Comments and Addenda

Correlated-effective-field theory for an effective spin-$\frac{1}{2}$ system

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An effective spin-$\frac{1}{2}$ antiferromagnetic system has been studied using correlated-effective-field theory, which, in contrast to mean-field theory, can explain the first-order magnetic transitions observed in many antiferromagnetic compounds. In this theory fluctuation is introduced phenomenologically via the temperature-dependent correlation parameter. The magnetic susceptibilities in the ordered, as well as in the paramagnetic phase, are calculated for K_2IrCl_6 and $(NH_4)_2IrCl_6$ compounds and an excellent agreement with the experimental results is obtained.

Magnetic susceptibilities of ammonium and potassium hexachloroiridates [$(NH_4)_2IrCl_6$, K_2IrCl_6] were measured by Cooke et al.[1] in powdered samples as early as 1959. The results were compared with the theories available at the time, viz. molecular-field theory and high-temperature series-expansion formula of Danielian and Stevens.[2] The agreement in the ordered phase was not good. Later De et al.[3] have obtained better agreement using self-consistent molecular-field theory. Since in mean-field theory fluctuation is not considered, this theory fails in the critical region where fluctuation becomes important. Moreover, mean-field (MF) theory always overestimates the transition temperature. Correlated-effective-field (CEF) theory, on the other hand, predicts a transition temperature very close to the experimental one.[4,5] Neutron-diffraction measurements[6,7] at low temperature reveal the magnetic structure of the compounds under investigation. In MF theory there is no scope for introducing the magnetic structure. The magnetic structure can be incorporated in the CEF theory developed by Lines,[8] and therefore more realistic models can be solved with the help of this theory.

The hexachloroiridates have an antifluorite type of lattice.[9] The $(IrCl_6)^{2-}$ octahedra are in a closed packed (fcc) arrangement with K atoms (NH_4 groups) occupying all the tetrahedral sites. The Ir^{4+} ion, in an octahedral crystal field of Cl^- ions, has t_{2g}^5 configuration and the ground state is $^2T_{2g}$. This state splits up into a doublet Γ_7 and a quartet Γ_8 by the spin-orbit interaction and the doublet lies lowest. Ir^{4+} belongs to the third series of transition-metal ions $5d^n$ and therefore, has strong crystal-field and spin-orbit interactions and larger covalency than the $3d^n$ ions. Though there is no direct overlap between two Ir^{4+} ions, there is an indirect overlap via Cl^- ions. This is because $5d$ wave functions are extended and therefore, the $5d$ electrons of Ir^{4+} ions are partially delocalized. This delocalization phenomenon which results in covalent bonds, also plays a decisive role in the origin of exchange interactions in magnetic insulators. As a result, phase transitions are observed in magnetic insulators at temperatures depending on the strength and path of the superexchange interactions.

The spin-orbit interaction being high, only the lowest doublet Γ_7 contributes to the magnetic properties in the range of temperature 0–20 K. The magnetic structure of K_2IrCl_6 was found to be of type $IIIA$[6,7] in which the spins are aligned along the stacking axis. Assuming the direction of spin alignment to be in the Z direction, the problem has been solved numerically. In fcc type-$IIIA$ magnetic structure, each ion has four nearest neighbors parallel and eight

nearest neighbors antiparallel. Out of six next-nearest neighbors, four are parallel and two are antiparallel. This magnetic structure has been included in the present calculation.

In the CEF theory developed by Lines,[8] static spin correlations are taken into account. In this theory each spin S_j appearing in the equations of motion of a particular spin S_i is replaced by the sum of two terms as follows:

$$S_j^\gamma \rightarrow \langle S_j^\gamma \rangle + A_{ij}^\gamma (S_i^\gamma - \langle S_i^\gamma \rangle), \quad (\gamma = x,y,z) ,$$

where $\langle S_j^\gamma \rangle$ represents the thermal average of S_j^γ, and A_{ij}^γ is the temperature-dependent static correlation parameter. Using the above replacement of the spin operators the effective Hamiltonian for the ith ion in absence of applied magnetic field can be written.

$$\mathcal{H}_i^{eff} = -\sum_{\gamma,j} J_{ij}^\gamma \alpha^\gamma (S_i^\gamma)^2 - 2\sum_{j,\gamma} J_{ij}^\gamma S_i^\gamma (\langle S_j^\gamma \rangle - \alpha^\gamma \langle S_i^\gamma \rangle) ,$$

$$(1)$$

where α^γ ($\gamma = x,y,z$) are parameters defined by

$$\sum_j A_{ij}^\gamma J_{ij} = \alpha^\gamma \sum_j J_{ij} .$$

In the above equation the first term represents an effective anisotropy energy and the second term represents the interaction of ith spin with the correlated effective field. The static magnetic susceptibility χ^γ is then given by[8]

$$\chi^\gamma(q) = \frac{1}{kT} \left[\langle\langle \mu_i^\gamma : \mu_i^\gamma \rangle\rangle \right.$$
$$\left. + \frac{2[J^\gamma(q) - \alpha^\gamma J(0)] \langle\langle \mu_i^\gamma : S_i^\gamma \rangle\rangle^2}{kT - 2[J^\gamma(q) - \alpha^\gamma J^\gamma(0)] \langle\langle S_i^\gamma : S_i^\gamma \rangle\rangle} \right] ,$$

$$(2)$$

where

$$J(q) = \sum_{r=NN,NNN} J e^{i\vec{q}\cdot\vec{r}} , \qquad (3)$$

$$\vec{\mu}_i = (K\vec{L}_i + 2\vec{S}_i)\mu_B , \qquad (4)$$

$$\langle\langle \vec{A} : \vec{B} \rangle\rangle = \langle \vec{A} : \vec{B} \rangle - \langle \vec{A} \rangle \langle \vec{B} \rangle , \qquad (5)$$

$$\langle \vec{A} : \vec{B} \rangle = \sum_n \rho_n \left[A_{nn} B_{nn} \right.$$
$$\left. + kT \sum_{m \neq n} \frac{A_{nm} B_{mn} + A_{mn} B_{nm}}{E_m - E_n} \right] ,$$

$$(6)$$

$$\langle \vec{A} \rangle = \sum_n \rho_n A_{nn} . \qquad (7)$$

ρ_n denotes the probability of occupation of the eigenstate $|n\rangle$ of the effective Hamiltonian (1). Now summing over q in the first Brillouin zone we have

$$kT\chi^\gamma = \sum_q kT\chi^\gamma(q) = N\left\langle \langle \mu_i^\gamma : \mu_i^\gamma \rangle \right\rangle$$
$$+ \sum_q U^\gamma(q) , \qquad (8)$$

where

$$U^\gamma(q) = \frac{2[J^\gamma(q) - \alpha^\gamma J^\gamma(0)] \left\langle \langle \mu_i^\gamma : S_i^\gamma \rangle \right\rangle^2}{kT - 2[J^\gamma(q) - \alpha^\gamma J^\gamma(0)] \left\langle \langle S_i^\gamma : S_i^\gamma \rangle \right\rangle} .$$

Again from the fluctuation theorem we have

$$\sum_q kT\chi^\gamma(q) = N\langle\langle \mu_i^\gamma : \mu_i^\gamma \rangle\rangle .$$

Therefore, the condition $\sum_q U^\gamma(q) = 0$ has to be satisfied, and from this condition the correlation parameters are determined. Using this condition,

$$\alpha^\gamma = \frac{\displaystyle\sum_{\vec{q}} \frac{J^\gamma(\vec{q})kT}{kT - 2[J^\gamma(\vec{q}) - \alpha^\gamma J^\gamma(0)]\langle S_i^\gamma : S_i^\gamma \rangle}}{\displaystyle\sum_{\vec{q}} J^\gamma(0)} , \quad (9)$$

which is computationally more convenient than the expression used by Lines,[8] Eq. (9) is solved self-consistently through Eqs. (5)−(7).

For the compounds of interest the ground state is an effective spin-$\frac{1}{2}$ state so that we have

$$\mu_i^\gamma = g\mu_B S_i^\gamma ,$$

where g is the effective-spectroscopic splitting factor. The susceptibility given by Eq. (2) then reduces to

$$\chi^\gamma = \frac{g^2\mu_B^2 \left\langle \langle S_i^\gamma : S_i^\gamma \rangle \right\rangle}{kT - 2[J^\gamma(q) - \alpha^\gamma J^\gamma(0)] \left\langle \langle S_i^\gamma : S_i^\gamma \rangle \right\rangle} \qquad (10)$$

and the uniform molar susceptibility ($q = 0$) is given by

$$\chi^\gamma = \frac{Ng^2\mu_B^2 \left\langle \langle S_i^\gamma : S_i^\gamma \rangle \right\rangle}{kT - 2J(0)(1 - \alpha^\gamma) \left\langle \langle S_i^\gamma : S_i^\gamma \rangle \right\rangle} . \qquad (11)$$

As the magnetic structure shows the spins to be aligned in a given direction, say z, then for fcc type-IIIA structures, the Hamiltonian (1) becomes

$$\mathcal{H}_i^{eff} = -(12J_1 + 6J_2)[\alpha^x(S_i^x)^2 + \alpha^y(S_i^y)^2 + \alpha^z(S_i^z)^2]$$
$$+ \langle S_i^z \rangle [(8J_1 - 4J_2) + 12(2J_1 + J_2)\alpha^z]S_i^z , \qquad (12)$$

where J_1, J_2 are the isotropic nearest neighbor and next-nearest-neighbor interactions respectively. In the paramagnetic phase we have $\langle S_i^z \rangle = 0$ and we have $\alpha^x = \alpha^y = \alpha^z$. For spin-$\frac{1}{2}$ systems, the first term in the Hamiltonian (12) can be ignored for statistical averaging as it gives a constant term in the energy. Using the Hamiltonian (12), Eqs. (5) and (7) become

$$\langle S_i^z \rangle = -\frac{1}{2}(\tanh x) \ ,$$

$$\left\langle \langle S_i^z : S_i^z \rangle \right\rangle = \frac{1}{4}(1 - \tanh^2 x) \ ,$$

$$\left\langle \langle S_i^x : S_i^x \rangle \right\rangle = \langle S_i^y : S_i^y \rangle = (\tanh x)/4x \ ,$$

where

$$x = [(8J_1 - 4J_2) + 12(2J_1 + J_2)\alpha^z] \langle S_i^z \rangle /2kT \ .$$

These equations are solved simultaneously with Eq. (9). Once a self-consistent solution is obtained for $\langle S^z \rangle$ and α^γ at a particular temperature, the susceptibility is calculated from Eq. (11). The average susceptibility is given by

$$\chi_{av} = \frac{1}{3}(\chi_{||} + 2\chi_{\perp}) \ ,$$

where $\chi_{||}$ corresponds to χ_z, and $\chi_{\perp}$ to either χ_x or χ_y. We have $\chi_{||} = \chi_{\perp}$ in the paramagnetic phase, and in the ordered phase we have

$$\chi^z(\alpha^z) \neq \chi^x(\alpha^x) = \chi^y(\alpha^y) \ .$$

Type IIIA magnetic structure is stabilized by both nearest neighbor and next-nearest-neighbor interactions of antiferromagnetic nature.[10,11] Therefore, with a suitable choice of the parameters J_1, J_2, susceptibilities are calculated. For K_2IrCl_6,[7] $g = 1.55$ is used and for $(NH_4)_2IrCl_6$,[12] $g = 1.79$ is used. The results are shown in Fig. 1, where the experimental results
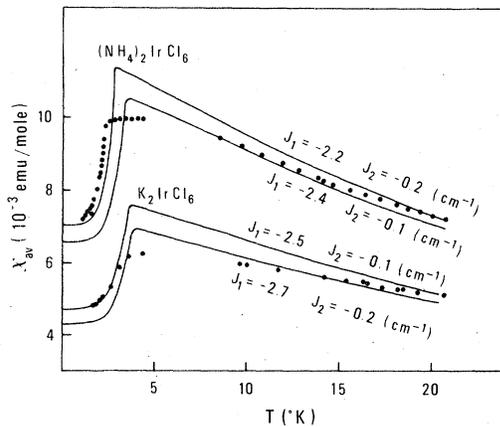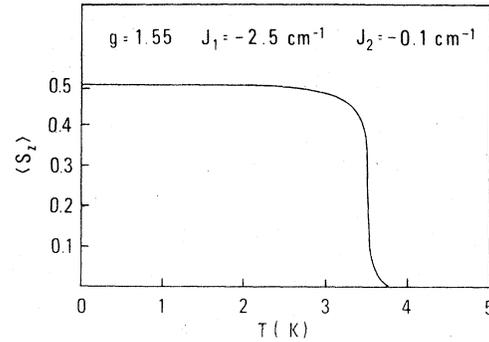

FIG. 2. Variation of order parameter with temperature.

are also shown by dots for comparison. As the figure shows there is very good agreement over the whole range of temperature excepting the critical region.

The variation of the order parameter with temperature is shown in Fig. 2, which shows a discontinuous change in the order parameter, demonstrating that the phase transition is of first order. This is in agreement with the remarks made by Benguigui[13] on CEF theory as a general case of self-consistent phonon (SCP) approximation,[14,15] and the generalized spherical model of Brout.[16] The first-order transition in type III antiferromagnets such as K_2IrCl_6 has already been predicted by Bak[17] by renormalization-group calculation. The appropriate Landau-Ginzberg-Wilson-Hamiltonian has no stable accessible fixed point with symmetry consistent with the observed symmetry of the state.

The variations of $\alpha_{||}$, $\alpha_{\perp}$ and $\chi_{||}$, $\chi_{\perp}$ with temperature are shown in Fig. 3 and Fig. 4, respectively.
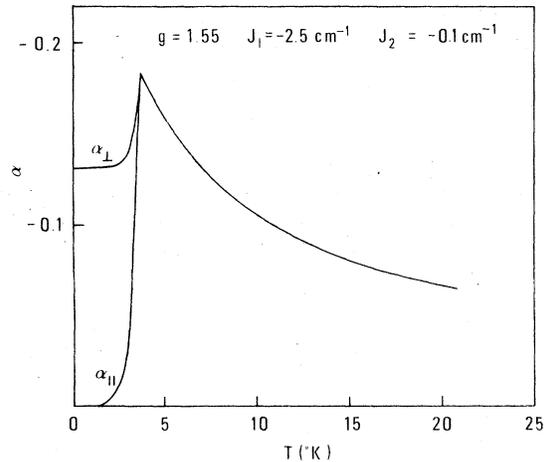

FIG. 1. Variation of average susceptibilities with temperature.

FIG. 3. Correlation parameters as a function of temperature.
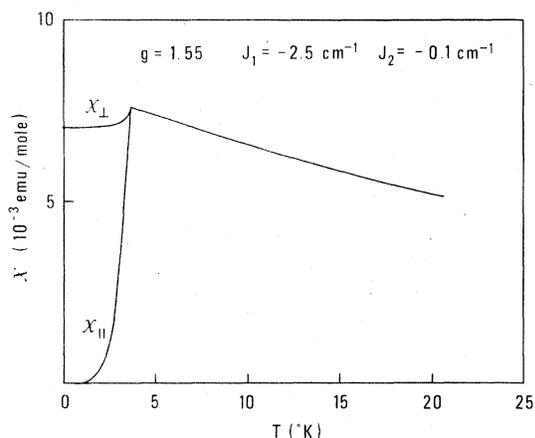
FIG. 4. Variation of longitudinal and transverse suscepti-
bilities with temperature.

ordered and paramagnetic phases. Since there is no
experimental data for the order parameter and no an-
isotropy measurements of the susceptibilities are
available, only the average susceptibilities are com-
pared. The compounds under investigation are ex-
pected to show first-order magnetic phase transition.
For a better understanding of the nature of phase
transition in these compounds, magnetic measure-
ments in single crystals are suggested. Because of the
discontinuity of the order parameter, it is difficult to
obtain a stable solution numericaly at the critical tem-
perature. This numerical instability of the order
parameter near the critical temperature is consistent
with the results obtained from a renormalization-
group calculation,[17] and it is similar to finite size
effects observed in Monte Carlo calculation.[18]

From the results it is evident that the CEF theory
developed by Lines can give a good description of the
order parameter and the susceptibilities, both in the

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