{151} in the energy region of interest. Their resonance parameters are given in Table I.

In order to bring out the essentials of the argument, we write Eq. (2) in a symbolic form. If Sg(x) means "the sign of x" (+ or −) then we have

$$\begin{aligned} \mathrm{Sg}(\mathcal{E}) &= -\mathrm{Sg}(\rho)\mathrm{Sg}(f_N) \\ &= -\mathrm{Sg}(\rho)\mathrm{Sg}(g_N)\mathrm{Sg}(H_{\mathrm{eff}}) \end{aligned} \tag{3}$$

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where g_N is the nuclear gyromagnetic ratio and H_{eff} the effective field acting at the nucleus.

If we determine that, say, $\mathcal{E}>0$, as we actually have in both Eu and EuS, we do not know whether we are dealing with an $I+\frac{1}{2}$ resonance and a negative field or an $I-\frac{1}{2}$ resonance and a positive field. However we note that, all other things being equal, $\mathcal{E}$ is smaller for $I+\frac{1}{2}$ resonances than for $I-\frac{1}{2}$ resonances due to the presence of the factor $\rho<1$ for the former. This is the basis of the "weighting factor method" used by Postma *et al.*[6] in their study of Tb and also applied successfully to Gd by Stolovy[10] and by Shore *et al.*[7] This technique can be applied whenever resonances of opposite J values are available. With this method in mind we have studied the three Eu^{151} resonances listed in Table I, using an Eu metal sample. We concluded, as did Stolovy,[10] that these three resonances are in the same spin state, all giving an $\mathcal{E}>0$. Therefore, the "weighting factor method" is inapplicable. Furthermore, using Kienle's value[3] of the hyperfine field in the metal $|H|=264$ kOe, we likewise found that the effects we observed were only about 10% of the expected value. However, the metal did not depolarize the beam, as might have been expected if it were an incompletely saturated ferromagnet. The only reasonable explanation is that the metal is antiferromagnetic, as Arnold *et al.*[11] have reported, and that the applied field caused a slight breakdown of the strict antiferromagnetic arrangement.

One direct possibility remains, however. Since we know the hyperfine splitting, a measurement of the sample temperature allows us to calculate f_N. With all factors except ρ known on the right side of Eq. (2), a careful determination of the *magnitude* of $\mathcal{E}$ thus suffices to determine the magnitude of ρ, from which one can infer the sign. The effect is actually very large: for Eu^{151}, $I=5/2$ and $\rho=+5/7$ or -1. Since it turns out that $\mathcal{E}$ is proportional to ρ over a wide range of values of f_N, this factor of 5/7 is directly reflected in the measured values of $\mathcal{E}$. Further, the applied field will add to the hyperfine field if the latter is positive, but will oppose it if it is negative. In the cases under consideration here, this acts to further increase the difference between the two possible cases. The over-all effect in EuS is to make the expected magnitude of $\mathcal{E}$ for an $I-\frac{1}{2}$ resonance and a positive field a factor of 1.57 larger than for an $I+\frac{1}{2}$ resonance and a negative field. The factor in Eu metal is somewhat larger, since the hyperfine field is slightly smaller. However, the experiment cannot be done in Eu metal because of its antiferromagnetic nature. The degree to which the antiferromagnetism is broken down in the applied field is unknown; hence the degree of nuclear polarization is also unknown. EuS, on the other hand, is a cubic ferromagnet,[12] easily saturated with our available field, so that this compound provided a very convenient sample.

TABLE I. Breit-Wigner parameters[a] for low energy resonances in Eu^{151}.

E_0 eV	σ_0 barns	Γ meV
0.327	3850±310	70±10
0.461	24 000±600	93±3
1.056	3190±60	94±3

[a] Calculated from Ref. 9 using an isotopic abundance of 47.82%.

NUCLEAR POLARIZATION IN EuS

EuS was obtained as a fine powder, with particles averaging $\sim 10^{-3}$ cm in size. We were confronted with the problem of making a thin, homogeneous, uniform foil of this material with good heat transfer properties. These requirements were satisfied quite simply and adequately as follows. A mixture of 7.79 wt% EuS powder with lead metal powder[13] (about 200 mesh) was tumbled under argon in a ball mill. 6.939 g of this mix were poured into a die and pressed at ~50 tons/sq in. into a foil 1.012×0.762×0.054 in. thick. This sample was soldered to a copper holder attached to our refrigerating salt.

The calculated thickness of Eu^{151} was $Nt_{151}=1.70\times10^{20}$ atoms/cm², while the actual thickness, as calculated from the neutron transmission at 0.364 eV, was $Nt_{151}=1.62\times10^{20}$ atoms/cm². It is not known whether the discrepancy is due to a fault in the sample preparation procedure—it may be that the act of pouring part of the mixture into the die slightly favors the lead powder—or whether it is due to uncertainty in the resonance parameters of Table I or the spectrometer resolution. If it is one of the latter, its effect on the final calculation of $\mathcal{E}$ may be largely eliminated by using the value of Nt_{151} determined from the neutron transmission. This fact is contained in the argument concerning the ratio R utilized by Postma *et al.*[6] We therefore used the value $Nt_{151}=1.62\times10^{20}$ atoms/cm² in all our calculations.

We monitored the thermal behavior of this sample after demagnetization by measuring $\mathcal{E}$ as a function of time. In the temperature region above 0.15°K, an initial 10 minute wait was sufficient to establish thermal equilibrium. At lower temperatures, however, the final temperature, and particularly the time needed for equilibrium, were very strongly dependent upon the magnetic field applied to the sample. We are studying this behavior in more detail. At present we believe it is due to spin-lattice relaxation, and that the lag due to thermal conductivity of the sample is too small to measure at the lowest temperatures (~0.05°K) reached. To avoid any possibility of systematic error we followed the usual procedure of using only the data after the effect had

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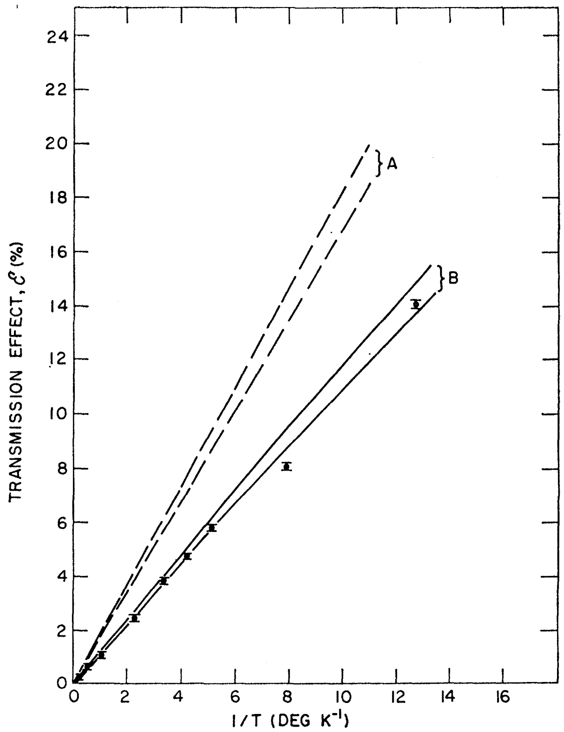

FIG. 1. Transmission effect $\mathcal{E}$ in percent versus reciprocal temperature for EuS at a neutron energy of 0.364 eV. Solid points are experimental data and the error bars give the standard deviation due to counting statistics. The solid curves bracket a region of ±4% about the theoretical result for $I+\frac{1}{2}$ resonances and a negative effective field. The dashed curves bracket the theoretical result for $I-\frac{1}{2}$ resonances and a positive field.

passed through a maximum, indicating that the salt had warmed up to the sample temperature.

Figure 1 shows the results of our measurements of $\mathcal{E}$ in EuS, as a function of the reciprocal of the average thermodynamic temperature T of the cooling salt during the time over which the neutron measurement was made. We have calculated T from the measured magnetic temperature T^* by applying an appropriate shape correction and using the T^*-T data of Kurti and Simon.[14] The solid curves bracket, with a deviation of ±4%, our calculation, using Eq. (2), for $I+\frac{1}{2}$ resonances and a negative effective field; the dashed curves bracket the calculation for $I-\frac{1}{2}$ resonances and a positive effective field. The observed positive sign of $\mathcal{E}$, combined with the known positive value of the Eu^{151} magnetic moment,[15] eliminates the other two possibilities for sign combinations of ρ and H_{eff}.

In performing these calculations we have used the following constants and formulas:

(a) $f_n^0[(1+\phi)/2]=0.84\pm0.02$ as measured by analyzing the beam polarization.

(b) $Dt=0.071\pm0.007$ obtained by measuring the beam polarization with the sample in and sample out, as described above. Similar depolarization has been observed with homogeneous, fully saturated samples.[7] We believe it is due to distortion of the field by the ferromagnetic sample.

(c) $Nt=(1.62\pm0.02)\times10^{20}$ atoms/cm², as described above.

(d) σ calculated from the resonance parameters of Table I with Doppler broadening given as usual by an effective temperature $T_{\mathrm{eff}}\approx(3/8)\theta_{\mathrm{Debye}}$. θ_{Debye} is not known for Eu metal or EuS, and we assumed $\theta_{\mathrm{Debye}}=150°\mathrm{K}$. The effect of a large variation in this quantity is small, and is minimized with any other uncertainties in resonance parameters by using the Nt value derived from the transmission measurement.

(e) Resolution function calculated according to Sailor *et al.*[16] for the (111) planes of fcc cobalt with an angular resolution $\Delta\theta=15.1$ min. At 0.364 eV this leads to an energy resolution of 2.75×10^{-2} eV (full width at half-maximum).

(f) $f_N=B_{5/2}(\beta)$, where $B_{5/2}$ is the Brillouin function for spin 5/2 and $\beta=\mu_N H_{\mathrm{eff}}/IkT$. $\mu_N=+3.419$ nm,[15] $I=5/2$. $H_{\mathrm{eff}}=H_{\mathrm{hfs}}+H_{\mathrm{app}}+\frac{4}{3}\pi M-DM$.

There seems to be some inconsistency among the values given by Charap and Boyd[1] for the hyperfine splitting in various units. However, taking their value for the resonant frequency of Eu^{151} at 0°K, $\nu_0=343.0$ Mc/sec, we calculate that in their experiment $|H_{\mathrm{eff}}|=328.8$ kOe, uncorrected for the Lorentz field. (The Mössbauer value of Shirley *et al.*[2] is 328±15 kOe at 5°K.) We have made a sufficiently accurate correction for the temperature variation of this quantity by using Fig. 4 of Ref. 1.

In our experiment we have $H_{\mathrm{app}}=+15$ kOe, and we assume that the EuS sample is magnetically equivalent to a collection of small, independent spherical samples, so that the demagnetizing field cancels the Lorentz field. In any case, the maximum systematic error caused by this procedure would be at most $\frac{4}{3}\pi M\approx5$ kOe out of a total of ~300 kOe, or <2%.

DISCUSSION OF RESULTS

The experimental points in Fig. 1 are seen to lie very close to the calculated curve for a *negative* H_{eff} and $I+\frac{1}{2}$ resonances and to completely rule out any alternate possibility. The only possibility for a systematic error of the order of magnitude required to shift the measured points to the other curve would be if the sample contained some nuclei which contributed to the cross section but not to the effect. Since the calculated and measured values of Nt_{151} are so close, the only possibility for this

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to happen would be if a reasonable fraction (~36%) of the sample were actually Eu_2S_3. However, an x-ray study of the EuS powder revealed no detectable trace of a second phase. Since the transmission effects in Eu metal and EuS are of the same sign, so are the effective fields. The field in the metal is thus also negative, as has generally been assumed. Any conduction electron effects are thus contained in the difference between $H_{\mathrm{hfs}}=-329$ kOe in EuS and $H_{\mathrm{hfs}}=-264$ kOe in the metal (both values are corrected to 0°K).

We had originally hoped to be able to see the direct effect of H_{app} on $\mathcal{E}$. Since H_{hfs} is negative, lowering H_{app} from 15 to 9 kOe would in principle have caused an *increase* of 2.5% in $\mathcal{E}$. This would be just detectable, were it not for the fact that there are uncertainties introduced by the field dependence of the depolarization correction and the spin-lattice relaxation.

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Trapping Centers in Thermoluminescent Calcite

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Trapping levels which account for most of the thermoluminescence in natural calcite have been investigated. Results are based on a study of color centers which are shown to be closely associated with the traps involved in thermoluminescence. Optical absorption measurements in a variety of Iceland-spar crystals show that the prominent calcite glow peaks at 350, 500, 600, and ~700°K are accompanied by thermal bleaching of the color centers. Results indicate that the color centers are due to one kind of trapped-hole center and at least four kinds of trapped-electron centers. Recombinations resulting from thermal bleaching of each of these centers excites emission at Mn^{++} impurity ions and produces the observed glow peaks. The mechanism for exciting the Mn^{++} ions appears to be the same nonradiative transfer process which accounts for sensitized luminescence in calcite.

I. INTRODUCTION

THERMOLUMINESCENCE in natural calcite is usually associated with the presence of divalent manganese, a common impurity.[1] There are three prominent glow peaks in most samples at 350, 500, and 600°K and a weaker peak near 700°K. The orange emission of these glow peaks is produced by the $^4G(T_{1g})\rightarrow {}^6S$ transition in the Mn^{++} ion,[2] which occupies substitutional sites in the lattice.[3] This transition is forbidden so it cannot be directly excited by optical absorption. But indirect excitation through host lattice absorption of ionizing radiation is possible; and it is by this method that luminescence is produced. Another form of indirect excitation occurs through the action of sensitizing agents such as Pb, Tl, or Ce. These impurities absorb radiation in their own characteristic absorption bands and transfer energy through a nonradiative, resonance mechanism to Mn^{++} centers. This produces sensitized luminescence,[4] which has the same emission characteristics as thermoluminescence and x-ray excited luminescence.

Trapping centers in calcite are somewhat analogous to sensitizing ions. Both provide indirect processes for exciting the forbidden Mn^{++} transitions. The properties of sensitizing centers in calcite have been studied in detail.[4] But comparatively little is known about the trapping centers or about the mechanism for exciting emission when the traps are emptied.

There is good evidence that the traps which produce thermoluminescence are associated with color centers. Thermoluminescent crystals are visibly darkened by x-ray irradiation whereas nonthermoluminescent crystals remain uncolored. This suggests that a study of the relation between color centers and thermoluminescence may provide information about trapping centers associated with the glow peaks.

In this paper we describe the results of an investi-

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