and Giauque,[4] while those below 5°K are due to Corak *et al.*[5] The experimental C_v at lower temperatures are corrected for the electronic contribution. It is seen that the calculated values are systematically greater than the measurements. In Fig. 3, the more sensitive plot, Θ vs T is given. The discrepancy between the theory and the experiment here can be attributed to the approximate method of calculating the frequency spectrum and the neglect of anharmonic effects.

ACKNOWLEDGMENTS

The authors are grateful to Professor K. Banerjee for his interest in the investigation and Dr. S. S. Mitra of Ontario Research Foundation, Canada, for discussion.

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Paramagnetic Behavior of Metallic Cerium and Europium

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The magnetic behavior of metallic polycrystalline cerium and europium has been studied above room temperatures. The measured paramagnetic behavior of cerium can be explained using the interacting Ce^{+++} ion model ($\theta=-50$°K) and the Van Vleck theory of paramagnetism with an additional temperature-independent paramagnetic term $\chi_c=1.00\times10^{-6}$ g^{-1} cm^3 resulting from the conduction electrons. Europium metal has an unusual magnetic behavior. Its paramagnetic properties in the solid state cannot be explained on the basis of the noninteracting Eu^{++} model. Near the melting point metallic europium behaves as a collection of weakly interacting Eu^{+} ions. The Bohr magneton number of liquid europium is very close to that of Eu^{++} ions.

INTRODUCTION

RECENTLY we have been studying the paramagnetic behavior of polycrystalline rare-earth metals in order to enlarge our knowledge about their electronic structures. Our results on neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, and thulium have been reported earlier.[1–3] These measurements have clearly indicated that the $4f$ electrons in the rare earth metals are quite localized and that the Van Vleck theory can approximately explain the observed magnetic susceptibilities. In this paper we present further results on this problem by discussing our magnetic measurements on metallic europium and cerium.

EXPERIMENTAL CONSIDERATIONS

Distilled and recast europium used in this investigation was obtained from Lindsay Chemical Division of American Potash and Chemical Corporation. This material contained 0.3% oxygen, less than 0.1% other rare-earth elements, and traces of calcium and tantalum. About 4.5 grams of material was cut from a larger piece in a dry-box containing argon. This sample was weighed, wrapped in a tantalum foil, and enclosed in a silica capsule filled with argon gas at 20 cm Hg at room temperature. All these operations were performed in argon atmosphere, and during these operations the europium sample maintained a bright surface.

Cast polycrystalline cerium was purchased from the St. Eloi Corporation and according to the manufacturer was at least 99.5% pure. A sample having a mass of about 4.3 grams was sealed in a silica container using the same procedure as for europium.

The magnetic susceptibilities of europium and cerium metals were measured using the Faraday method. The apparatus has been described in detail earlier.[4]

THEORY

The electronic configuration of a Ce^{+++} ion is $1s^2$, $2s^22p^6$, $3s^23p^63d^{10}$, $4s^24p^64d^{10}4f^1$, $5s^25p^6$. The lowest multiplet consists of two energy levels $^2F_{5/2}$ and $^2F_{7/2}$, the term $^2F_{5/2}$ representing the ground state. The position of the level $^2F_{7/2}$ with respect to the ground state can be approximately calculated using the modified Goudsmit formula[5,2]:

$$\Delta E=\frac{8\pi^4me^2}{c^3h^5}\frac{2L+1}{n^3l(l+1)(2l+1)}(Z-\sigma)^4, \qquad (1)$$

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where ΔE is the width of the energy multiplet, m the mass of an electron, c the velocity of light, h the Planck constant, n the principal quantum number, l the orbital quantum number of an electron, L the total orbital quantum number of the incomplete $4f$ shell, Z the atomic number, and σ the nuclear screening constant. The energy levels of a Ce^{+++} ion for various σ values are given in Table I together with the results of calculations by Elliott and Stevens[6] and an experimental determination by Lang.[7]

The electronic configuration of a Eu^{+++} ion is $1s^2$, $2s^22p^6$, $3s^23p^63d^{10}$, $4s^24p^64d^{10}4f^6$, $5s^25p^6$. The lowest multiplet consists of seven energy levels ${}^7H_0$, ${}^7H_1$, ${}^7H_2$, ${}^7H_3$, ${}^7H_4$, ${}^7H_5$, and ${}^7H_6$, where ${}^7H_0$ is the ground state. The energy level structure can be approximately calculated using Eq. (1) and the Landé interval rule. The results are summarized in Table II which also gives more refined theoretical calculations by Judd,[8] and Elliott and Stevens,[6] and the spectroscopic results on some trivalent rare earth salts.[9–11]

TABLE I. Energy levels of the lowest multiplet of Ce^{+++}.

Term	$E_J[\mathrm{cm}^{-1}]$ $\sigma=32$	$\sigma=33$	$\sigma=34$	$\sigma=35$	$\sigma=36$	Elliott & Stevens[a]	Experimental
${}^2F_{7/2}$	3476	2972	2524	2129	1782	2100	2253[b]
${}^2F_{5/2}$			0			0	0

[a] See reference 6.
[b] See reference 7.

TABLE II. Energy levels of the lowest multiplet of Eu^{+++}.

Term	$E_J[\mathrm{cm}^{-1}]$ $\sigma=32$	$\sigma=33$	$\sigma=34$	$\sigma=35$	$\sigma=36$	Judd[a]	Elliott & Stevens[b]	Experimental
${}^7F_6$	7026	6162	5381	4676	4043	5100		5100[c]
${}^7F_5$	5018	4402	3843	3340	2888	3990		3900[d]
${}^7F_4$	3346	2934	2562	2227	1925	2850		2900[d]
${}^7F_3$	2007	1761	1537	1336	1155	1800		1900[d]
${}^7F_2$	1004	880	769	668	578	940		1100[d] 1000[e]
${}^7F_1$	335	293	256	223	192	320	270	300[d] 350[e]
${}^7F_0$			0			0	0	0

[a] See reference 8.
[b] See reference 6.
[c] See reference 9.
[d] See reference 10.
[e] See reference 11.

Knowing the energy levels E_J, the paramagnetic susceptibility can be evaluated numerically using the Van Vleck theory.[12] When the quantity kT is comparable with the energy intervals of the lowest multiplet, the paramagnetic susceptibility per gram can be written as

$$\chi=\frac{(N/M)\sum_J[(g^2\beta^2J(J+1)/3kT)+\alpha](2J+1)\exp(-E_J/kT)}{\sum_J(2J+1)\exp(-E_J/kT)},\tag{2}$$

where N is the Avogadro number, M the atomic weight of the particular rare earth metal, k the Boltzmann constant, T the absolute temperature, β the Bohr magneton, and

$$\alpha=\frac{\beta^2}{6(2J+1)}\left[\frac{F_{J+1}}{E_{J+1}-E_J}-\frac{F_J}{E_J-E_{J-1}}\right],\tag{3}$$

with

$$F_J=[(S+L+1)^2-J^2][J^2-(S-L)^2]/J.\tag{4}$$

The quantity g is the Landé splitting factor,

$$g=1+[S(S+1)+J(J+1)-L(L+1)]/2J(J+1).$$

The paramagnetic susceptibility for noninteracting Eu^{+++} ions has been evaluated numerically by means of a Burroughs Datatron 205 computer. The $1/\chi$ vs T plots for various energy level separations are shown in Fig. 1.

RESULTS AND DISCUSSION

Values of the paramagnetic susceptibility of cerium were obtained from the measured susceptibility by correcting for the diamagnetism of the silica capsule and the paramagnetism of the tantalum foil. These values were then corrected for the diamagnetic con-

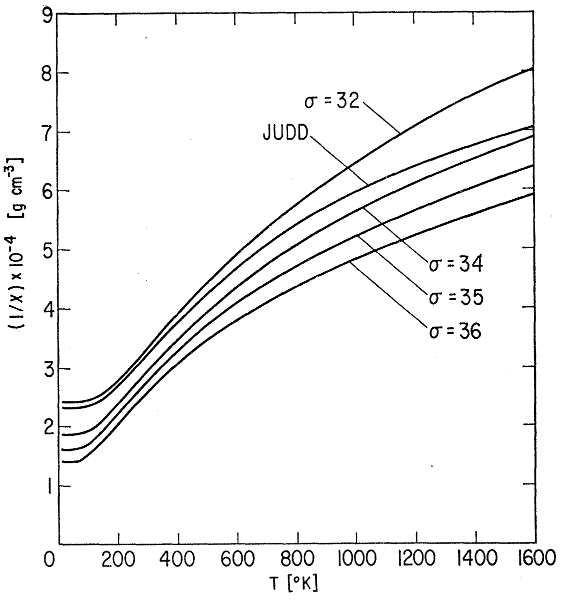

FIG. 1. Calculated inverse paramagnetic susceptibility of noninteracting Eu^{+++} ions.

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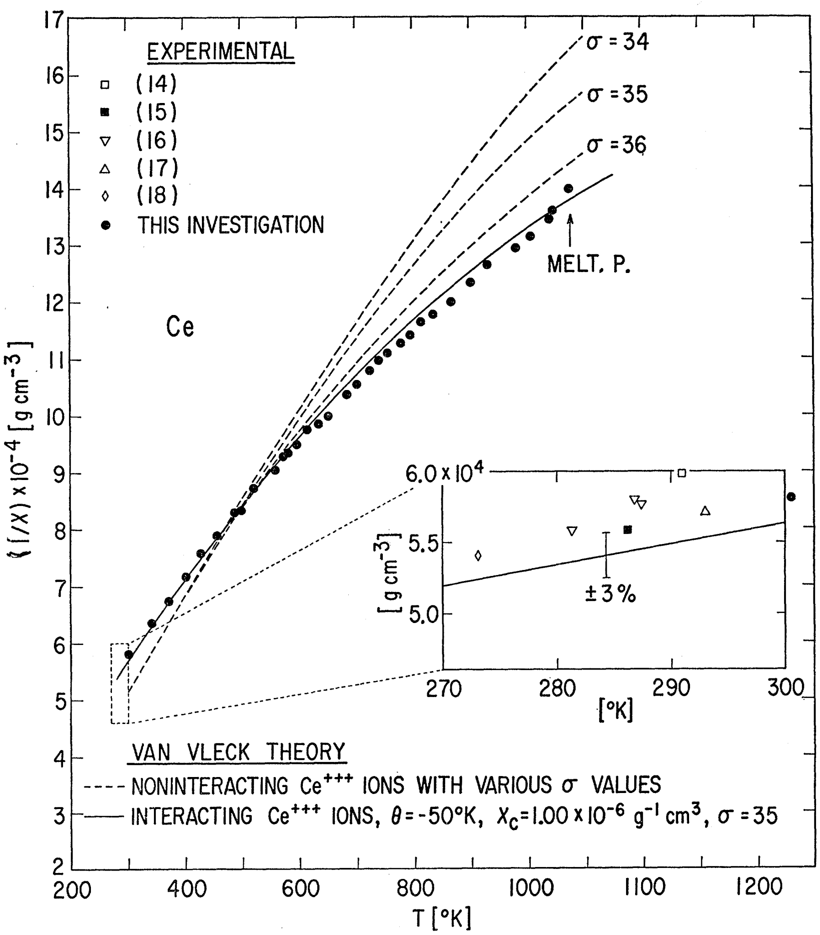

FIG. 2. Inverse paramagnetic susceptibility of Ce as a function of temperature.

tribution which was taken to be -0.19×10^{-6} g^{-1} cm^3.[13] The inverse paramagnetic susceptibility of metallic cerium as a function of temperature is shown in Fig. 2. Our room temperature measurement is in fair agreement with those of other investigators[14–22] in this temperature range. The results of some of the previous studies,[14–18] where the authors have provided numerical susceptibility data, are shown in Fig. 2. Our high-temperature magnetic susceptibility measurements are also in fair agreement with the earlier studies by Blanchetais[19] and Bates *et al.*[17] Figure 2 also shows the theoretical curves for noninteracting Ce^{+++} ions with various screening constants. It is obvious that the calculations of this type can provide only an order-of-magnitude agreement with the experimental data. The reason for the imperfect agreement between the simple theory and the experimental observations is due to the interactions between the Ce^{+++} ions and the contribution of conduction electrons to the observed paramagnetism of cerium metal. These latter contributions, which we designate by χ_c, are particularly important for cerium since at high temperatures they are comparable with the paramagnetism of the localized f electrons of Ce^{+++} ions. The solid curve shown in Fig. 2 represents the paramagnetic behavior of interacting Ce^{+++} with $\theta=-50$°K, $\sigma=35$, and $\chi_c=1.0\times10^{-6}$ g^{-1} cm^3. The agreement with the measurements of the paramagnetic susceptibility of metallic cerium is satisfactory. It should be mentioned that the choice of value of θ is very reasonable in light of the experimental work by Bates *et al.*[17] and Lock[21] who have determined the paramagnetic Curie temperatures to be -42°K and approxi-

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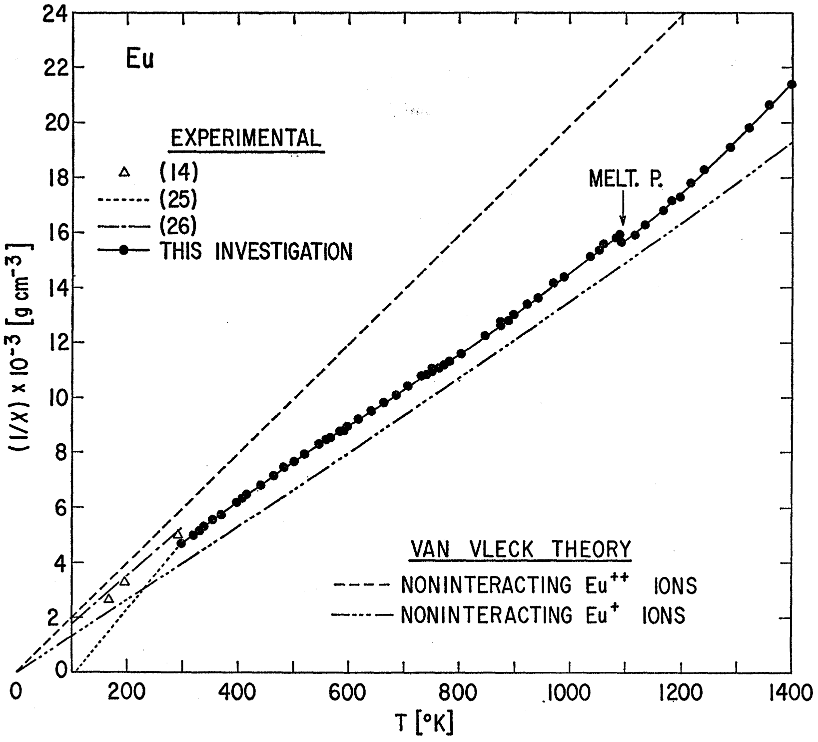

FIG. 3. Inverse magnetic susceptibility of Eu as a function of temperature.

mately −46°K, respectively. The value $\chi_c = 1.00 \times 10^{-6}$ g^{-1} cm^3 is also quite reasonable since the room temperature value of the paramagnetic susceptibility of lanthanum, which does not have any *f* electrons, measured by Trombe,[23] Bommer,[24] and Lock[21] are 1.19×10^{-6}, 0.99×10^{-6}, and 0.74×10^{-6} g^{-1} cm^3, respectively. Moreover, we have also found that for dysprosium $\chi_c = 1.15 \times 10^{-6}$ g^{-1} cm^3.[3] Thus it appears that the paramagnetic behavior of metallic cerium can be satisfactorily explained using the localized *f*-electron model and the Van Vleck theory of paramagnetism with the above-described additional contributions.

The magnetic behavior of metallic europium from 300°K to 1400°K, as determined in this investigation, is shown in Fig. 3. This graph also gives all the known previous measurements[14,25,26] of the magnetic susceptibility between the Néel temperature (about 90°K) and 300°K. The agreement between the data of Bozorth and Van Vleck[26] and those of Klemm and Bommer[14] is fairly satisfactory. It should be mentioned that Klemm and Bommer studied a powdered mixture of Eu+3 KCl while Bozorth and Van Vleck made their measurements on a polycrystalline metallic europium. The results of the investigation by Blanchetais and Trombe[25] deviate considerably from those of Bozorth and Van Vleck, and Klemm and Bommer. Our value of the magnetic susceptibility of europium at 300°K is about 10% larger than that measured by Bozorth and Van Vleck. It is very possible that this discrepancy is due to different amounts of impurities in the samples. In Table III the Bohr magneton numbers and the paramagnetic Curie temperatures, obtained by various investigators, are summarized.

Comparing the measured inverse magnetic susceptibility curve shown in Fig. 3 with the theoretical curves given in Fig. 1 immediately reveals that the Eu^{+++} model cannot explain the observed magnetic susceptibility of metallic europium. It has been suggested that europium metal should be considered to be made up

TABLE III. Comparison of the results on europium of this study with magnetic susceptibility data of others.

Investigator	Temperature range [°K]	μ_{eff} [Bohr magnetons]	θ_p [°K]
Klemm and Bommer[a]	167–293	8.2	15
Henry La Blanchetais and Trombe[b]	140–300	7.12	108
Bozorth and Van Vleck[c]	100–300	8.3	0
This investigation	300–400	9.17±0.05	−3.26±0.05

[a] See reference 14.
[b] See reference 25.
[c] See reference 26.

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of Eu^{++} ions imbedded in a sea of electrons.[26,27] Although this model can approximately account for the magnetic susceptibility above the Néel temperature, our high-temperature measurements of the magnetic behavior of solid europium clearly show that the noninteracting Eu^{++} model is not a correct approximation. In fact, it appears that at high temperatures, say between 800°K and the melting point of europium (1099°K[27]), the magnetic susceptibility values are quite close to those resulting from noninteracting Eu^{+} ions. The Bohr magneton number in this range is equivalent to that of Eu^{+} ion in its ground state $^7F_6$.

The melting process produces a small anomaly in the plot of $1/\chi$ vs T curve as can be seen in Fig. 3. Liquid europium metal approximately follows the Curie-Weiss law. The magnetic moment in this state is very close to that expected from the interacting Eu^{++} system. These observations indicate that metallic europium has unusual magnetic properties and that europium is not a well-behaved rare-earth metal. This supports some previous studies on the crystal structure, density, compressibility, thermal expansion, electrical resistivity, etc.[27–30] which are out of line with the corresponding behavior for most of the rare-earth elements. At the present time we are unable to provide a theoretical justification for the possible change of valency of europium ions with respect to the temperature.

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Note added in proof. Dr. Anthony Arrott of the Scientific Laboratory of the Ford Motor Company has suggested (private communications) that the valency change of europium ions is not needed for explaining our experimental results. The interacting Eu^{++} model may be applicable to metallic europium if the anomalous thermal expansion (reference 30) is taken into account.

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Photochemically Produced Color Centers in KCl and KBr†

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KCl and KBr crystals were exposed to unfiltered mercury arc radiation at 15°K. If an "OH" band was present in the crystals before irradiation, the ultraviolet irradiation produced an optical absorption spectrum similar to that produced by x rays at 15°K. The optical absorption spectrum and the changes in the absorption produced by annealing at higher temperatures were measured and compared with the spectra observed during similar annealing of x-irradiated crystals. In KCl the 335-mμ band, formed by the uv irradiation, bleaches thermally at 56°K as does the 335-mμ H band of x-irradiated KCl. In KBr the 381-mμ band bleaches in steps at 35°, 46°, 56°, and 80°K as compared with the 381-mμ H band in x-irradiated KBr which bleached at 30°, 46°, 56°, and 80°K. In both KCl and KBr the V_1 band appears with the disappearance of the H band. Illumination in the V_1 band causes regeneration of the H band as occurs in x-irradiated KCl and KBr. In both KCl and KBr the photoproduced H band grows by about 10% at approximately 25°K. It is concluded that the H centers bleach thermally by diffusing to and combining with other color centers. Recombination with F and α centers annihilates the H centers and leads to the formation of V_K centers, while recombination with a third center (possibly a positive-ion vacancy) results in the formation of V_1 centers.

U, U_1, U_2, O^-, and α centers are produced by the uv irradiation as well as F and H centers. The photoproduced F band may be bleached optically with negligible effect on the H band.

INTRODUCTION

WHEN an alkali-halide crystal, which has been exposed to ionizing radiation at liquid helium temperature, is warmed, changes occur in the optical absorption spectrum. In general, at definite temperatures during warmup the various absorption bands change in magnitude and in shape. This effect, together with the appearance of thermoluminescence and free electrical charge within the crystal at some of these characteristic temperatures, leads to the conclusion that some of the original color centers become unstable while new centers are formed.

In a recent publication[1] a study was reported of the

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