

STUDY OF MAGNETISM IN THE LAYERED TRANSITION METAL COMPOUND



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Abstract-We have investigated the quasi-two-dimensional magnetism for the layered transition metal compound $(C_nH_{2n+1}NH_3)_2CuCl_4$ ($n=10, 14$) in the high temperature regions by means of EPR (Electron Paramagnetic Resonance) and SQUID measurements. As a result, the magnetic transitions were reflected in the EPR linewidths and the magnetic susceptibilities in a sensitive manner. Fluctuations of the magnetic susceptibility and a similar variation of the $\Delta g=(g_{||}-g_{\perp})/g_{||}$ value were also observed around the structural phase transition temperatures.

I. INTRODUCTION

Perovskite-type layer compounds of general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ (C_nM for short) show a rich variety of order-disorder structural phase transitions which are governed by the dynamics of the alkylammonium groups and by the rotational motions of the MCl_4^{2-} macroanions about their crystallographic axes. It has been known that the types of structural disorder and the sequence of the thermotropic phase transitions depend on the type of the metal ion M . It is thus essential to understand the role of the metal ions. Electron Paramagnetic Resonance (EPR) and magnetic susceptibility measurements are powerful tools for studying the paramagnetic metal ions. In this work, we have studied the static and dynamic magnetism of Cu^{2+} in $C10Cu$ and $C14Cu$ by the DC and EPR magnetic susceptibility, and explained them in the view of the structural phase transitions.

For $M=Cd, Mn, \text{ or } Cu$, the mineral layers in C_nM are constituted of more or less distorted corner-sharing MCl_6 octahedra forming a two dimensional matrix, with hydrocarbon layers sandwiched between them. The NH_3 groups are attached to the layers by weak $NH \cdots Cl$ hydrogen bonds. Van der Waals interactions and long-range Coulomb forces account for the interlayer bonding.

For $C10Cu$, five structural phases are present above 100 K. On increasing temperature, two discontinuous transitions, a conformational transition of the hydrocarbon chains and an order-disorder transition of the NH_3 groups, known to occur at 306 and 310 K, respectively, take place accompanied by changes in the interlayer distances. A high temperature transition at 338 K is athermic and implies only a continuous structural modification from the monoclinic to the orthorhombic symmetry[1, 2]. For $C14Cu$, the major conformational and the minor order-disorder transition temperatures are 344 K and 357 K, respectively[3].

Linear temperature dependence of EPR linewidths in C_nM has been found and discussed in terms of the temperature dependent exchange integral $J(\delta R)=\exp(\delta R/R_0)$ [4, 5], phonon modulation of the Dzialoshinsky-Moriya (DM) antisymmetric exchange interaction $\vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j$ [6, 7, 8] or the two-dimensional spin diffusion[9]. Susceptibility in the paramagnetic region has been discussed in terms of the isotropic exchange and the DM antisymmetric exchange interaction.

II. EXPERIMENTAL

Powder samples of $C10Cu$ and $C14Cu$ were synthesized and investigated in this work. The

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EPR measurements were carried out at 9.4 GHz (X-band) using a Bruker ESP 300M spectrometer in the temperature range 110-420 K. The EPR linewidths were obtained from the lineshapes and the EPR magnetic susceptibilities by the integration of the lineshape. The DC magnetic susceptibilities were measured by a SQUID magnetometer (Quantum Design MPMS).

III. RESULTS AND DISCUSSION

Fig. 1 shows the differential EPR lineshape at 293 K in C14Cu exhibiting the g -anisotropy, with two well resolved Lorentzian lines. In Fig. 1, g_{\parallel} and g_{\perp} are the g values for the external magnetic fields parallel and perpendicular to the CuCl_4^{2-} magnetic plane, respectively.

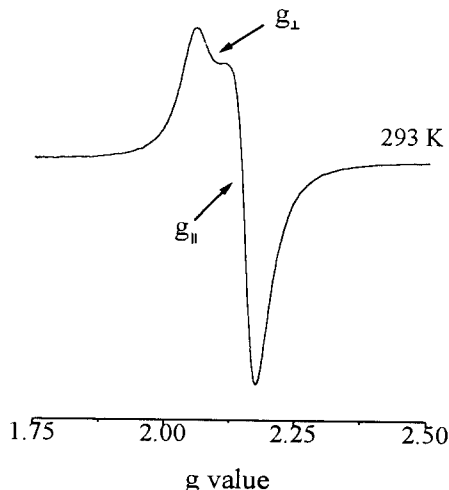


Fig. 1. EPR lineshape of C14Cu at 293 K.

The FWHM linewidths for C10Cu and C14Cu are shown in Fig. 2 as a function of temperature. It shows roughly three temperature regions with distinct slopes.

The lower and higher temperature regions show linear temperature dependences of the linewidth while the linewidth exhibits sharp transitions in the intermediate region. Since the symmetry of the system is low enough for an antisymmetric exchange, phonon modulation of the antisymmetric DM interaction can be considered. In the case of

phonon modulation of the antisymmetric exchange term, the linewidth is linearly proportional to the temperature, $\Delta H \sim J^4 (\Delta g/g)^2 T$ [6, 7, 8].

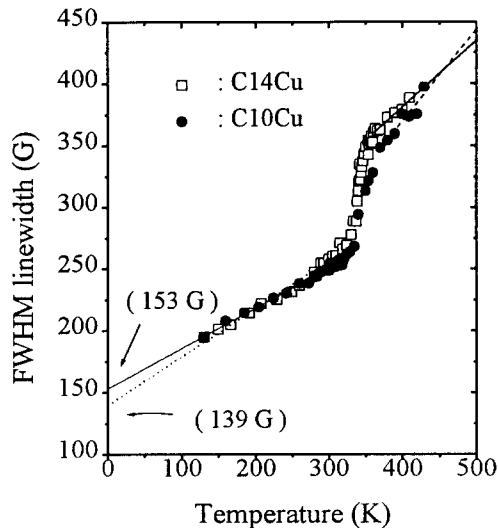


Fig. 2. Temperature dependence of EPR linewidths for C10Cu and C14Cu.

In the intermediate region, the sharp transition of the linewidths can be related to the conformational transition or an order-disorder transition of the CuCl_4^{2-} matrix plane, which may correspond to the dynamic Jahn-Teller distortions. It has been known that a number of the CnM compounds have a thermochromism, which is closely related to the static and dynamic Jahn-Teller distortions [10]. In fact, the color of C10Cu and C14Cu changes from yellow at room temperature to dark green at higher temperatures. This fact cannot be explained in terms of the exchange integral, $J(T)$, or phonon modulation of the DM antisymmetric exchange $\vec{D}_i \cdot \vec{S}_i \times \vec{S}_j$. Instead, either compression or elongation of the Cu-Cl bond perpendicular to the CuCl_4^{2-} plane would allow the g_{\perp} to depend on the temperature.

Fig. 3 and Fig. 4 shows the variation of the values of g_{\parallel} and g_{\perp} for the C10Cu and C14Cu as a function of temperature. It is noticed that the g_{\parallel} values remain relatively fixed, especially in C14Cu, whereas the g_{\perp} values have a marked

temperature dependence, reflecting the critical fluctuations around the structural phase transition temperatures. This indicates that the distortion of the CuCl_6 octahedra mainly occurs in the direction perpendicular to the basal plane.

In Fig. 5, the DC and EPR magnetic susceptibilities are shown. It is apparent that the susceptibilities deviate from the conventional Curie-Weiss law.

While the DC magnetic susceptibility does not reflect the critical fluctuations around the structural phase transitions, they are apparent in the EPR magnetic susceptibility measurements. Thus, the EPR susceptibility proves to be a much more effective probe for the dynamical properties than the DC susceptibility.

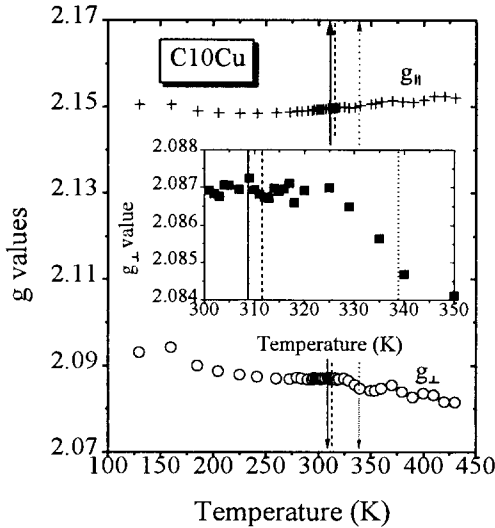


Fig. 3. g values of C_{10}Cu as a function of temperature.

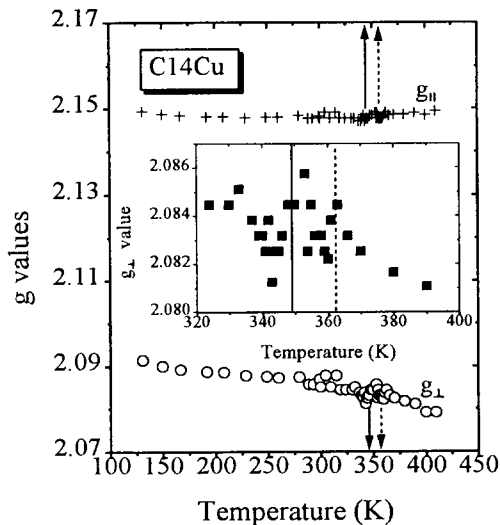


Fig. 4. g values of C_{14}Cu as a function of temperature.

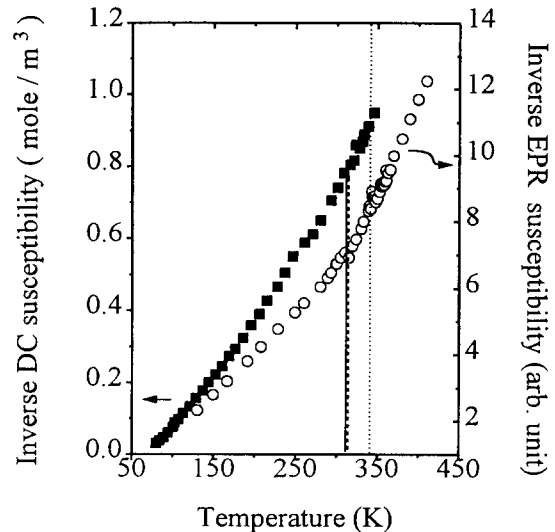


Fig. 5. Inverse DC and EPR susceptibilities for C_{14}Cu .

IV. SUMMARY

We have studied the magnetism in the perovskite-type layer compounds $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ ($n=10, 14$) in the paramagnetic high temperature regions by means of EPR and magnetic susceptibility measurements. The EPR linewidths have a characteristic temperature dependence and sensitively reflect the structural phase transitions. In the lower and higher temperature regions, the linewidth is linearly proportional to the temperature, while sharp transition are observed at intermediate temperatures. The exchange energies could be estimated from the EPR linewidth measurements. In addition, critical fluctuations of the g -values and the EPR magnetic susceptibility were observed around the structural phase transition temperatures.

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