Magnetic Susceptibility and Fluorescence Spectra of SmI$_2$ in THF

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Introduction

Magnetic susceptibility measurements have been used widely for the characterization of oxidation states of lanthanide elements. Calculation of the molar susceptibilities and effective magnetic moments for Sm^{2+} at 35°C is about 3.64 μ_B. The magnetic moments of Sm^{2+} and Eu^{3+} are nearly the same, indicating that both ions have the electronic configuration (Xe) $4f^6$ (*1*). Magnetic susceptibility of SmBr$_2$ measured by Selwood used the Groy method (*2*). The NMR method was first employed by D. F. Evans (*3*); the NMR method is very simple to use and is quite applicable in the case of species soluble in an organic medium. Namy *et al.* (*4*) measured magnetic susceptibility of SmI$_2$ in THF using NMR, but the magnetic susceptibility of SmI$_2$ powder has not been reported.

The ultraviolet–visible absorption spectra of divalent samarium in a number of systems have been measured. These include Sm^{2+} in a lattice of CaF$_2$, SrF$_2$, and BaF$_2$ (*5, 6*); SmI$_2$ dissolved in THF (*7*), in HMPA, ethanol, and acetonitrile (CH$_3$CN) (*8*); and solutions of SmI$_2$, SmBr$_2$, and SmCl$_2$ in HMPA (*9*). All of these spectra

are basically similar, supporting Namy's contention (*10*) that THF solutions of Sm^{2+} are stable. He went on to interpret the absorption spectrum in terms of energy levels. Kamenskaya *et al.* also interpreted the absorption spectrum of Sm^{2+} and compared it to other divalent lanthanides.

Przibram (*11*) investigated fluorescence of SmI$_2$ in water and found a diffuse red band at 6300 Å and a line spectrum with lines at 6900 Å and further on into the near infrared. Butement (*12*) measured the fluorescence of SmCl$_2$ in SrCl$_2$ and BaCl$_2$ and reported a brilliant red diffuse band from 6550 to 6900 Å with a maximum at 6760 Å. Dieke and Sarup (*13*) studied the fluorescence spectrum of Sm^{2+} in LaCl$_3$ and found that the fluorescence spectrum resembles in all details that of isoelectronic Eu^{3+}.

Dieke and Sarup excited the very strong continuous absorption band in the visible around $4f^6$ to the $4f^55d$ state. The energy is transferred to the closely spaced (1330 cm^{-1}) stable states $^5D_0$ and $^5D_1$ of the $4f^6$ configuration. From these states strong red emission is observed back to the ground ^7F multiplet. This has been utilized in an optical laser by placing the Sm^{2+} in CaF$_2$.

In this paper we report the magnetic susceptibility and the magnetic moment of SmI$_2$, calculate λ (the spin–orbit coupling constant), and compare the data with the

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fluorescence spectrum of Sm^{2+} in $LaCl_3$. We also investigate the fluorescence spectrum of SmI_2 in THF. This has not been reported before, and we believe that such measurements in different solvent systems would be of interest. We tried Nujol and found that Nujol has its own fluorescence.

Experimental

Sm^{2+} was measured by a SHEVTS (Variable Temperature Susceptometer) 905 with superconducting devices (SQUID) from 5 to 300 K at 10 kG.

SmI_2 was prepared by reacting Sm with HgI_2 (*14*). The sample was sealed under vacuum (2×10^{-6} Torr) and was heated, first at 300°C and then at 500°C. It was checked by X-ray analysis. The melting point is 526°C. The SmI_2 contained no less than 99.4% of the theoretical amount. The sample bucket is made of derlin, which is diamagnetic. SmI_2 was stored in a bucket and sealed in glass in a dry box; it was quickly transferred to the SQUID and put under vacuum. After measurement, SmI_2 does not change color, i.e., SmI_2 is not oxidized.

The THF must be quite anhydrous. It was dried over CaH_2 for several days until no more bubbles were evolved. After this, some $LiAlH_4$ was added and it was recycled under N_2 for 1 hr and then stored under N_2.

At least two fluorescence spectra were measured for each sample, excitation and emission, each of those being duplicated or triplicated at different sample concentrations. No concentration dependence was found within experimental error.

The spectra were obtained using a method very similar to the one described by Lehman (*15*). The light source was a 500-W high-pressure xenon arc lamp, whose beam was focused onto the entrance slit of a Jobin-Yvon Model M25 holographic grating monochromater. This beam (with about a 6-

nm bandwidth) was chopped at about 15 Hz and then focused onto a Maxlight UV fiber optic light guide, which randomized the light.

The sample was irradiated from the side, not the top as in Lahman's work, because our samples were sensitive to air and had to be sealed at the top.

The fluorescence perpendicular to the exciting light was focused by two lenses into a Jobin-Yvon Model H-20 monochromater. After exiting, the light was focused onto an RCA-31034 gallium arsenide photomultiplier which was connected to a PAR Model 1140 quantum photometer. This signal (of between 0 and 10 mV) was amplified by a Dynatrac 3 Lock-In Amplifier to a range of 0 to 10 VDC (but never exceeding 10, to stay in the linear amplification range of the amplifier). A diode measured the chopping frequency at the chopper itself, and this signal was used as the reference frequency for the Lock-In Amplifier.

An IBM-PC sampled the output of the Lock-in-Amp and also drove the stepper motor of the appropriate monochromater.

The light source does not emit the same number of photons per second for each wavelength. Therefore a "blackbody" spectrum was taken each day. The setup for this measurement was the same as for the other spectra, until the light reached the chopper, which was turned off. The same light guide as before then focused the light into a Molectron Model PR-20 power meter, which had its own chopper. The output of this, in the range of 0 to 20 mVDC, was amplified by a PAR 113 preamp to between 0 and 5 VDC, its linear amplification range. The signal was again sampled by the IBM-PC and corrected to give the photon flux from the lamp by dividing the power reading by the energy per photon at that wavelength.

Figure 1 shows the emission spectrum of SmI_2 in THF from 450 to 850 nm, excited at 418 nm. There is a strong continuous band
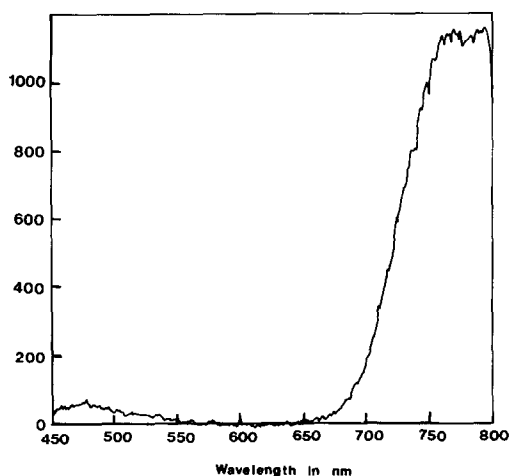
FIG. 1. Fluorescence spectrum of SmI_2 in THF excitation at 418 nm.

FIG. 3. I: Electronic spectrum of SmI_2 in THF. II: Electronic spectrum of EmI_2 in THF during air oxidation. III: Electronic spectrum of Sm^{3+} in THF

of red emission from 650 to 800 nm. The failure of the spectrum to fall back to the baseline from 800 to 850 nm is probably an artifact of the instrumentation.

Figure 2 shows the corrected excitation spectrum of SmI_2 from 400 to 700 nm, with the emission monitored at 735 nm.

Figure 3 shows the absorbance spectrum of pure SmI_2 and additional spectra that were taken as the SmI_2 was air-oxidized.
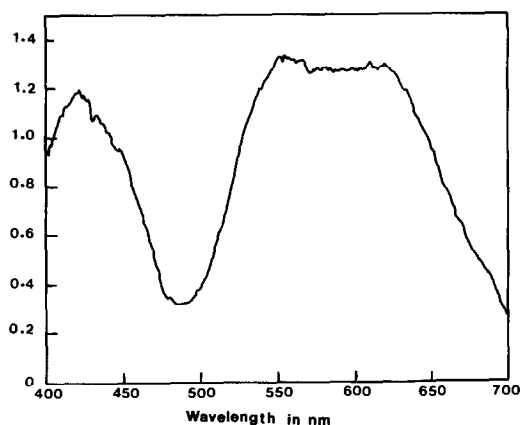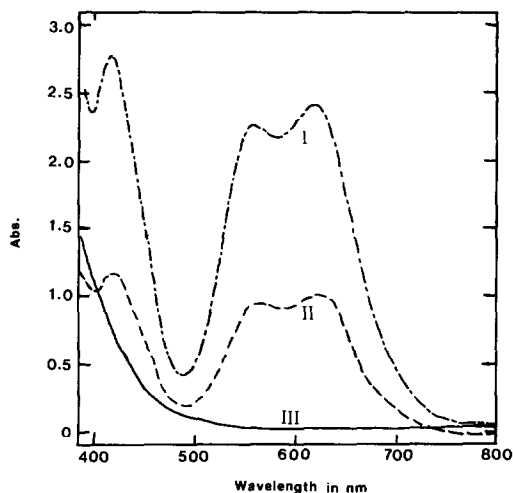
Results and Discussion

1. Magnetic Susceptibility of SmI_2

At room temperature (295°K) the magnetic moment of SmI_2 is 3.58 μ_B. The magnetic susceptibility is 5.425×10^{-3} emu/GS mole Sm^{2+}. The following data show that the magnetic susceptibility of SmI_2 per mole of Sm^{2+} changes with an elevation in temperature (Fig. 4). χ_M increases with decreasing temperature down to about 40 K; above 40 K it flattens out, after which χ_M decreases with increasing temperature. For comparison, magnetic susceptibility measurements of Eu_2CuO_4 (16) were made in the range 4.2–300 K using a Faraday apparatus. The magnetic susceptibility of Eu_2CuO_4 behaves with temperature as shown in Fig. 5. The magnetic susceptibility data of SmI_2 agree with Selwood's suggestion of SmI_2 (1).

The temperature dependence of the magnetic susceptibility of Eu_2CuO_4 per mole of Eu^{3+} is very similar to that of SmI_2.

The data show that Sm^{2+} and Eu^{3+} have an isoelectronic configuration $4f^6$, which

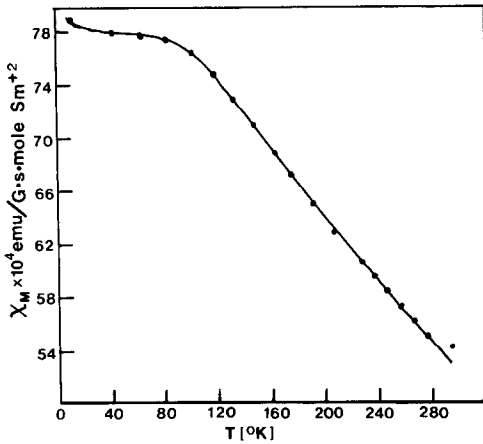FIG. 2. Excitation spectrum of SmI_2 in THF monitored at 735 nm.

FIG. 4. Temperature dependence of the magnetic susceptibility of SmI₂ per mole of Sm²⁺. The dots are experimental values and the solid line represents the best fit of Eq. (2) to the experimental data at elevated temperature.

gives rise to seven energy levels: $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^7F_5$, $^7F_6$, with ^7F being the ground state. Glaunsinger et al. (16) suggested that $4f^6$ is particularly interesting because the energy-level differences are usually comparable to kT at elevated temperatures, so that the effect of temperature on the magnetic susceptibility is pronounced. Assuming Russell–Saunders coupling, the energy levels of the multiplets can be written

$$W_J = \frac{\lambda}{2} [J(J + 1) - L(L + 1)$$
$$- S(S + 1)] + C, \quad (1)$$

where λ is the spin–orbit coupling constant and C is a constant which is independent of J. Van Vleck has shown that the susceptibility per mole of Eu³⁺ is given by

$$\chi_M(Eu^{3+}) = (0.1241/\gamma T)$$
$$[24 + (13.5\gamma - 1.5)e^{-\gamma} + (67.5\gamma - 2.5)e^{-3\gamma}$$
$$+ (189\gamma - 3.5)e^{-6\gamma} + \ldots]$$
$$\div (1 + 3e^{-\gamma} + 5e^{-3\gamma} + 7e^{-6\gamma} + \ldots), \quad (2)$$

where γ is 1/21 of the ratio of the overall multiplet width, i.e., $\gamma = \lambda/kT$. The best fit of Eq. (2) to the experimental data for Eu₂CuO₄ at elevated temperatures is shown in Fig. 5, for which λ has the value 280 cm⁻¹. Using Eq. (1) the multiple splittings are shown in Fig. 6. We used the data of the magnetic susceptibility of SmI₂ vs T and Eq. (2) to calculate γ. λ was then obtained from $\gamma = \lambda/kT$ as 243 cm⁻¹. From λ we can obtain the ground-state level (see Fig. 6). If using (17)
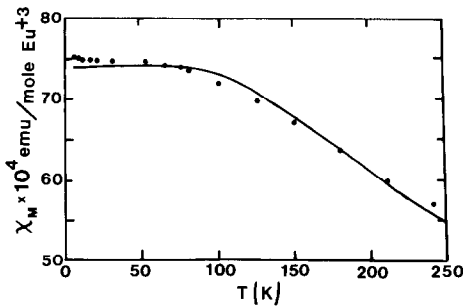

FIG. 5. Temperature dependence of the magnetic susceptibility of Eu₂CuO₄ per mole of Eu³⁺. The dots are experimental values and the solid line represents the best fit of Eq. (2) to the experimental data at elevated temperature.
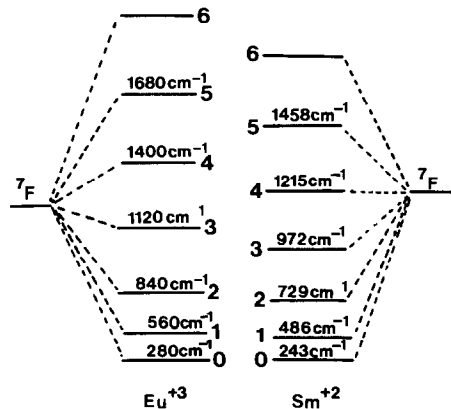

FIG. 6. Multiplet splittings for Eu³⁺ and Sm²⁺ in Eu₂CuO₄ and SmI₂ derived by using Eq. (2) with the experimental susceptibility data at elevated temperatures.

$$\frac{1}{c}\,\Delta U \text{ total} = \pm\,\frac{5.82(2L + 1)(z - \sigma)^4}{n^3 l(l + 1)(2l + 1)}, \quad (3)$$

where ΔU total is the "overall" multiplet width, z is atomic number, $\sigma = 34$ for Sm is the screening constant, l is the orbital angular momentum quantum number for a single electron, and L is that of the whole term, then $\gamma = 365/T$ and $\lambda = 255$ for Eu^{3+} and $\gamma = 319/T$ and $\lambda = 222$ for Sm^{2+}.

These conclusions, especially the latter, agree very well with the fluorescence spectra of Sm^{2+} in $LaCl_3$ (13) and SmI_2 (this work). Dieke and Sarup suggest that if the constant Slater integral F_2 and the spin–orbit coupling constant λ of Eu^{3+} are decreased by 20 and 22.2%, respectively, they obtain the levels shown in the middle of Fig. 7. We see that these agree very closely with the observed levels of Sm^{2+} and SmI_2 (see Figs. 6 and 7). This is a fairly convincing proof that the energy levels of the fluo-

rescence spectrum of SmI_2 and the magnetic susceptibility of SmI_2 correspond.

2. Fluorescence Spectrum of SmI_2 in THF

Figure 1 shows the strong fluorescence of SmI_2 in the red, which is compared to Sm^{2+} fluorescence in a host, and in THF, in Table I.

This table shows that a red fluorescence was observed in all samples. The spectra of the free divalent ions show that the $4f^{n-1}5d$ configuration is much closer to $4f^n$. In Sm^{2+}, $4f^55d$ is slightly less than 500 nm above $4f^6$ so that the transitions should fall in the visible. The $5d$ levels are so broad as to produce a continuous absorption spectrum which has an intrinsic strength five orders of magnitude larger than the forbidden transitions among the $4f^n$ levels. The excitation that leads to the fluorescence of Sm^{2+} thus has a mechanism quite different from that involved in the fluorescence of the trivalent ions. Since the exciting transitions are allowed it means that very small quantities of Sm^{2+} can produce noticeable fluorescence. We have synthesized a series of polycrystalline mixed fluorides to obtain new phosphors, which would fluoresce under 365-nm light excitation. The phosphors exhibit emission lines assigned to the transition. The excitation spectrum consists of band characteristics of the $4f^55d$ configuration and of a few $4f^6$ lines.

Table I compares our results to other investigations of SmI_2 fluorescence. One can see that our results are indeed similar to previous work, and hence lead us to believe that the red fluorescence band of SmI_2 is not altered significantly by solvent or host lattice effects. Also, the excitation spectrum of SmI_2 agrees with the electronic absorption spectrum.

The change of the absorption spectrum of SmI_2 over time as it oxidizes lets us suggest that this spectrum may be used to detect Sm^{2+} and Sm^{3+}. Recently Wood et al. (18)
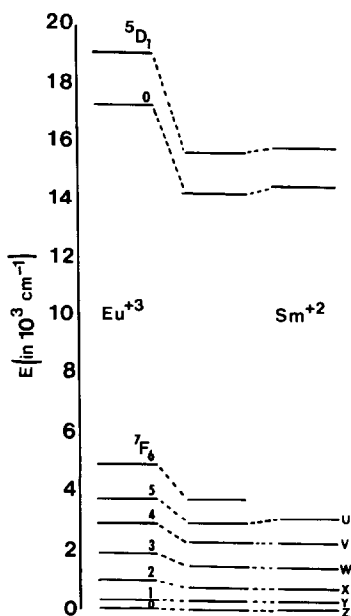

FIG. 7. Observed energy level diagrams of Sm^{2+} (right) and Eu^{3+} (left). The middle diagram is that of Eu^{3+} with appropriate scale changes.

TABLE I

THE FLUORESCENCE SPECTRUM OF SmI_2 UNDER VARIOUS CONDITIONS

Compound	Host or solvent	300°K	77°K	4°K	Reference
SmI_2	THF	650–800 nm			This work
$SmCl_2$	$BaCl_2$	655–690 nm max 676 nm			(8)
	$SrCl_2$	620–685 nm max 670 nm			(8)
Sm^{2+}	$LaCl_3$		644–680 nm	644–668.5 nm	
			692–707 nm	692–707 nm	(9)
			731–741 nm	731–741 nm	
			770–771 nm	787–791 nm	

used this method to confirm the presence of SmOBr in $SmBr_2$.

The fluorescence spectrum of SmI_2 in THF and magnetic susceptibility of SmI_2 were measured and the data from these studies were complementary in confirming our conclusions.

Acknowledgments

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