

## Low-Temperature Magnetic Studies of the Expanded-Metal Compounds $\text{Eu}(\text{NH}_3)_6$ and $\text{Yb}(\text{NH}_3)_6$ <sup>1</sup>

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The magnetic susceptibilities of the metallic compounds  $\text{Eu}(\text{NH}_3)_6$  and  $\text{Yb}(\text{NH}_3)_6$  have been measured by the Faraday method in the range 2–200 K. The susceptibility of  $\text{Eu}(\text{NH}_3)_6$  obeys a near-Curie law down to 10 K, below which it flattens out. These results are attributed to  $\text{Eu}^{2+}$  ions that are weakly coupled by short-range antiferromagnetic interactions.  $\text{Yb}(\text{NH}_3)_6$  exhibits a near-Curie increase in susceptibility below 50 K, which is intrinsic to this compound and possibly originates from a partial localization of conduction electrons.

Metal-ammonia solutions exhibit a rich variety of electronic behavior as the metallic concentration is increased (1). Upon freezing concentrated solutions containing Li, Ca, Sr, Ba, Eu, and Yb, low-electron-density metallic compounds are formed which have the approximate compositions  $\text{Li}(\text{NH}_3)_4$  and  $M(\text{NH}_3)_6$ , where  $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}, \text{or Yb}$  (2). The metallic nature of these compounds is believed to originate from the loss of one valence electron in the case of  $\text{Li}(\text{NH}_3)_4$ , and two valence electrons in the case of  $M(\text{NH}_3)_6$ , from each molecular complex to a conduction band. The  $M(\text{NH}_3)_6$  compounds crystallize in a bcc structure, with  $M(\text{NH}_3)_6$  complexes occupying the lattice sites. Recent research has indicated that the alkaline earth hexammines have novel structures, molecular motions, and electronic properties (3, 4).

Magnetic susceptibility ( $\chi$ ) measurements have played an important role in elu-

cidating the electronic nature of metal-ammonia compounds. In  $\text{Li}(\text{NH}_3)_4$ ,  $\chi$  shows an abrupt 25% drop at 82 K, where there is a structural transition, and then displays Curie-Weiss behavior down to 15 K, below which  $\chi$  flattens out (5). In  $\text{Ca}(\text{NH}_3)_6$ ,  $\chi$  is strongly dependent on temperature, showing a broad minimum near 120 K, paramagnetic behavior between 110 and 20 K, and a sharp peak near 10 K (6). It has been suggested that changes in  $\chi$  near 82 K in  $\text{Li}(\text{NH}_3)_4$  and 110 K in  $\text{Ca}(\text{NH}_3)_6$  may result from a partial localization of conduction electrons originating from strong electron-electron interactions in these compounds (5, 6). The observation by electron paramagnetic resonance (EPR) of possible local-moment signals in  $\text{Li}(\text{NH}_3)_4$  below 80 K (7) and in  $\text{Sr}(\text{NH}_3)_6$  below 200 K (8) supports this interpretation. Both  $\text{Sr}(\text{NH}_3)_6$  and  $\text{Ba}(\text{NH}_3)_6$  are diamagnetic, and the magnitude of their diamagnetism increases sharply as the temperature is lowered, with  $\text{Ba}(\text{NH}_3)_6$  exhibiting the largest diamagnetic mass susceptibility of any non-

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superconducting metal at low temperatures (6).

There are conflicting reports in the literature of the magnetic properties of  $\text{Eu}(\text{NH}_3)_6$ . The original susceptibility measurements indicated that  $\text{Eu}(\text{NH}_3)_6$  was ferromagnetic, with a Curie temperature ( $T_c$ ) of 5.5 K (9). Moreover, it was found that the effective magnetic moment ( $\mu_{\text{eff}}$ ) per  $\text{Eu}^{2+}$  ion was  $10.2 \beta$  between 5.5 and 47 K, and above 47 K it changed to the spin-only value of  $7.9 \beta$ . Another most unusual result of this study was that  $T_c$  was nearly unchanged upon magnetic dilution with Yb. It was also found that even  $\text{Yb}(\text{NH}_3)_6$  was not magnetically inert, but was diamagnetic at high temperatures and crossed over to paramagnetic below 31 K. The first Mössbauer studies of  $\text{Eu}(\text{NH}_3)_6$  also indicated that this compound ordered magnetically just above 4.2 K (10). However, subsequent Mössbauer resonance studies (11, 12) showed that  $\text{Eu}(\text{NH}_3)_6$  does not order magnetically and that Eu remains divalent down to 1.2 K, with an estimated ordering temperature of only 0.1 K, which is lower than any known europous compound. Recent EPR studies of  $\text{Eu}_x\text{Yb}_{1-x}(\text{NH}_3)_6$  alloys (13), in which only  $\text{Eu}^{2+}$  was detected above 10 K and an ordering temperature of 0.2 K was predicted, are in excellent agreement with the latter Mössbauer studies. Hence it appears that the magnetic ordering found in the first susceptibility and Mössbauer studies of  $\text{Eu}(\text{NH}_3)_6$  was due to magnetic impurities in the samples, with the most likely candidates being  $\text{Eu}(\text{NH}_2)_2$  ( $T_c = 5.4$  K) (14) and  $\text{Eu}_3\text{O}_4$  ( $T_c = 6.2$  K) (15).

In view of the substantial impurity effects in the previous susceptibility work, we have reexamined the susceptibility of both  $\text{Eu}(\text{NH}_3)_6$  and  $\text{Yb}(\text{NH}_3)_6$  using high-purity metals and special sample-handling techniques to ensure sample homogeneity and minimize decomposition. Below we report and discuss the results of this investigation.

Samples having a 6 : 1 ammonia-to-metal

stoichiometry were used in all experiments. The magnetic measurements were made using the Faraday technique between 2 and 200 K at several magnetic fields ( $H$ ) between 6 and 13 kG. The sample preparation and handling procedure as well as the measurement technique have been described elsewhere (6, 16). Since  $\chi$  varied linearly with  $H^{-1}$  at all temperatures for both compounds, the Honda–Owen method was applied to derive infinite-field susceptibilities. The difference between the measured and extrapolated susceptibilities was about 20% at the lowest temperatures and decreased rapidly with increasing temperature, becoming negligible above 150 K. The reported susceptibilities have been corrected for the diamagnetism of the Kel F bucket containing the sample, but not for the constituent ions and molecules, since the standard values may not be valid in view of the unusual structures of these materials (4). The temperature dependence of  $\chi$  for both compounds reported below is much more pronounced than that of the pure metals, and that of  $\text{NH}_3$  is independent of temperature.

The susceptibilities of five different samples of  $\text{Eu}(\text{NH}_3)_6$  were determined in the course of this research, and two samples were investigated in detail. The temperature dependence of the reciprocal molar magnetic susceptibility ( $\chi_m^{-1}$ ) of these two

TABLE I  
SUMMARY OF MAGNETIC PARAMETERS FOR  
 $\text{Eu}(\text{NH}_3)_6$

Sample	$\mu_{\text{eff}}$ ( $\beta$ )	$\theta$ (K)
I	$7.19 \pm 0.06$	$-2 \pm 2$
II	$9.23 \pm 0.06$	$0 \pm 2$
III	$7.90^a$	$18^a$
	$10.15^b$	$-5.5^b$

<sup>a</sup>  $T > 47$  K.

<sup>b</sup>  $T < 47$  K.

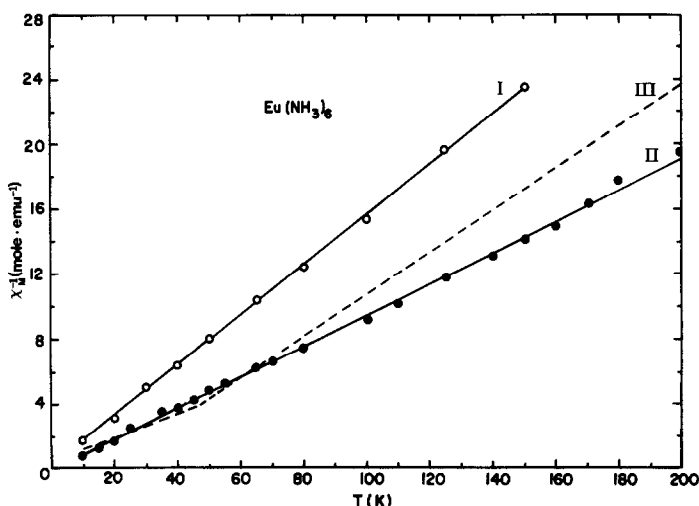


FIG. 1. Reciprocal molar susceptibility vs temperature for  $\text{Eu}(\text{NH}_3)_6$ . Samples I and II represent this work, whereas the data for sample III was taken from Ref. (9).

samples (I and II) is shown in Fig. 1. For comparison, the original susceptibility data for  $\text{Eu}(\text{NH}_3)_6$  (III) (9) is also displayed in Fig. 1. A comparison of  $\chi_m^{-1}$  vs  $T$  at low temperatures for samples II and III is shown in Fig. 2. The magnetic parameters for these samples are summarized in Table I. No corrections are necessary for either the diamagnetism of the  $\text{Eu}(\text{NH}_3)_6^{2+}$  complexes ( $\chi_d \approx -120 \times 10^{-6}$  emu/mole) (17) or the Pauli–Peierls susceptibility of the conduction electrons ( $\chi_p \approx 64 \times 10^{-6}$  emu/mole) (18), since they are negligible compared to the sample susceptibility over the entire temperature range.

The effective moments evaluated from the slope of the  $\chi_m^{-1}$  vs  $T$  plot are in qualitative agreement with the spin-only value for  $\text{Eu}^{2+}$  of  $7.94 \beta$  determined from EPR studies of  $\text{Eu}(\text{NH}_3)_6$  (13). The variation in  $\mu_{\text{eff}}$  for different samples reflects some of the problems associated with susceptibility measurements on these reactive materials. In the course of these studies we discovered that  $\chi$  was strongly dependent upon the extent of sample decomposition. It has been noted that magnetic susceptibility measurements of metals are extremely sen-

sitive to even slight surface decomposition (19, 20). In particular, we found that  $\chi$  decreases with increasing sample decomposi-

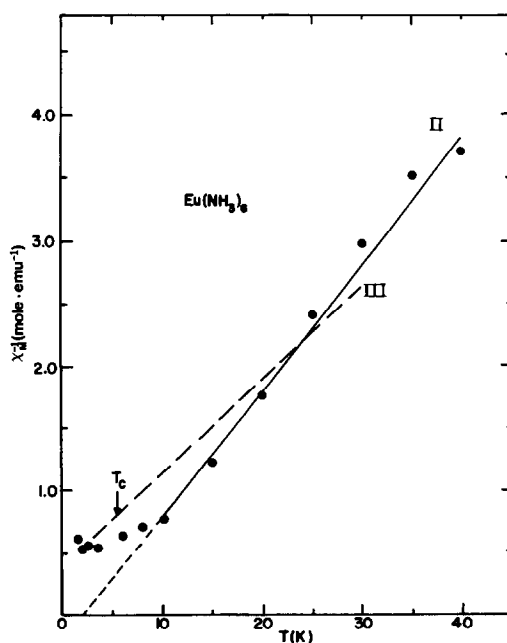


FIG. 2. Temperature dependence of the reciprocal molar susceptibility of  $\text{Eu}(\text{NH}_3)_6$  at low temperatures. Samples II and III represent data from this work and Ref. (9), respectively.

tion and actually becomes diamagnetic after the decomposition is complete. In some experiments, even warming the sample from 100 to 200 K and then remeasuring  $\chi$  at 100 K resulted in a 20% decrease in  $\chi$ . These results are surprising, because the expected primary decomposition reaction is  $\text{Eu}(\text{NH}_3)_6 \rightarrow \text{Eu}(\text{NH}_2)_2 + 4\text{NH}_3 + \text{H}_2$  (14, 21–23). In this case,  $\chi$  should exhibit essentially no change at elevated temperatures, since (1) the  $\text{Eu}^{2+}$  concentration does not change, (2)  $\text{Eu}^{2+}$  in  $\text{Eu}(\text{NH}_2)_2$  has a spin-only magnetic moment (14), and (3) the paramagnetism of  $\text{Eu}^{2+}$  is much stronger than the diamagnetism of  $\text{NH}_3$  and  $\text{H}_2$  (17). Moreover, the presence of any substantial quantity of  $\text{Eu}(\text{NH}_2)_2$  should be easily detected, because it orders ferromagnetically at 5.4 K (14).

An X-ray diffraction study was performed in order to better characterize the yellow–orange decomposition product. Using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), six weak lines were observed at the following  $d$  spacings: 1.80, 1.82, 1.83, 2.15, 3.03, and 3.16  $\text{\AA}$ . Comparison with the known patterns of  $\text{Eu}(\text{NH}_2)_2$ ,  $\text{EuNH}$ ,  $\text{EuN}$ ,  $\text{EuO}$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Eu}_3\text{O}_4$ ,  $\text{Eu}(\text{OH})_3$ , and  $\text{Eu}$  revealed that it was not any of these compounds. At present we do not understand the nature of the decomposition product or its possible interaction with  $\text{Eu}(\text{NH}_3)_6$ . In an attempt to avoid this decomposition problem, the samples were inserted rapidly into the pre-cooled cryostat ( $\approx 30$  sec), and the magnetic measurements were made from lower to higher temperatures. However, even then it was not possible to eliminate completely the effects of decomposition. Although the susceptibility trends are reproducible for different samples, the values of the magnetic parameters presented in Table I should be regarded in a qualitative fashion. With this precaution in mind, we proceed to a discussion of the magnetic data for  $\text{Eu}(\text{NH}_3)_6$ .

In contrast to the previous study (sample

III) (9), in which a magnetic change was observed at 47 K and magnetic ordering was found at 5.5 K, we find that  $\chi$  obeys a single Curie–Weiss law,  $\chi = C/(T - \theta)$ , above 10 K. The origin of the magnetic change at 47 K observed in previous work is uncertain. It may be due to excess Eu in the samples, which we have found to undergo a pronounced increase in  $\chi$  near 50 K, but the change in  $\chi$  is in the wrong direction to explain the previous results. Also, there is no change in  $\chi$  near 160 K, where an EPR lineshape transition has been detected (13). This transition is believed to be associated with  $\text{NH}_3$  vacancies, which apparently have little effect upon the average magnetic moment of Eu. The average Weiss constant for samples I and II is only  $-1 \pm 2$  K, which is in good agreement with that predicted from Mössbauer (12) and EPR (13) studies. However, as shown in Fig. 2, low-temperature measurements on one of the  $\text{Eu}(\text{NH}_3)_6$  samples (sample II) reveals that  $\chi$  deviates from the Curie–Weiss law below 10 K and begins to flatten out in a manner similar to that found for  $\text{Li}(\text{NH}_3)_4$  below 15 K (5). Magnetic measurements below 10 K were not attempted on the other  $\text{Eu}(\text{NH}_3)_6$  samples. This behavior coincides with the observation by EPR of the onset of critical broadening of the  $\text{Eu}^{2+}$  resonance below 10 K in  $\text{Eu}(\text{NH}_3)_6$ . The flattening in  $\chi^{-1}$  below 10 K as well as the slight upturn at 1.5 K suggests that the balance of the magnetic interactions in  $\text{Eu}(\text{NH}_3)_6$  is antiferromagnetic. Since Mössbauer studies have provided no evidence of any long-range magnetic ordering down to 1.2 K (11, 12), the low-temperature susceptibility behavior apparently reflects only short-range antiferromagnetic interactions between the  $\text{Eu}^{2+}$  moments, which are probably a precursor to long-range antiferromagnetic order below 1.2 K. Hence these results, as well as those from recent Mössbauer (11, 12) and EPR (13) studies, provide no evidence for conduc-

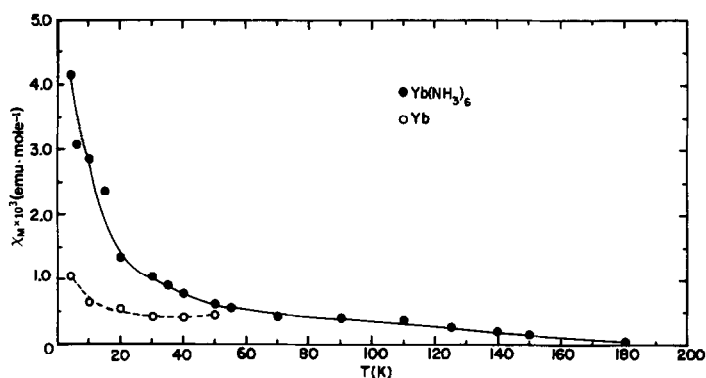


FIG. 3. Molar susceptibility vs temperature for  $\text{Yb}(\text{NH}_3)_6$  and Yb.

tion-electron localization at low temperatures in  $\text{Eu}(\text{NH}_3)_6$ , as suggested in the original susceptibility work (9).

In contrast to  $\text{Eu}(\text{NH}_3)_6$ , susceptibility runs on different  $\text{Yb}(\text{NH}_3)_6$  samples were reproducible to better than 20% over the whole temperature range, and  $\chi$  did not change upon thermal cycling. The temperature dependence of  $\chi_m$  for  $\text{Yb}(\text{NH}_3)_6$ , as well as that of the Yb metal used to prepare this compound, are shown in Fig. 3. The relatively small increase in  $\chi$  for Yb at low temperatures reflects its high purity. In a previous study (19), the paramagnetic increase in  $\chi$  of Yb with decreasing temperature has been attributed to the presence of a small amount of  $\text{Yb}^{3+}$  ( $\approx 0.4\%$ ) having a  $^2F_{7/2}$  ground state and a magnetic moment of  $4.5 \beta$  (assuming Russel-Saunders coupling), but the origin of the  $\text{Yb}^{3+}$  was unspecified. More recently, this increase has been attributed to strain in crystals of Yb metal (24). Since we find only about a two-fold increase in  $\chi$  of Yb in going from 50 to 4.2 K, whereas about a fivefold increase has been found in the previous work (25), it appears that small amounts of lanthanide impurities probably play an important role in determining the low-temperature behavior. Moreover, since  $\chi$  of  $\text{NH}_3$  is diamagnetic ( $\approx -16 \times 10^{-6}$  emu/mole) and independent of temperature above 4 K, it

follows that the strong paramagnetic increase in  $\chi$  of  $\text{Yb}(\text{NH}_3)_6$  at low temperatures is intrinsic to this compound.

In contrast to the previous susceptibility study of  $\text{Yb}(\text{NH}_3)_6$  (9), in which  $\chi$  crossed over from diamagnetic to paramagnetic below 31 K, we find that  $\text{Yb}(\text{NH}_3)_6$  is paramagnetic below 180 K. Although corrections for the diamagnetic susceptibility of the  $\text{Yb}(\text{NH}_3)_6^{2+}$  complexes ( $\chi_d \approx -120 \times 10^{-6}$  emu/mole) (17) and the Pauli-Peierls susceptibility of the conduction electrons ( $\chi_p \approx 61 \times 10^{-6}$  emu/mole) (18) would change  $\chi$  at higher temperatures substantially, at low temperatures their effect is much smaller ( $\approx 10\%$  at 50 K). In this case it is possible to try to fit  $\chi$  to the Curie-Weiss law appropriate for a fixed concentration of localized moments. A plot of  $\chi_m^{-1}$  vs  $T$  at low temperatures for  $\text{Yb}(\text{NH}_3)_6$  is shown in Fig. 4, where it can be seen that  $\chi$  indeed obeys the Curie-Weiss law below about 50 K, with  $\mu_{\text{eff}} = 0.52 \beta$  and  $\theta = -3.2$  K. The low-temperature moment is in good agreement with the value  $0.50 \beta$  obtained in the previous study (9), even though  $\chi$  at 4.2 K is about twice our value. Although there are differences in the absolute values of  $\chi$  between this and the previous work, the relative increase in  $\chi$  at low temperatures is reproducible and hence is believed to be real. However, the origin of this behavior is

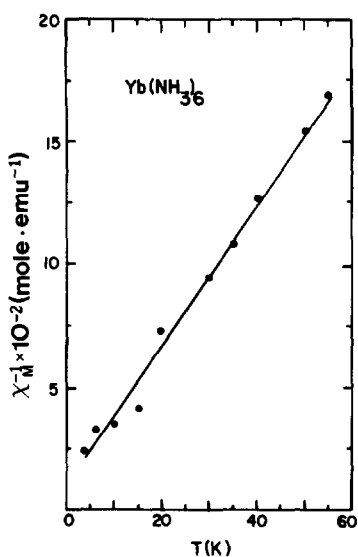


FIG. 4. Temperature dependence of the reciprocal molar susceptibility of  $\text{Yb}(\text{NH}_3)_6$  at low temperatures.

uncertain. If, in analogy to Yb metal, we attribute the paramagnetism to  $\text{Yb}^{3+}$  having  $\mu_{\text{eff}} = 4.5 \beta$ , then about 1.3% of the Yb must be in the trivalent state to account for our measured low-temperature behavior of  $\text{Yb}(\text{NH}_3)_6$ . However, since  $\text{Yb}(\text{NH}_3)_6$  is a low-electron-density metal in which electron-electron interactions probably play a prominent role, it is also possible that the low-temperature paramagnetism could arise from a partial localization of conduction electrons. If we assume that  $\text{Yb}^+$  is produced by the localization process and that its electronic configuration is  $4f^{14}5d^1$  with a quenched orbital moment, then  $\mu_{\text{eff}} = 1.73 \beta$  and about 9% of the Yb must be in this state to account for the low-temperature susceptibility. In either case, the small value of  $\theta$  is consistent with weak interac-

<sup>2</sup> Using a simple model for Yb— $\text{NH}_3$  bonding, the  $4f^{14}5d^1$  configuration should be favored for  $\text{Yb}^+$ , since this leaves the 6s orbitals of Yb available for  $d^2sp^3$  bonding to  $\text{NH}_3$ . The lack of metallic s character in the conduction-electron wavefunction is supported by the small s-f exchange integral ( $J_{sf} \approx 3.5 \times 10^{-3}$  eV) derived from EPR measurements in  $\text{Eu}(\text{NH}_3)_6$  (13).

tions between well-separated magnetic moments. In this regard, a relatively small localization of conduction electrons would be difficult to detect for  $\text{Eu}(\text{NH}_3)_6$  due to the large background moment of  $\text{Eu}^{2+}$ . EPR measurements on  $\text{Yb}(\text{NH}_3)_6$  in the helium range should help to elucidate the electronic nature of Yb at low temperatures, and such measurements will be undertaken in this laboratory in the near future.

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