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Magnetic susceptibility of antiferromagnetic Ir^{4+} complexes

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Magnetic susceptibility in the antiferromagnetic and the paramagnetic phase is calculated by using a molecular-field model, wherein the molecular field is calculated self-consistently. When applied to the hexachloroiridates, it is shown that the observed and the calculated susceptibility in the antiferromagnetic phase agree well. As in the case of rare-earth compounds, this model is adequate to treat the crystal-field effects in the compounds of the transition-metal ions.

I. INTRODUCTION

The concentrated and dilute hexachloroiridates [$K_2(Ir, Pt)Cl_6$, $(NH_4)_2(Ir, Pt)Cl_6$] have attracted considerable attention[1-18] because of their unusual magnetic properties. These complexes undergo antiferromagnetic transitions at the Néel temperatures 3.08 and 2.16 K, respectively. These show an unusually large θ/T_N ratio, ~10. (θ is the paramagnetic Curie-Weiss temperature). Experimentally, magnetic susceptibility,[1] EPR[2-7] Nuclear-quadrupole-resonance[8,9] (NQR), antiferromagnetic-resonance[10] (AFMR), neutron-diffraction[11,12] and specific-heat[13] studies have been made on these complexes. All the studies confirm the above-mentioned phase transitions and the magnetic ordering in the antiferromagnetic phase is found to be of the type III*A*.[11,12] Among the theoretical works in these salts, we may mention the study of superexchange interaction between the magnetic ions,[14] covalency effects,[15] and the application of molecular-field theory and the spin-wave theory.[16-18] In Ref. 18 an attempt was made to explain the observed large θ/T_N ratio, but the molecular-field theory was shown to be unable to explain this. Although the spin-wave theory indicated a large θ/T_N ratio, the results are not very reliable, since in this case $S=\frac{1}{2}$ and the spin-wave theory gives large zero-point deviations.[16-18]

Our interest is in the magnetic susceptibility of these compounds. We have calculated the magnetic susceptibility by assuming an internal magnetic field due to antiferromagnetic coupling between the ions and also have calculated the internal field self-consistently. In our model it is not possible to compare θ/T_N ratio, but we have compared the susceptibility data.

In Sec. II we have given a brief potpourri of the known facts about these compounds. In Sec. III the theory is given and in Sec. IV the results are compared with the experimental data.

II. REVIEW OF FACTS

The hexachloroiridates have an antifluorite type of lattice. The $IrCl_6$ octahedra are in a closed-packed (fcc) arrangement with K atoms (NH_4 groups) occupying all the tetrahedral sites.[19] Unlike the analogous compounds of Re, the ground state of Ir^{4+} ion is Jahn-Teller insensitive (the ground state is a Γ_7 Kramers doublet) and the $IrCl_6$ octahedra are perfect. The lattice constants a_0 and the parameter u (a_0u is Ir-Cl separation) from x-ray measurements are 9.7189 Å and 0.2374 for K_2IrCl_6[8] and 9.87 Å and 0.25 for $(NH_4)_2IrCl_6$.[19] The position of the atoms on a face of the unit cell is shown in Fig. 1, where the paths of the superexchange interaction between an Ir-Ir pair are also shown. An order-of-magnitude calculation of the exchange interaction[2,14] supports the antiferromagnetic coupling in these compounds. Values of exchange integral derived from the EPR pair spectrum of semidilute crystals also confirm this coupling. The orbital reduction factor k estimated from the g-value measurements[15] is 0.76. In our model, the covalency is treated semiempirically via the orbital reduction factor in the magnetic moment operator. Table I summarizes the different experimental observations on the compounds of our interest.

III. THEORY

The Hamiltonian for the problem can be written

$$\mathcal{H}=\mathcal{H}_0+V_c+\sum\left[\zeta_i\vec{L}_i\cdot\vec{S}_i-\mu_B H_{\text{int}}(K L_i^z+2S_i^z)-\mu_B H_{\text{app}}\cdot(K\vec{L}_i+2\vec{S}_i)\right], \qquad (1)$$

where the summation is over all the d-shell electrons and $\mathcal{H}_0$ is the free-ion Hamiltonian, V_c is the crystal-field operator for cubic symmetry, ζ is the spin-orbit interaction constant, H_{app} is the Zeeman field, and H_{int} is the internal magnetic field in the molecular-field approximation. The ground term of the Ir^{4+} ion ${}^2T_2$, comes from the strong-field configuration t_{2g}^5. Due to the spin-orbit coupling, this term is split, resulting in the Kramers doublet Γ_7 as the ground state. This coupling is sufficiently strong to mix other terms from the first-excited configuration $t_{2g}^4 e_g$. Apart from the spin-orbit interaction, the electrostatic interaction also leads to configuration mixing. Taking into account these admixtures, the wave function for one component of Γ_7 can be written as[15]

$$\begin{aligned}|\Gamma_7 a\rangle = {} & \sqrt{\tfrac{2}{3}}\,|{}^2T_2;-\tfrac12,1\rangle - \frac{1}{\sqrt3}\,|{}^2T_2;\tfrac12,0\rangle + \frac{6B}{E_2}\,|{}^2T_2';-\tfrac12,1\rangle - \frac{2B}{E_3}\,|{}^2T_2'';-\tfrac12,1\rangle \\ & - \frac{3\sqrt2\,B}{E_2}\,|{}^2T_2';\tfrac12,0\rangle + \frac{\sqrt2\,B}{E_3}\,|{}^2T_2'';\tfrac12,0\rangle + \frac{\zeta}{E_1}\,|{}^2A_2';\tfrac12,a_2\rangle + \frac{\zeta}{3E_2}\left(|{}^2T_2';-\tfrac12,1\rangle - \frac{1}{\sqrt2}\,|{}^2T_2';\tfrac12,0\rangle\right) \\ & - \frac{\zeta}{E_3}\left(|{}^2T_2'';-\tfrac12,1\rangle - \frac{1}{\sqrt2}\,|{}^2T_2'';\tfrac12,0\rangle\right) - \frac{\zeta}{E_4}\left(|{}^4T_1';-\tfrac32,0\rangle + \sqrt{\tfrac32}\,|{}^4T_1';-\tfrac12,-1\rangle - \frac{1}{\sqrt2}\,|{}^4T_1';\tfrac32,1\rangle\right) \\ & + \frac{\zeta}{3E_5}\left(|{}^4T_2';\tfrac12,0\rangle - \frac{1}{\sqrt2}\,|{}^4T_2';-\tfrac12,1\rangle - \sqrt{\tfrac32}\,|{}^4T_2';\tfrac32,-1\rangle\right),\end{aligned} \qquad (2)$$

where we have used Griffith's complex orbital bases.[20] The primes denote the states from the excited configuration $t_{2g}^4 e_g$. E_1, E_2, E_3, etc. can be shown to be[15]

$$\begin{aligned} E_1 &= \Delta - 3B - C, \\ E_2 &= \Delta + 12B - C, \\ E_3 &= \Delta + 2B - C, \\ E_4 &= \Delta - 5B - 4C, \\ E_5 &= \Delta + 3B - 4C, \end{aligned} \qquad (3)$$

where B and C are Racah parameters. Applying the time-reversal operator, one gets the other component of the wave function. Using these wave functions, we obtain

$$g = -\frac{4k+2}{3} - k\left(\frac{8\zeta}{3E_1} + \frac{4}{E_2}(6B + \tfrac13\zeta) - \frac{4}{E_3}(2B+\zeta)\right), \qquad (4)$$

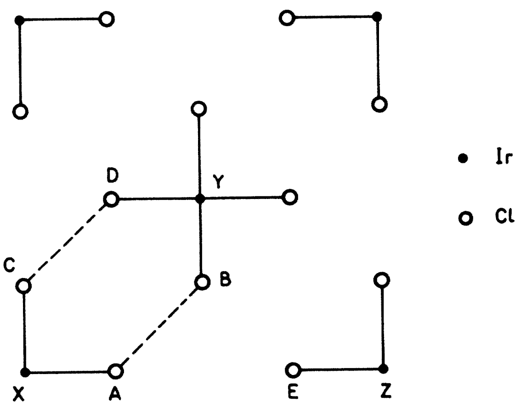

FIG. 1. Section in (100) plane of lattice showing disposition of atoms on the face of an unit cell. Broken lines show paths of superexchange.

where k is the orbital reduction factor. Taking[15] $k = 0.76$, $B = 300\ \mathrm{cm}^{-1}$, $C/B = 4.0$, $\Delta = 28\,000\ \mathrm{cm}^{-1}$, $\zeta = 2000\ \mathrm{cm}^{-1}$, g comes out to be 1.795 which agrees with the experiment. In the rest of our calculations we have, therefore, made use of these values.

As usual, in the molecular-field theory the internal field can be written as

$$H_{\mathrm{int}} = \lambda\langle M\rangle, \qquad (5)$$

where λ is the molecular-field parameter. $\langle M\rangle$ denotes the magnetization given by

$$\langle M\rangle = \left(\frac{\sum -(\partial E_i/\partial H)\,e^{-E_i/kT}}{\sum e^{-E_i/kT}}\right)_{H\to H_{\mathrm{int}}}, \qquad (6)$$

where E_i are the eigenvalues of the Hamiltonian (Eq. 1). Solving Eqs. (1), (5), and (6) self-consistently for a given value of λ and temperature T, H_{int} is obtained. In Eq. (6), the summation is over all the Zeeman levels of the ion. In our case the separation between the lowest Γ_7 and the first-excited Γ_8 state is $\frac32\zeta$ ($\zeta = 2000\ \mathrm{cm}^{-1}$). This state ($\Gamma_8$) and other excited states are omitted from the summation, as their contribution to the magnetic moment is insignificant. However, the Γ_8 contribution to the susceptibility is included, which is nothing but Van Vleck temperature-independent susceptibility,

$$\chi_{\mathrm{VV}} = \frac{N(g+2)^2\mu_B^2}{6\zeta}. \qquad (7)$$

The susceptibility calculated by the usual methods can be written as[21]

$$\chi_{\parallel} = \frac{\chi_{\parallel}^0}{1 - \bar\lambda\,\chi_{\parallel}^0}, \qquad (8)$$

TABLE I. A summary of the experimental results.

Experiments	Complexes	Dilution (Ir : Pt)	*g* values	*J*/*k* (°K)	*θ* (°K)	T_N (°K)	Refs.
EPR	$(NH_4)_2(Ir, Pt)Cl_6$	1 : 200	1.82				5
			1.775 ± 0.01				6
			1.786 ± 0.004				15
		1 : 20	1.79 ± 0.01	7.5 ± 1.0			2, 7
	$K_2(Ir. Pt)Cl_6$	1 : 200	1.82				6
			1.79 ± 0.005				15
		1 : 20	1.79 ± 0.01	11.5 ± 1.0			2
Susceptibility	$(NH_4)_2IrCl_6$				20 ± 3	2.16	1
	K_2IrCl_6				32 ± 4	3.08	1
Specific heat	$(NH_4)_2IrCl_6$					2.15	13
	K_2IrCl_6					3.05	13
NQR	K_2IrCl_6					3.05	8
						3.08	9
AFMR	K_2IrCl_6					3.0	10
Neutron diffraction	K_2IrCl_6					3.05 ± 0.04	12
						3.05	11

where

$$\chi_{\parallel}^0 = \frac{N\mu_B^2}{kT}\left[\frac{\sum W_1^2 e^{-W_0/kT}}{\sum e^{-W_0/kT}} - \left(\frac{\sum W_1 e^{-W_0/kT}}{\sum e^{-W_0/kT}}\right)^2\right] + \chi_{VV} \tag{9}$$

and

$$W_1 = \langle \Gamma_7 | (k L_z + 2S_z) | \Gamma_7 \rangle . \tag{10}$$

W_0 is the energy of the state without applying Zeeman perturbation, and the summation is over the components of the Γ_7 ground state.

Similarly,

$$\chi_\perp = \frac{\chi_\perp^0}{1 - \lambda \chi_\perp^0} , \tag{11}$$

where

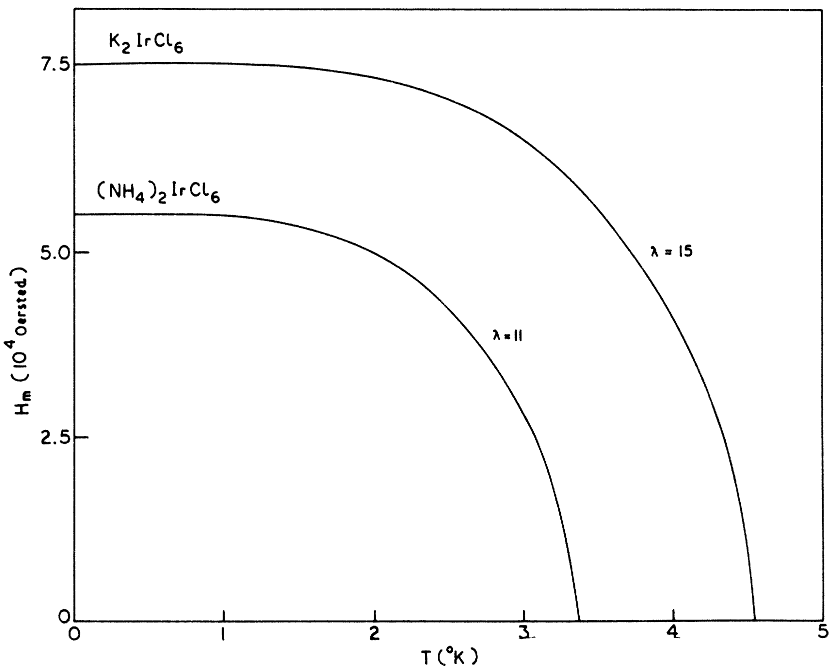

FIG. 2. Variation of molecular field with temperature.

$$\chi_{\perp}^{0}=2\mu_B^2\sum_{a,b}{}' \frac{|\langle\Gamma_7 a|(K\,L_x+2S_x)|\Gamma_7 b\rangle|^2}{E_b-E_a}\,e^{-E_a/kT}\Big/\sum e^{-E_a/kT}+\chi_{\mathrm{vv}}\,. \tag{12}$$

The total susceptibility is given by

$$\chi=\tfrac{1}{3}\chi_{\parallel}+\tfrac{2}{3}\chi_{\perp}\,. \tag{13}$$

In Eqs. (8) and (11), $\bar{\lambda}$ is the paramagnetic molecular-field constant. For a fcc lattice,

$$\bar{\lambda}=12\bar{\lambda}_1+6\bar{\lambda}_2\,, \tag{14}$$

where $\bar{\lambda}_1$ and $\bar{\lambda}_2$ are the molecular-field coefficients[22] giving the effective field exerted on a spin by each of its nearest neighbors and next-nearest neighbors, respectively. $\bar{\lambda}$ is related to the paramagnetic Curie-Weiss temperature ($\bar{\lambda}=\theta/C_M$) and this can be used in the ordered phase if there is no distortion on ordering.

IV. RESULTS AND DISCUSSION

The variation of the molecular field with temperature is shown in Fig. 2. The magnetic susceptibilities were measured by Cooke *et al.*[1] and are shown by black circles in Fig. 3. They attempted to explain the susceptibilities by the high-temperature expansion method (Heisenberg-Kramers-Opechowski) and the simple molecular-field model. But neither explained the very sharp variation of susceptibility below the antiferromagnetic transition point. Since, the anisotropy measurements are not available, we have calculated the total susceptibilities from Eqs. (8), (11), and (13) and are shown in Fig. 3 by continuous lines for a few suitable choice of the parameters λ and $\bar{\lambda}$. For a single set of the parameters (λ, $\bar{\lambda}$) the variations of $\chi_{\parallel}$ and $\chi_{\perp}$ with temperature are shown in Fig. 4. It is evident from Fig. 3 that the susceptibility below the transition point agrees quite well with the experiment. However, in our model, the susceptibilities in the paramagnetic phase do not agree for the same set of parameters. This may be attributed to two possible causes. It is quite possible that the antiferromagnetic transition can be accompanied by a distortion. If this is so, then $\bar{\lambda}$ cannot remain the same below and above the transition. Indeed, Armstrong and Van Driel, by comparing the temperature variation of ^{35}Cl NQR-frequency data in K_2IrCl_6, show that the rotary lattice mode softens, which may lead to such a distortion.[23] It is also quite possible that some short-range order persists above the transition point. As in the molecular-field theory, in our model too, the magnetic order completely vanishes at the transition temperature. Analysis of NQR data by Lindop indicates that some short-range order persists above the transition[8]; as a result of which the susceptibilities get enhanced.

In conclusion it may be pointed out that this model is useful to treat the influence of crystal field on the susceptibility of antiferromagnetic

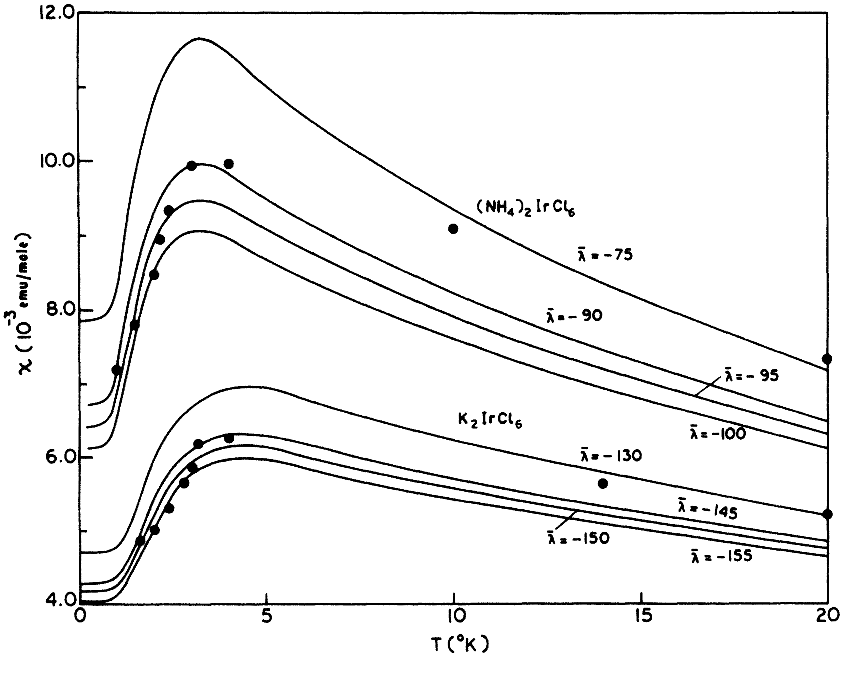

FIG. 3. Variation of susceptibility with temperature.

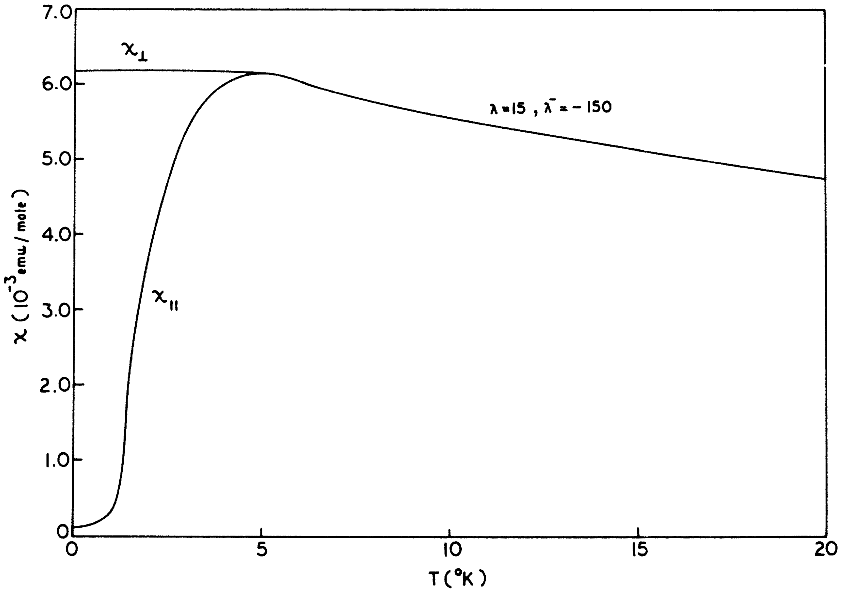

FIG. 4. Variation of longitudinal and transverse susceptibilities with temperature.

phase in the compounds of the transition-metal ions, as in the case of the rare-earth compounds.[21] In the particular compounds discussed in this paper, however, because of the large spin-orbit coupling and strong crystal field, the problem is simplified to a great extent. These interactions lifted all but the Kramers degeneracy, resulting in a ground state which can be considered as an effective spin-$\frac{1}{2}$ doublet. All the other states of importance were far removed from the ground state taking kT as a yardstick and therefore the mixing due to the internal field was insignificant. In the case of analogous compounds, where such fortuity does not exist, this model is likely to show the effect of crystal field on the susceptibility.

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