

EPR of Europium Amide: $\text{Eu}(\text{NH}_2)_2$ †

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Received September 3, 1969

The x -band electron paramagnetic resonance spectrum of europium amide $[\text{Eu}(\text{NH}_2)_2]$ has been observed at room temperature and at liquid nitrogen temperature. The Lorentzian shaped line is approximately 1000 G wide and the effective g factor is 2.015 ± 0.008 . No spectral changes were noted with temperature. The theory of Anderson and Weiss [*Rev. Mod. Phys.* **25**, 269 (1953)] is used to account for the linewidth in terms of an exchange interaction. The interpretation suggests that europium (II) amide is ferromagnetic and long-range order will occur in the 10–50°K range. A comparison of the physical properties of this compared with other divalent europium (II) compounds is also presented.

There has been a continuing interest in the magnetic properties of divalent europium compounds(1): of the chalcogenides EuO , EuS , and EuSe are ferromagnetic while EuTe is antiferromagnetic; all have the NaCl structure. Among the halides, EuCl_2 and EuBr_2 are paramagnetic, EuF_2 is antiferromagnetic, and EuI_2 is ferromagnetic. The magnetic properties of the pure metal are not well understood, but it seems clear that it has a divalent core with an antiferromagnetic Néel point at about 90°K (2). The related "metal," $\text{Eu}(\text{NH}_3)_6$ is ferromagnetic (3).

The electron paramagnetic resonance (EPR) data have been obtained on four europium chalcogenides at both 100°K and 300°K (4). Bach et al. have shown that these data, notably the linewidths, are consistent with the results of magnetic susceptibility investigations. Furthermore, this consistency has been shown in four binary gadolinium (III) compounds (4).

In this note, the EPR data of another $\text{Eu}(\text{II})$ compound, $\text{Eu}(\text{NH}_2)_2$ is presented. The original report of this compound was by Warf and Korst in their investigation of europium metal-liquid ammonia solutions (5). The solid precipitating from the decomposing solution was inferred, by analogy with other metal-ammonia systems, to be $\text{Eu}(\text{NH}_2)_2$. The compound does not seem to have been further investigated until 1968 when Juza and Hadenfeldt (6) reported some ir and crystallographic data. $\text{Eu}(\text{NH}_2)_2$ crystallized in the space group D_{4h}^{19} —

† Supported by SUNY Research Foundation and Research Corporation.

$I4_1/amd$, the same space group as anatase, a polymorph of TiO_2 and calcium and strontium amides. With $a = 5.45 \text{ \AA}$ and $c = 10.86$, the c to a ratio is 1.99. The ideal anatase structure may be derived from the NaCl structure by the removal of half of the Na atoms (7). This hypothetical structure would obey the relation $c = 2a$, quite close to the value actually found in $\text{Eu}(\text{NH}_2)_2$ (6). This corresponds to the removal of eight of the twelve nearest neighbors in NaCl and two of the six next nearest neighbors.

For this work the amide was prepared by the decomposition of a dilute solution of europium metal in liquid ammonia at room temperature. The orange solid obtained was transferred in a nitrogen atmosphere to a glass capillary and sealed for the EPR measurements. EPR spectra were obtained with a reflection x -band spectrometer and incident microwave energy of about 50 MW. The magnetic field modulation frequency was 1000 Hz. Most data were obtained at room temperature, but a preliminary measurement at liquid nitrogen temperature revealed no change in the spectral line shape, linewidth, or g factor. The effective g factor was measured to be 2.015 ± 0.008 and the derivative peak to peak linewidth was about 1000 G. The signal-to-noise ratio was about 30 at room temperature and, to within experimental uncertainty, the line shape is Lorentzian.

Several observations may be made concerning these results. Firstly, the sample is in polycrystalline form and the local environment about an individual europium (II) ion is nearly axial. Under these circumstances the EPR spectrum is dominated by

the "perpendicular" spectrum; that is by the spectrum from crystallites whose unique axis is perpendicular to the external magnetic field (8). For ions such as Eu(II) or Gd(III), the second order shifts in the spectrum can produce an effective g value which is greater than 2.0023 although the actual g value is less than this. For example, Lancaster and Gordy (9) measured a g value of 2.02 for polycrystalline $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ at 35 GHz while Hutchison, Judd, and Pope (10) obtained 1.991 for GdCl_3 diluted in the LaCl_3 lattice. Similarly the g values for three of the four europium complexes measured by Busch and coworkers were greater than 2.00 (4). The theoretical understanding of the actual g factor being less than 2.0023 has been discussed by Lacroix (11) and our results are consistent with such a value.

Secondly, and of somewhat greater interest, is the Lorentzian lineshape. A simple dipole-dipole interaction between spins would produce a Gaussian lineshape and a linewidth of over 3000 G (12). Furthermore, crystal field fine structure and nuclear hyperfine structure for known Eu(II) ions are often greater than a few hundred gauss (13). The observed shape and width thus suggest the effects of exchange narrowing (12). This is analogous to the results and conclusion of Busch et al. (4). The Anderson-Weiss theory can be used to estimate the magnitude of J , the parameter in the Heisenberg exchange Hamiltonian. With the assumption of a simple cubic lattice, an exchange field (H_e) greater than the external magnetic field (H_o), and much greater than the dipolar field (H_d), the calculated linewidth is

$$H_{\text{cal}} = [(10/3) H_d^2 + H_H^2] / H_e,$$

where H_H is assumed to be of the same order of magnitude or smaller than H_d and represents the contributions from crystal field induced zero field splittings and nuclear hyperfine effects. For convenience this will be taken as zero in the rest of this analysis. This has the effect of placing a lower limit to $|J|$. With the following simple cubic lattice equations (12)

$$H_d^2 = 5.1 (g\beta n)^2 S(S+1),$$

$$H_e = 2.83 \cdot |J| [(S)(S+1)]^{1/2} / g\beta.$$

The experimental linewidth may be related to an effective J value. This is $|J| = 0.20^\circ\text{K}$. In order to at least partially compensate for the use of the simple cubic expressions for this lattice, $6|J|$, in the theory of Anderson and Weiss (12) can be replaced (4) by $4|J_1| + 4|J_2|$, where J_1 and J_2 are the nearest and next nearest neighbor exchange constants. J_2 is believed not to be sensitive to lattice parameter (1a) and may be taken as about -0.07°K by interpolation

between EuO and EuS. Thus the value for $|J_1|$ is found to be 0.23°K . Comparison with EuO ($a = 5.144 \text{ \AA}$, $J_1 = 0.65^\circ\text{K}$, $J_2 = -0.06^\circ\text{K}$) and EuS ($a = 5.97 \text{ \AA}$, $J_1 = 0.20^\circ\text{K}$, $J_2 = -0.08^\circ\text{K}$) indicates that a value $|J_1| = 0.23^\circ\text{K}$ for $\text{Eu}(\text{NH}_2)_2$ ($a = 5.45 \text{ \AA}$, $J_2 = -0.07^\circ\text{K}$) fills out a consistent pattern for these europium (II) compounds. These values suggest the onset of long-range order in the 10–50 $^\circ\text{K}$ range. Furthermore if the sign of J_1 is the same as in EuO and EuS, the interaction should be ferromagnetic. Magnetic susceptibility investigations below 77 $^\circ\text{K}$ should be quite interesting in this regard.

Acknowledgments

The authors wish to thank M. Linzer and T. Chang for valuable discussions, U. Favreau for aid in the construction of the spectrometer, and the SUNY Research Foundation and Research Corporation for support.

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