Magnetic Susceptibility of LiUO₃

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LiUO₃ was prepared, and its magnetic susceptibility was measured in the 4.2–300 K temperature range. Magnetic transition occurred at 16.9 K, and below this temperature large field dependence of the magnetic susceptibility was observed. The crystal field parameters of LiUO₃ were determined from the optical absorption spectrum of U⁵⁺ doped in LiNbO₃. The susceptibility and the g-value of electron paramagnetic resonance were calculated and compared with the experimental results. © 1992 Academic Press, Inc.

Introduction

The magnetic and optical properties of actinides are characterized by the behavior of $5f$ electrons. For the $5f$ compounds, the crystal field, spin–orbit coupling, and electronic repulsion interactions are of comparable magnitude, which makes the analysis of the experimental results complicated. However, in the case of actinide ions having the $[Rn]5f^1$ electronic configuration such as a U^{5+} ion, the situation is considerably simplified, because the electron–electron repulsion interactions vanish. Therefore, we can make the theoretical treatments of such ions much easier and then may obtain a deeper

understanding of the behavior of $5f$ electrons in solids.

There have been several reports on the measurements of optical absorption spectra and electron paramagnetic resonance (EPR) spectra for LiUO₃ and U^{5+} ion doped in LiNbO₃, and of magnetic susceptibilities for LiUO₃. However, the results are inconsistent with each other and not sufficiently discussed. Lewis et al. (1) measured the EPR and optical spectra of U^{5+} doped in LiNbO₃ and found that the U^{5+} ion gave rise to an EPR signal at $g = 0.727$ which suggests that the crystal field has almost regular octahedral symmetry. They also mentioned that the EPR spectrum was not detected for magnetically condensed compounds of uranium such as LiUO₃, while Miyake et al. (2, 3) reported that an EPR spectrum was measured for

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pure $LiUO_3$. The signal was extremely broad and the g-value was 2.49–2.57. Kemmler-Sack et al. (4) measured the magnetic susceptibility of $LiUO_3$ from 83 to 473 K and found that it did not obey the Curie–Weiss law but could be represented by $\chi = 0.050/T + 320 \times 10^{-6}$. Keller (5) extended the temperature range of the magnetic susceptibility measurements of $LiUO_3$ down to 4.2 K and found the large field dependence of the magnetic susceptibility below 19 K. Miyake et al. (2, 3) also measured the magnetic susceptibility of $LiUO_3$ and found a sharp spike in the susceptibility vs temperature curve at 16 K. Kanellakopulos et al. (6) remeasured the electronic spectra and detailed magnetic susceptibilities for $LiUO_3$ and other uranates (U^{5+}), neptunates (Np^{6+}), and one plutonate (Pu^{7+}), and fitted the data to the Eisenstein–Pryce model (7) with an additional parameter δ to account for a tetragonal component of the crystal field. The low temperature magnetic susceptibility data were basically the same as the results reported previously by Keller (5). However, Edelstein and Goffart (8) questioned that the spin–orbit coupling constant used by Kanellakopulos et al. were approximately constant for U^{5+}, Np^{6+}, and Pu^{7+}, because the spin–orbit coupling constant is known to increase markedly with higher atomic number and higher charge on the ion (9).

In order to clarify the inconsistent experimental results and to elucidate the behavior of the 5f electron in an octahedral crystal field, we prepared $LiUO_3$ and measured magnetic susceptibility in the 4.2–300 K temperature range. The crystal field parameters were obtained from the analysis of the optical absorption spectrum of $LiUO_3$, diluted with $LiNbO_3$. The magnetic susceptibility was calculated and compared with the experimental data. We also derived the g-value of EPR and discussed the reported experimental data.

Experimental

1. Preparation

$LiUO_3$ was prepared by the following reactions:

$$U_3O_8 + 3Li_2CO_3 \xrightarrow{\text{in air}} 3Li_2UO_4 + 3CO_2, \quad (1)$$

$$Li_2UO_4 + UO_2 \rightarrow 2LiUO_3. \quad (2)$$
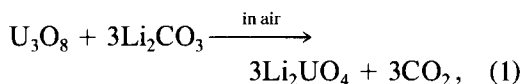
Li_2UO_4 was prepared by repeatedly grinding and firing to 850°C mixtures of U_3O_8 and Li_2CO_3 in air for 1 day. $LiUO_3$ was prepared by heating mixtures of Li_2UO_4 and UO_2 in an evacuated quartz tube at 740°C for 38 hr. Since traces of UO_2 reactant impurity were found, we tried to prepare $LiUO_3$ from Li_2UO_4 and UO_2 of which the ratio is over one. However, such UO_2 impurity could not be excluded completely. We also tried to prepare $LiUO_3$ by the reaction of Li_2CO_3 and UO_2 in a dry argon atmosphere at 800°C for 180 hr (2, 3). However, the yield of dark violet $LiUO_3$ was low.

2. Analysis

2.1. X-ray diffraction analysis. An X-ray diffraction study was performed with $CuK\alpha$ radiation on a Philips PW 1390 diffractometer equipped with a curved graphite monochromator. The lattice parameter of the sample was determined by a least-squares method applied to the diffraction lines.

2.2. Determination of oxygen amount. The oxygen nonstoichiometry in the specimen was checked by the back-titration method (10, 11). First, 20–30 mg of the sample was weighed out and dissolved in excess cerium (IV) sulfate solution. The cerium (IV) sulfate solution was standardized in advance with stoichiometric UO_2. The excess cerium (IV) was titrated against a standard iron (II) ammonium sulfate solution with ferroin indicator. The oxygen amount was determined for predetermined Li/U ratio.

3. Magnetic Susceptibility Measurement

The magnetic susceptibility was measured with a Faraday-type torsion balance in the 4.2–300 K temperature range. The apparatus was calibrated with a Manganese Tutton's salt (χ_g = 10,980 × $10^{-6}/(T$ + 0.7)). The temperature of the sample was measured by a "normal" Ag vs Au-0.07at% Fe thermocouple (4.2 K ~ 40 K) (12) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (13).

Results and Discussion

The X-ray diffraction analysis shows the specimen prepared in this study is rhombohedral and the lattice parameters are a = 5.9145 Å and α = 54.54°. From the chemical analysis of the oxygen concentration, it was $LiUO_{3.008(10)}$. In view of the error limits for this analysis, this result indicates that the specimen was oxygen stoichiometric.

Kemmler (14) showed that the crystal structure of $LiUO_3$ is $LiNbO_3$ type, which is rhombohedral with space group $R3C(C_{3v}^6)$ (15). In this crystal, the oxygen atoms are arranged in planar sheets, forming a network of distorted octahedra. The deviations from octahedral symmetry seem to be quite small, since an isotropic single EPR signal was observed for uranium-doped $LiNbO_3$ single crystal and since all the signals in the optical absorption spectrum were assigned on the basis that the transitions were purely electronic, assuming the coordination of oxygen atoms around the U^{5+} is octahedral (1). The following discussions will be made assuming an octahedral crystal field for $LiUO_3$.

Figure 1 shows the effects of perturbing the f^1 orbital energy levels successively by an octahedral field and spin–orbit coupling. In an octahedral crystal field, the sevenfold degenerate energy state of the f orbitals is split into Γ_2, Γ_5, and Γ_4 states, where Δ and
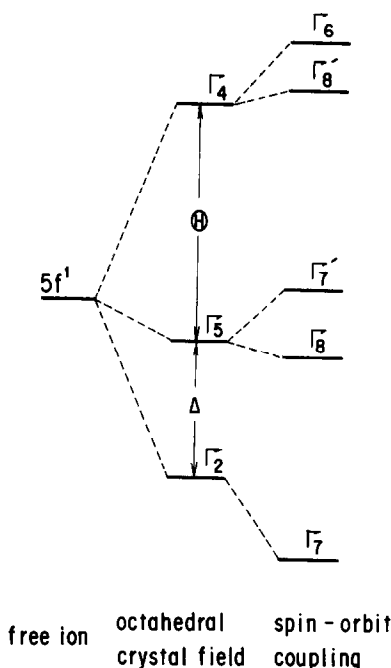

FIG. 1. f^1 orbital splitting perturbed by octahedral crystal field and spin–orbit coupling.

Θ represent the parameters of the crystal field strength. If spin–orbit coupling is taken into account, the Γ_2 orbital state is transformed into Γ_7, whereas the Γ_5 and Γ_4 states are split into Γ_7^* and Γ_8, and Γ_6 and Γ_8^*, respectively (16). The ground state Kramers doublet is the Γ_7 state and is coupled to the excited Γ_7^* state arising from the Γ_5 orbital, by spin–orbit coupling. The Γ_8 state arising from the Γ_5 orbital state is also coupled to the Γ_8^* state arising from the Γ_4 orbital state by the same spin–orbit coupling interaction. The energy matrices for the Γ_7, Γ_8, and Γ_6 states are

$$\Gamma_6: \left| \Delta + \Theta + \tfrac{3}{2} k_{\Gamma_4\Gamma_4}\zeta \right|$$

$$\Gamma_8: \begin{vmatrix} \Delta + \tfrac{1}{4} k_{\Gamma_5\Gamma_5}\zeta & \tfrac{3}{4}\sqrt{5}\, k_{\Gamma_4\Gamma_5}\zeta \\ \tfrac{3}{4}\sqrt{5}\, k_{\Gamma_4\Gamma_5}\zeta & \Delta + \Theta - \tfrac{3}{4} k_{\Gamma_4\Gamma_4}\zeta \end{vmatrix}$$

$$\Gamma_7: \begin{vmatrix} 0 & \sqrt{3}\, k_{\Gamma_2\Gamma_5}\zeta \\ \sqrt{3}\, k_{\Gamma_2\Gamma_5}\zeta & \Delta - \tfrac{1}{2} k_{\Gamma_5\Gamma_5}\zeta \end{vmatrix}. \qquad (3)$$

Here ζ is the spin–orbit coupling constant and $k_{\Gamma_i\Gamma_j}$ are the orbital reduction factors. It does not appear profitable to attempt to interpret the experimental data with so many parameters. Therefore, we assume, as Eisenstein and Pryce (7) and Hecht et al. (17) did, that there are only two orbital reduction parameters k and k', which are characteristic of the Γ_5 and Γ_4 states, respectively. This is to set $k_{\Gamma_4\Gamma_4} = k'$, $k_{\Gamma_5\Gamma_5} = k$, $k_{\Gamma_2\Gamma_5} = k^{1/2}$, and $k_{\Gamma_4\Gamma_5} = k^{1/2}k'^{1/2}$ in the above energy matrices, which are now

$$\Gamma_6 : |\Delta + \Theta + \tfrac{3}{2}k'\zeta|$$

$$\Gamma_8 : \begin{vmatrix} \Delta + \tfrac{1}{4}k\zeta & \tfrac{3}{4}\sqrt{5kk'}\,\zeta \\ \tfrac{3}{4}\sqrt{5kk'}\,\zeta & \Delta + \Theta - \tfrac{3}{4}k'\zeta \end{vmatrix}$$

$$\Gamma_7 : \begin{vmatrix} 0 & \sqrt{3k}\,\zeta \\ \sqrt{3k}\,\zeta & \Delta - \tfrac{1}{2}k\zeta \end{vmatrix}. \tag{4}$$

Diagonalization of the energy matrix produces the ground state Γ_7 and the excited state Γ_7', and the corresponding wavefunctions are written as

$$|\Gamma_7\rangle = \cos\theta |{}^2F_{5/2}, \Gamma_7\rangle - \sin\theta |{}^2F_{7/2}, \Gamma_7^*\rangle,$$

$$|\Gamma_7'\rangle = \sin\theta |{}^2F_{5/2}, \Gamma_7\rangle + \cos\theta |{}^2F_{7/2}, \Gamma_7^*\rangle, \tag{5}$$

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state with the relation

$$\tan 2\theta = \frac{2\sqrt{3k}\,\zeta}{\Delta - \tfrac{1}{2}k\zeta}. \tag{6}$$

The g-value for the ground Γ_7 doublet is obtained as follows:

$$g = 2\langle\Gamma_7|L + 2S|\Gamma_7\rangle$$

$$= 2\cos^2\theta - 4\sqrt{(k/3)}\sin 2\theta - \tfrac{2}{3}(1 - k)\sin^2\theta. \tag{7}$$

To obtain the crystal field parameters and orbital reduction factors, we applied the above-mentioned treatments to the optical absorption spectrum and EPR spectrum

data for uranium-doped LiNbO₃ measured by Lewis et al. (1). The obtained parameters and factors are listed in Table I. The spin–orbit coupling constant is 1930 cm⁻¹, which is a reasonable value for U^{5+} in solids (18–20), and is quite close to the value obtained from linear interpolation of the ζ values between Pa^{4+} and Np^{6+} compounds, 1950 cm⁻¹ (21). Kanellakopulos et al. (6) had to let ζ and k be independent because they did not use the g-value derived from EPR experiments, and obtained $\zeta = 1800$ cm⁻¹ for both uranates and neptunates, which is smaller than the well-known spin–orbit coupling constant for U^{5+} ion in compounds (18–20). Lewis et al. (1) used the free ion value of $\zeta = 2172$ cm⁻¹ for U^{5+} as calculated from the relativistic wavefunctions (9). This value is known to be larger than the value for U^{5+} in compounds (22). The obtained orbital reduction factor $k = 0.95$, for an electron in a Γ_5 orbital has also been obtained by Edelstein for the same Γ_5 orbital in UF_6^- compounds (23). The transition energies calculated from the crystal field parameters obtained and the g-values calculated from the wave functions are very well in agreement with the experimental data for U^{5+} ion in LiNbO₃ (Table I). From
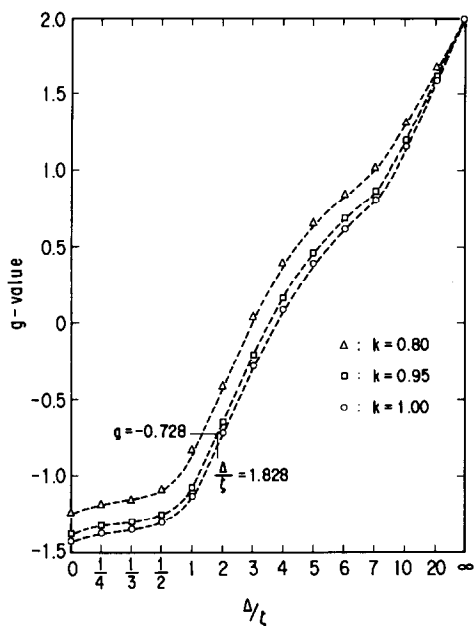
FIG. 2. The variation of g-value with Δ/ζ.

the orbital reduction factors, k and k', a considerable degree of covalency is found to exist in this uranate.

Next, we will discuss the EPR data. Using Eq. (7), we may draw in Fig. 2 the variation of g-value for the cases of $k = 1, 0.95$, and 0.80 as a function of the relative strengths of the crystal field and spin–orbit interactions. For $\Delta/\zeta = 0$, only the spin–orbit interaction is considered; for $\Delta/\zeta = \infty$, only the crystal field interaction is considered. The g-value is found to increase with decreasing k value. This figure clearly shows that the g-value for an f electron in an octahedral crystal field should be between -1.43 and 2.00. Therefore, we consider that the EPR spectrum with $g = 2.49–2.57$ for magnetically condensed $LiUO_3$ (2, 3) is not due to the $5f$ electron perturbed by an octahedral ligand field, but due to the magnetic interaction of the $5f$ electron. In fact, Miyake $et\ al.$ found magnetic interactions in MUO_3 (M = Li, Na, K, and Rb) which have distorted perov-

skite structures and measured EPR spectra with large g-values (2, 24).

The temperature dependence of the reciprocal magnetic susceptibility is shown in Fig. 3. When the temperature is increased and exceeds 16.9 K, the magnetic susceptibility suddenly decreases. Below this temperature, large field dependence of the magnetic susceptibility was found. In this figure, the susceptibility data measured by other research groups are also drawn. Our susceptibility data are also inconsistent with them. Figure 4 shows the dependence of magnetic susceptibility on the field strength at 4.2, 77.3, and 298 K, indicating large field dependence of susceptibility at 4.2 K. Kanellako-
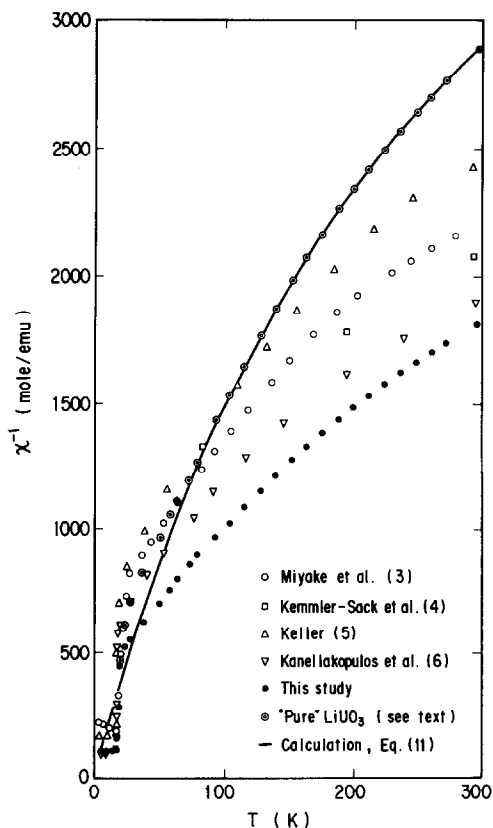

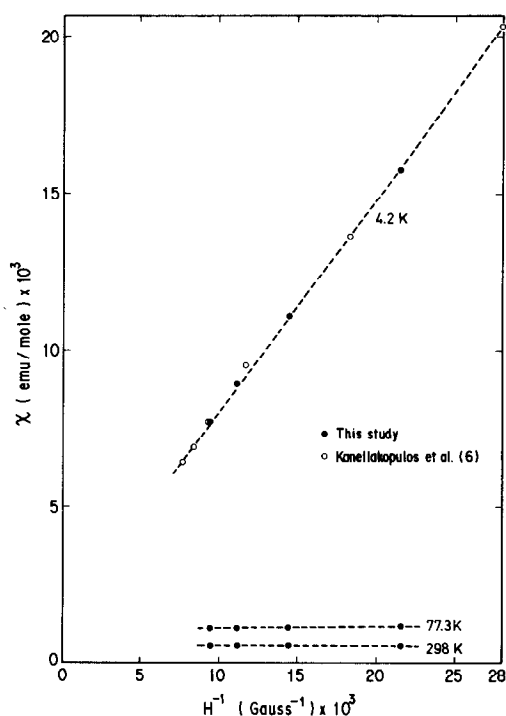FIG. 3. Reciprocal magnetic susceptibility versus temperature.

FIG. 4. Field dependence of magnetic susceptibility.

pulos *et al.* (*6*) also found the similar field dependence of magnetic susceptibility, which is depicted in the same figure. The magnetic susceptibility of the molecule is given by the equation

$$\chi = \frac{N \sum_{n,m} [(E_{n,m}^{(1)})^2/kT - 2E_{n,m}^{(2)}] \exp(-E_{n,m}^0/kT)}{\sum_{n,m} \exp(-E_{n,m}^0/kT)},$$

(8)

where N is the Avogadro's number, $E_{n,m}^0$ is the zero-field energy, $E_{n,m}^{(1)}$ and $E_{n,m}^{(2)}$ are the first- and second-order Zeeman terms, and n and m are quantum numbers. If the separation of levels within the ground state is much smaller than and the energy of the next excited state is much larger than kT, the susceptibility is expressed by the form (*25*)

$$\chi = \frac{Ng^2\beta^2}{4kT} + \text{TIP},$$

(9)

where

$$g = 2\langle\Gamma_7|\mathbf{L} + 2\mathbf{S}|\Gamma_7\rangle$$

$$\text{TIP} = 2N\beta^2 \sum_i \frac{|\langle\Gamma_i|\mathbf{L} + 2\mathbf{S}|\Gamma_7\rangle|^2}{E(\Gamma_i) - E(\Gamma_7)}.$$

(10)

Since we have already obtained the wavefunctions for the ground doublets and excited states, the magnetic susceptibility of LiUO₃ is easily calculated by Eq. (9) as follows:

$$\chi = 0.050/T + 179 \times 10^{-6}.$$

(11)

Our susceptibility data are not consistent with the calculation results (Eq. (11)). From X-ray diffraction analysis, our sample contains small amount of the residual UO₂ impurity. In Fig. 3, the susceptibility of "pure" LiUO₃ obtained by subtracting the susceptibility of UO₂ impurity (8 mole%) from the measured susceptibility is also shown. The data show good agreement with those calculated (Fig. 3). The magnetic susceptibility data measured by other research groups are also larger than the calculation results. One reason for this, we consider, is that some reactant impurity such as UO₂ (starting material) contributes to this excess susceptibility. Below 60 K, the magnetic susceptibilities of "pure" LiUO₃ deviate greatly from those calculated. This is due to magnetic interactions found experimentally below 16.9 K. In addition to the large field dependence of magnetic susceptibility below the transition temperature, the susceptibility of magnetically condensed LiUO₃ is much larger than the susceptibility calculated from the crystal field model. These experimental results indicate that the magnetic interaction between uranium ions is not antiferromagnetic (*2, 3*) but ferromagnetic (*6*). We should mention the results that the crystal field parameters for the four transition energies obtained from magnetically

condensed $LiUO_3$ do scarcely change from the parameters listed in Table I and that the susceptibility calculated by using such parameters is quite near to the value in Eq. (11).

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