Note

A Study of the Solid Solutions (EuO)$_{1-x}$(*Ln*N)$_x$ (Where *Ln* = Nd, Eu, Gd) by Europium-151 Mössbauer Spectroscopy

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The magnitude of the magnetic hyperfine field at Eu^{II} in the cubic solid solutions (EuO)$_{1-x}$(*Ln*N)$_x$ (where *Ln* = Nd, Eu, Gd) has been determined at 4.2°K by ^{151}Eu Mössbauer spectroscopy. The resultant effective hyperfine field is found to be almost independent of composition because of a number of compensating effects.

Europium(II) oxide EuO and europium(III) nitride EuN both have the NaCl structure and their Mössbauer spectra have been well established (1, 2). More recently several solid solution phases of the type (EuO)$_{1-x}$(*Ln*N)$_x$ (where *Ln* = Nd, Eu, Gd) have been characterized (3). Compositions in the series (EuO)$_{1-x}$(EuN)$_x$ (0 ⩽ x ⩽ 0.30) are semiconductors at room temperature with an activation energy which decreases with increase in x; there is a semiconductor-metal transition in the neighborhood of 70°K, and at low temperatures the phase is ferromagnetic. The nitrogen-rich phase (0.92 ⩽ x ⩽ 1) is metallic and is not magnetically ordered. The phases (EuO)$_{1-x}$(NdN)$_x$ (0 ⩽ x ⩽ 0.26) and EuO)$_{1-x}$(GdN)$_x$ (0 ⩽ x ⩽ 0.26) are ferromagnetic semiconductors, except for the case of neodymium with x ⩾ 0.22 when the phase becomes metallic. It is known that the internal magnetic hyperfine field at the europium nucleus in EuO depends on transferred hyperfine interactions with neighboring atoms, and it is therefore of interest to investigate the effects of a systematic change in nearest neighbor environment in these solid solutions.

Mössbauer absorbers of natural isotopic composition and containing 5–15 mg cm^{-2} of europium-151 were prepared in an atmosphere of dry argon. The source was ca. 300 mCi of ^{151}Sm in a matrix of SmF$_3$, and the spectra were obtained at 4.2°K with both source and absorber immersed in liquid helium using apparatus previously described. The oxide-nitrides are very sensitive to moisture, and it proved difficult to prevent some decomposition (to a nonmagnetic Eu^{III} material) during handling and transfer between our two laboratories. However, this can easily be allowed for in the data analysis.

The 21.53-keV transition in ^{151}Eu is from the ground state ($I_g = 5/2+$) to the first excited state ($I_e = 7/2+$), the multipolarity of the radiation being pure $M1$. The presence of magnetic hyperfine splitting produces 18 Mössbauer absorption lines, but several of these overlap so that the observed spectrum appears as four intense lines with two weaker components on each side. The ratio of the nuclear magnetic moments is $\mu_e/\mu_g = 0.7465$ with $\mu_g = +3.4649 \, \mu_N$, but there is a substantial hyperfine anomaly in EuO (*4, 5*) so that an effective value of $\mu_e/\mu_g = 0.7523$ is more appropriate in the present instance. Using these values it is possible to analyze the hyperfine spectrum in terms of the magnetic hyperfine field (B), the chemical isomer shift (δ), and

the linewidth (Γ). Quadrupole interactions are absent in EuO, and also appear to be negligible in the solid solutions.

Typical spectra for $(EuO)_{0.05}(EuN)_{0.95}$ and $(EuO)_{0.90}(EuN)_{0.10}$ are shown in Fig. 1. The spectrum of $(EuO)_{0.05}(EuN)_{0.95}$ shows a dominant nonmagnetic line for Eu^{III} and an apparently magnetic Eu^{II} component (which is intensified in the spectrum by saturation effects). The half-life of the excited state ^{151}Eu nucleus is 9.7×10^{-9} s (*1*) and the observed spectrum is consistent with a slowing down of paramagnetic relaxation to approximately this time scale as the Eu^{II} ions ($4f^7 - {}^8S_{7/2}$) are diluted by the nonmagnetic Eu^{III} ions ($4f^6 - {}^7F_0$). Relaxation broadening has also been reported (*6*) for Eu^{II} ions ($\leqslant 5$ at.%) in CaF_2 and CaS, and a particularly pronounced effect has been observed for Eu^{II} ions in zeolites (*7*). A detailed analysis of the present data is not possible because of the overlap with the strong Eu^{III} component.

By contrast, the spectrum of $(EuO)_{0.90}$-$(EuN)_{0.10}$ in Fig. 1b, shows a well-developed magnetic Eu^{II} hyperfine pattern rendered somewhat asymmetric by the superposition of an additional nonmagnetic resonance from the Eu^{III} component. The spectra of all the oxygen-rich samples studied $(EuO)_{1-x}(EuN)_x$ ($x = 0.10, 0.20, 0.30$), $(EuO)_{1-x}(NdN)_x$ ($x = 0.06$, 0.09, 0.13, 0.16, 0.21, 0.23, 0.24, 0.26), and $(EuO)_{1-x}(GdN)_x$ ($x = 0.10, 0.18, 0.26$) were remarkably similar to Fig. 1b. The hyperfine field in EuO was found to be 28.99 ± 0.05 T (1 T $= 10^4$ Gauss), and all the solid solutions gave values within the range 28.8–29.8 T. The largest data set (for Nd) are consistent with a small compositional dependence which can be written as $|B| = (29.0 + 2.3x) \pm 0.2$ T. The other two series were less extensive but appeared to follow a similar trend. The chemical isomer shift for each series was in the range $\delta = -10.7 \pm 0.1$ mm s^{-1} relative to EuF_3, and was insensitive to composition. Increase in x caused no noticeable line broadening, implying that there was no significant distribution in the values of the hyperfine field in the solid solutions.
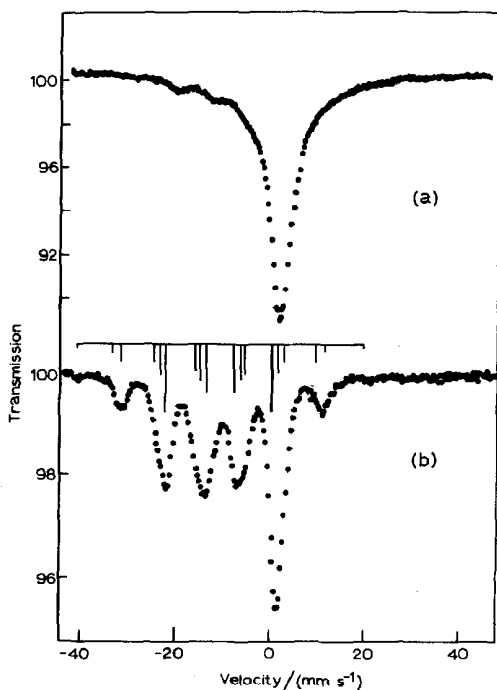

FIG. 1. The ^{151}Eu Mössbauer spectra at 4.2°K of: a, $(EuO)_{0.05}(EuN)_{0.95}$, the apparently magnetic spectrum from the weak Eu^{II} component is produced by a slow paramagnetic relaxation; b, $(EuO)_{0.90}(EuN)_{0.10}$, the 18 lines due to magnetic Eu^{II} are indicated and the additional absorption near zero velocity is from nonmagnetic Eu^{III}.

The lack of pronounced variation in the hyperfine field at the Eu^{II} ion in the ferromagnetic phases is remarkable. In EuO the observed magnetic field is given by $B_{eff} = B_I + B_d$ where B_I is the contact hyperfine field and B_d is the dipolar field (8, 9). For an S-state ion such as Eu^{II} the value of B_I at site i is given by

$$B_I^i = B_{4f} + 12\Delta B_1 + 6\Delta B_2,$$

where B_{4f} is the core s-electron polarization by the atomic $4f$-spins; $12\Delta B_1$ is the transferred hyperfine interaction from the 12 Eu^{II} nearest neighbors via an overlap of the $5d$–t_{2g} orbitals, and $6\Delta B_2$ is from the 6 next-nearest neighbors via an overlap of the $5d$–e_g orbitals with p-orbitals on the intermediate anion. B_d depends on sample geometry and domain size. In EuO itself, B_I is calculated to be -30.5 ± 0.5 T, compared to the value of -34.2 T for a pure $4f^7(^8S_{7/2})$ configuration, and a typical value (9) for B_{eff} of -29.0 T. B_I increases substantially with increase in pressure (and consequent decrease in the Eu–Eu distance) as a result of increased admixture of the $4f^7$ configuration with the $5d$-conduction band states. From data for EuSe and EuTe it appears (9) that $12\Delta B_1 + 12\Delta B_2 \sim -6$ T, i.e., about 20% of the total hyperfine field.

The lattice parameter a_0 decreases with increasing x for $Ln = $ Eu, Gd, but is virtually constant for Nd (3). The relevant (six-coordinate) ionic radii are (10): Eu^{2+} 1.7, Eu^{3+} 0.95, Nd^{3+} 1.00, Gd^{3+} 0.94 Å, so that the decrease in cation size from Eu^{2+} to Eu^{3+} or Gd^{3+} dominates the increase in anion radius of N^{3-} (1.50 Å) compared to O^{2-} (1.40 Å). In $(EuO)_{1-x}(EuN)_x$ the average environment about the Eu^{II} for $x = 0.30$ is only 8.4 nearest and 4.2 next-nearest Eu^{II} neighbors, the remainder being nonmagnetic Eu^{III}. Therefore B_I should be reduced, but this effect is presumably compensated by the decrease in the Eu–Eu distance. In $(EuO)_{1-x}(GdN)_x$ the Gd^{III} has the same $4f^7(^8S_{7/2})$ configuration as Eu^{II}, but the increasing Eu–Eu overlap will be compensated by a weaker Eu–Gd overlap

because of the smaller radius of Gd^{III}. The introduction of Nd^{III} $4f^3(^4I_{9/2})$ introduces further variables which again appear to compensate. The replacement of oxygen by nitrogen also seems to have no major effect on the magnetic exchange, implying either that ΔB_2 is an insignificant contribution to B_I or that it is not substantially different in the two cases.

In conclusion it can be seen that the magnetic properties of the Eu^{II} ion in the cubic, ferromagnetic solid-solution phases are very insensitive not only to changes in the electronic state and the size of the cation but also to replacement of oxygen by nitrogen. The various factors which must contribute to the observed magnetic field are mutually compensating.

Acknowledgments

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