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Superparamagnetic-like ac susceptibility behavior in the partially disordered antiferromagnetic compound Ca_3CoRhO_6

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We report the results of dc and ac magnetization measurements as a function of temperature (1.8 - 300 K) for the spin-chain compound, Ca_3CoRhO_6, which has been recently reported to exhibit a partially disordered antiferromagnetic (PDAF) structure in the range 30–90 K and spin-glass freezing below 30 K. We observe an unexpectedly large frequency dependence of ac susceptibility in the T range 30–90 K, typical of superparamagnets. In addition, we find that there is no difference in the isothermal remanent magnetization behavior for the two regimes below 90 K. These findings call for more investigations to understand the magnetism of this compound.

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Recently, the spin-chain compound, Ca_3CoRhO_6 (Ref. 1), has started getting attention due to the fact this compound exhibits an unusual type[2,3] of magnetic phase transition. This compound crystallizes in a K_4CdCl_6 type rhombohedral structure (space group $R\bar{3}c$). With this structure, in this compound, there are one-dimensional chains of alternating face-sharing CoO_6 trigonal prisms and RhO_6 octahedra. Ca cations separate these chains, and the magnetic ions form a triangular lattice with an interchain spacing of 5.313 Å. The dc magnetic susceptibility (χ) as well as neutron diffraction data reveal[1,2] that there are two magnetic transitions, one at 90 K (T_1) and the other at 30 K (T_2). In the magnetically ordered state, the magnetic ions along the chain couple ferromagnetically, whereas the interchain nearest neighbor interaction is antiferromagnetic. This type of interaction may cause magnetic frustration, as this compound is intrinsically a triangular lattice. As a consequence of this geometrical frustration, between T_1 and T_2, 2/3 of the ferromagnetic chains (present at the corners of the hexagon) have been reported to couple antiferromagnetically with each other and the other 1/3 (at the center of the hexagon) are proposed to be left incoherent with the other chains [see Fig. 1(a) of Ref. 3]. There are only few compounds known with this kind of triangular lattice of antiferromagnetic spin chains, e.g., $CsCoCl_3$ and $CsCoBr_3$.[4,5] However, the magnetism of this compound is proposed[3] to be unusual in the sense that, below T_2, the incoherent chains appear to freeze in a disordered state, whereas in the Cs compounds, a ferrimagnetic state is attained below the lower transition temperature. However, the ferrimagnetic phase can be obtained even in the present material by an application of a magnetic field (H) of the order of 20 to 30 kOe. In other words, this compound is characterized by an interesting magnetic phase diagram.[2]

While we believe that this magnetic compound will attract future attention for various investigations, it is of interest to look for further characteristics of such a complex magnetic material, in particular, to compare the anomalies due to the disordered nature of the magnetism in the two temperature ranges below 90 K. With this motivation, we have carried out magnetic measurements on this material, the results of which are reported in this article. The results apparently raise interesting questions.

The compound Ca_3CoRhO_6 in the polycrystalline form was prepared by solid state route. Stoichiometric amounts of high purity (>99.9%) $CaCO_3$, CoO and Rh powder were thoroughly mixed. Then the mixture was calcined at 900 C for one day. Subsequently, the preacted powder was finely ground, pelletized and heated at 1200 C for about 10 days with few intermediate grindings. The x-ray diffraction pattern confirmed that the sample is a single phase (a = 9.202 Å and c = 10.730 Å). The dc χ measurements were performed in the range 1.8–300 K at different fields (1, 30, and 50 kOe) both for zero-field-cooled (ZFC) as well as field-cooled (FC) state of the specimens employing a commercial (Quantum Design) superconducting quantum interference device (SQUID). The same magnetometer was employed to take ac χ data (1.8–300 K) at various frequencies

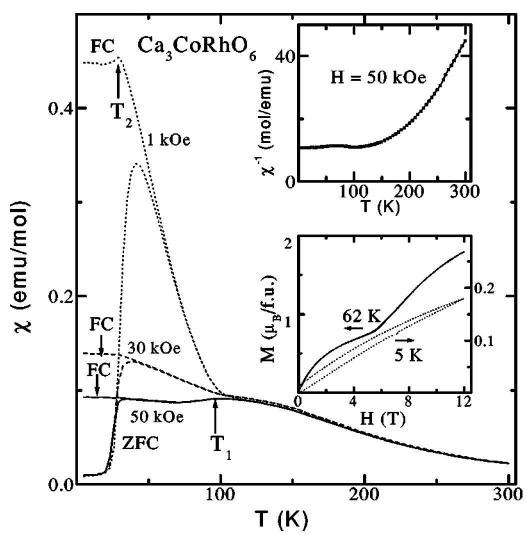

FIG. 1. Dc magnetic susceptibility (χ) as a function of temperature for Ca_3CoRhO_6 measured at different fields. The transition temperatures, T_1 and T_2, are marked. Insets show (a) inverse χ (H = 50 kOe) as a function of T to highlight paramagnetic behavior with the lines through the data points serving as a guide to the eyes and (b) isothermal magnetization at 5 and 62 K. For T = 5 K, the lower curve corresponds to increasing H and the upper one to decreasing H.

in zero field as well as in the presence of two dc fields (5 and 30 kOe). Isothermal magnetization (M) and remanent magnetization (M_{IRM}) behavior were also tracked at 5 and 62 K employing a commercial magnetometers both by vibrating sample magnetometer (VSM, Oxford Instruments) and SQUID and the results obtained from both the instruments agree quite well.

The T-dependence of dc χ measurements are shown in Fig. 1. There is a sharp drop of χ above about 35 K for ZFC-curves for all H as though there is a magnetic transition at this temperature. ZFC χ-T plots tend to merge below about 20 K for all the values of H. However, FC-curves at low temperatures show a different behavior in the sense that the values are found to be H-dependent, though the plots tend to a constant value below 20 K in all cases. Above about 35 K, χ values are field-dependent for both the ZFC and FC measurements and the features are suggestive of another transition in the range 90–100 K. As noted earlier,[1] the plot of inverse χ versus T (Fig. 1, inset) is highly nonlinear in the paramagnetic state (above 90 K). The Curie-Weiss temperature inferred from the near-linear range of 225–300 K is found to be about 175 K, the positive sign indicating strong ferromagnetic interaction; this value however is marginally higher than that reported (150 K) in Ref. 1. The findings are otherwise in good agreement with those reported in Ref. 1. There is a distinct difference[1] between the plots of isothermal M at 5 and 62 K (Fig. 1, inset) in the sense that there is a plateau in the H range 20–40 kOe at 62 K due to ferromagnetic alignment of the spins. There is a significant hysteresis in the plot for 5 K resulting in a remanence of M (*vide infra*) after reducing H to zero, which is in agreement with the proposed spin-glass behavior. We have observed similar magnitudes of remanence even at 62 K, which is not obvious from Fig. 1 inset, due to the compression of the scale on the y-axis. The ZFC-FC χ curves obtained in the presence of 1 kOe field tend to bifurcate at a temperature close to 70 K; however, applications of higher fields lower the temperature at which this bifurcation occurs, implying thereby that at much smaller fields (in few gausses) this feature may occur at temperatures higher than 70 K. There is a tendency for a broad peak in temperature range 100 to 150 K in χ versus T plots for $H=1$ and 30 kOe, but it is cut off around 100 K due to the onset of magnetic ordering. It is to be noted that this peak is clearly visible in the data for $H=50$ kOe. This maximum in χ resembles that of Bonner and Fischer's prediction for one-dimensional magnetism.[6] Alternatively, short-range correlations also may be responsible for this feature.

We now present the results of ac χ measurements (see Fig. 2). It is clearly seen that, in the zero-field data, there is a well-defined peak at 50 K in the real part (χ') of ac χ typical of spin-glasses. However, what is remarkable is that the anomalies associated with magnetic ordering start building at temperatures as high as 90 K. Therefore, it is very difficult to associate the ac χ anomalies (see further below) to the transition at T_2. This observation may be correlated to the ZFC-FC divergence at a temperature close to 90 K at low fields (say, at 1 kOe) as discussed above. The fact that the χ' peak arises from some kind of spin-glass freezing appears to be endorsed by the observation of an upturn in the imaginary part (χ'') of the ac χ as well (prominent below about 75 K). One does not expect such a feature at the magnetic transition temperature due to long range magnetic ordering.[7] It is also remarkable that the width of the χ'-feature is so large that it spans entire temperature range between T_1 and T_2. What is puzzling is the large frequency dependence of the temperature at which the peak appears, for instance, from 50 K at 1 Hz to 70 K at 1 kHz in the χ' data, in sharp contrast to that known in canonical spin glasses. Quantitatively speaking, the magnitude of the factor,[7] $\Delta T_f/T_f\Delta(\log\omega)$, turns out to be as large as about 0.1, which is typically seen in superparamagnetic materials.[7] The peak temperature in the χ' vs T plot typically represents the spin-freezing temperature (T_f). The value of this factor in canonical spin glasses is known to be below 0.01. It is to be noted that the values of χ are also practically frequency-independent below 30 K. We have also taken the data in the presence of a H of 5 and 30 kOe. While the ac chi features for 5 kOe resemble those of zero-field data, for $H=30$ kOe data, the χ' cusp vanishes and the peak gets broadened by the field with a significantly reduced intensity; also the χ''-anomaly is completely depressed. This finding is consistent with the proposed phase diagram[2] in the sense that the disordered magnetic state is destroyed at a field of 30 kOe.

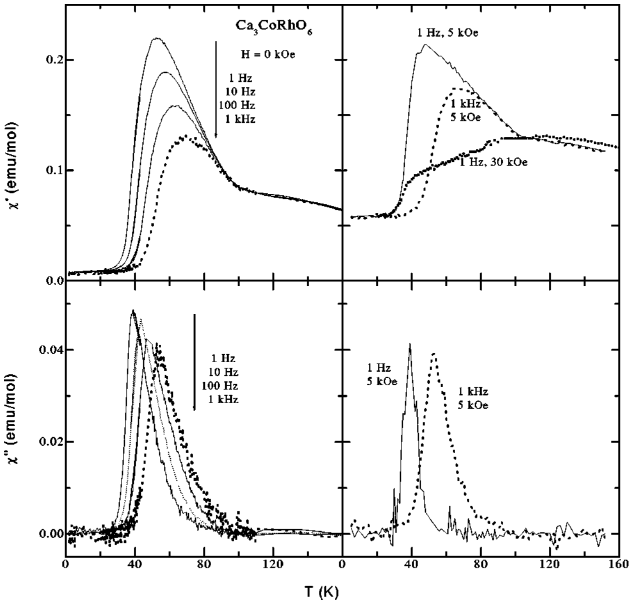

FIG. 2. Real (χ') and imaginery (χ'') parts of ac susceptibility for Ca_3CoRhO_6, measured at different frequencies with an ac driving field of 1 Oe. The ac χ behavior in the presence of a magnetic field of 5 kOe at two frequencies are also shown. The data for the presence of 30 kOe at various frequencies nearly overlap and hence shown only for one frequency (with the data for χ'' being featureless not shown in the plot). The curves shown are obtained by drawing lines through the experimental data points.

We have also probed the magnetic relaxation behavior in the two temperature ranges, by measuring at 5 and 62 K (Fig. 3). For this purpose, we have zero-field-cooled the specimen to respective temperatures, switched on the field of 5 kOe, waited for 5 min and then the decay of M_{IRM} was tracked as a function of time (t) for about an hour after the field was

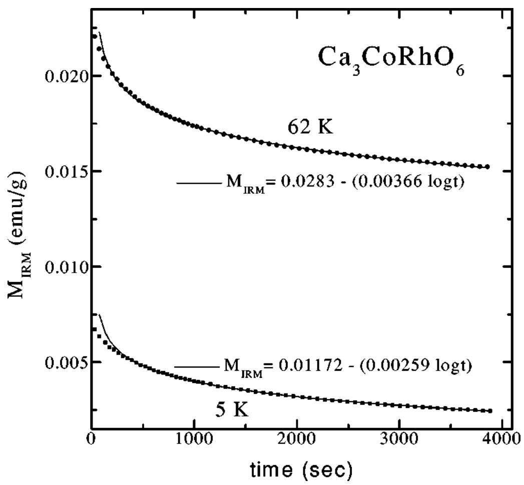

FIG. 3. Isothermal remanent magnetization behavior at 5 and 62 K for Ca_3CoRhO_6, obtained as described in the text. The continuous lines represent least squares fit to a logarithmic function mentioned in the figure.

switched off. We observed that M_{IRM} dropped to a value below the detection level of the instrument in the paramagnetic state (say, at 120 K) as expected. However, the values at 5 and 62 K are significant (in agreement with the *M* versus *H* behavior discussed above) and found to undergo slow decay with *t*. A quantitative analysis of the data to an exponential form popularly noted for canonical spin glasses is found to hold good for a narrow range of the plot (below about 1000 sec), but deviations occur for M_{IRM} curve at higher *t* values. It appears that, barring low-*t* region, M_{IRM} seems to vary logarithmically as shown in Fig. 3 with comparable values of the coefficient of the logarithmic term. It thus appears that a superimposition of exponential (for low *t* values) and logarithmic (at higher *t* values) terms describe the relaxation process. As the actual form of relaxation is a matter of great discussion even in conventional spin glasses,[7] a further discussion on this aspect for the present complex material is not desirable. What is important to note is that, while the slow relaxation of M_{IRM} at 5 K is consistent with the spin-glass freezing proposed in Ref. 3, similar behavior at 62 K is unexpected on the basis of the analysis of the neutron diffraction data. If the interpretation of previous results[3] are correct, one can argue that coexisting antiferromagnetic chains and paramagnetic chains can also give rise to this behavior which by itself will be an interesting conclusion. Alternatively, on the basis of the similarities of the relaxation behavior at 5 and 62 K quantitatively evidenced by a comparable values of the coefficients of the logarithmic term (see Fig. 3), one is also tempted to propose that the dynamics in the entire temperature range below 90 K observed here is the one due to superparamagnetic clusters formed between T_1 and T_2, the dynamics of which apparently gets frozen below T_2.

To conclude, we have observed a large frequency dependence of ac susceptibility in Ca_3CoRhO_6 in a temperature range in which a partially disordered antiferromagnetic phase has been previously proposed. If the interpretation of the neutron diffraction data[2] for the range 30-90 K is correct, the present results raise a very interesting question how the coexistence of antiferromagnetic and incoherent magnetic chains result in superparamagnetic-like behavior. It is also surprising that the magnetic relaxation behavior in the two temperature regimes in the magnetically ordered state is found to be similar, which prompts us to propose that the dynamics of the superparamagnetic clusters formed in the range 30-90 K freeze below about 30 K. We hope that this work motivates further microscopic investigations for a better understanding of the magnetism of this compound.

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