

A PRELIMINARY NOTE ON THE MAGNETIC ANISOTROPY AND SUSCEPTIBILITY OF $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

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ABSTRACT. The theory of magnetic anisotropy and susceptibility of Fe^{2+} in Tutton salts has been worked out on the basis of Abragam and Pryces' method. It is found that the anisotropic part of the crystal field changes with temperature due to the thermal expansion of the crystal lattice. The spin-orbit coupling coefficient has to be decreased by 20% from its free ion value of -103 cm^{-1} which indicates some amount of overlap between the $3d$ - Fe^{2+} and s and p - O^{2-} charge clouds. The agreement of the theoretical values with the experiment is excellent.

INTRODUCTION

The five-fold degeneracy of the ground state $3d^6, ^5D$ of Fe^{2+} ion in the free state is split up by the predominant cubic component of the crystal field into an orbital doublet and a triplet, the latter being lower by about 10^4 cm^{-1} , in the octahedrally co-ordinated Fe^{2+} salts, e.g., the Tutton salts (van Vleck, 1932). In these salts the octahedron of six water molecules surrounding each Fe^{2+} ion has very nearly a tetragonal symmetry with the z -axis elongated as observed from paramagnetic resonance measurements (Tinkham, 1955). This tetragonal component of the electric field and the spin-orbit coupling acting together partly removes the remaining degeneracy of the orbital levels inclusive of the five-fold spin degeneracy of each orbital level. The complete secular problem is highly complicated and a complete theory of the susceptibility of Fe^{2+} salts has not yet been worked out. In the case of the trigonal symmetry, the expression for the susceptibility has been approximately worked out by Pryce (1957) and in some details by Palumbo (1958), but the agreement with Jackson's (1959) measurements in $\text{Fe SiF}_6 \cdot 6\text{H}_2\text{O}$ is not very satisfactory at all ranges of temperature.

We have derived the theoretical expressions for the magnetic susceptibility and anisotropy in the tetragonal case i.e., for the Fe^{2+} Tutton salts on the basis of Abragam and Pryces' theory (1951) and compared these with the experimental results on $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ of Bose (1947) and Jackson (1924) and also with the resonance data of Tinkham.

Since the Fe^{2+} ion is in the D state, we have assumed $\alpha \approx \alpha' \approx 1$ (Abragam and Pryce) in this case. Under the action of the tetragonal field and the spin-orbit coupling, our fifteen order secular determinant breaks up into six $|j=1\rangle$, three $|j=0\rangle$, four $|j=2\rangle$, and two $|j=3\rangle$ levels, one of the six $|j=1\rangle$ levels, lying lowest. All these levels lie within a span of about 800 cm^{-1} . We next apply magnetic perturbation on these levels and get the expression for the magnetic susceptibility and finally for the square of the effective moment

$$= \frac{3k}{N\beta^2}$$

converted into ionic values of P^2 , taking two Fe^{2+} ions in the unit cell equally inclined to the crystallographic X_1 axis, in the usual manner.

Here again we find that unless Δ is varied appreciably as in Ti^{3+} (1959a) and Co^{2+} (1959b) salts, the agreement with experiment at all temperatures is impossible. Thus the crystal field changes quite appreciably due to thermal expansion of the crystal lattice. The facts that at high temperatures the spin-lattice relaxation time is very small making paramagnetic resonance lines too wide to be observable and that it increases sufficiently at about 20°K to give well-resolved lines are also indications that the crystal field changes considerably with temperature. Moreover, the spin-orbit coupling coefficient has to be decreased by 20% from its free ion value of 103 cm^{-1} . This indicates a corresponding overlap between the $3d$ Fe^{2+} and s - and p - O^{2-} charge clouds.

TABLE I
 $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\zeta = 80 \text{ cm}^{-1}$)

Temp in $^\circ\text{K}$	$\Delta \text{ cm}^{-1}$	P^2_{\parallel}	P^2_{\perp}	$P^2 - P^2_{\perp}$	g -values
300	650	36.26 (36.25)	26.31 (26.22)	9.95 (10.02)	—
160	500	44.12 (44.01)	24.72 (24.56)	19.39 (19.44)	—
90	400	51.80 (51.77)	21.28 (21.23)	30.51 (30.52)	—
20	270	—	—	—	$\left\{ \begin{array}{l} g_{\parallel} = 8.989 \\ \quad \quad (8.97 \pm .02) \\ g_{\perp} = 0(0) \end{array} \right.$

The values in the parentheses indicate the mean of the experimental moment results of Jackson (1924) and Bose (1948). The g -values within parentheses are Tinkham's (1955).

The agreement with the magnetic anisotropies is quite excellent as can be seen in Table I, but the theoretical absolute P^2_{\perp} -values agree with the mean values of Jackson and Bose. The g -values given by Tinkham at 20°K also agree quite closely with our theoretical values.

The mathematical details will be published elsewhere shortly.

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