Long-range magnetic ordering in the spin-chain compound Ca_3CuMnO_6 with multiple bond distances

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The results of ac and dc magnetization and heat-capacity measurements as a function of temperature (T = 1.8–300 K) are reported for a quasi-one-dimensional compound, Ca_3CuMnO_6, crystallizing in a triclinically distorted K_4CdCl_6-type structure. The results reveal that this compound undergoes antiferromagnetic ordering close to 5.5 K. In addition, there is an additional magnetic transition below 3.6 K. The existence of two long-range magnetic transitions is uncommon among quasi-one-dimensional systems. It is interesting to note that both the magnetic transitions are of long-range type, instead of spin-glass type, in spite of the fact that the Cu-O and Mn-O bond distances are multiplied due to this crystallographic distortion. In view of this, this compound could serve as a nice example for studying ''order-in-disorder'' phenomena.

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The spin-chain compounds of the type (Sr, Ca)$_3MXO_6$ (M, X= a metallic ion, magnetic or nonmagnetic), crystallizing in the K_4CdCl_6 (rhomhohedral) derived structure (space group $R\bar{3}c$), are attracting a lot of attention in the recent literature (see, for instance, Refs. 1–17 and references cited therein). The structure is characterized by the presence of chains of M and X ions running along the c direction arranged hexagonally forming a triangular lattice. These chains are separated by Sr (or Ca) ions. Within the chains, alternating MO_6 trigonal prism and XO_6 octahedra share one of the faces. The triangular arrangement of magnetic ions in the a-b plane may result in magnetic frustration in the event that the interchain interaction on the a-b plane is antiferromagnetic. A survey of the literature reveals that a variety of magnetic behavior, including ''partially disordered antiferromagnetic structure'' (a rare magnetic structure), has been observed[10,11] in this class of compounds. Among these spin-chain oxides, the Cu containing ones are especially of interest due to a lowering of crystal symmetry. For instance, Sr_3CuIrO_6 undergoes a monoclinic distortion (space group $C2/c$) due to Jahn-Teller effect, as a result of which the Cu ions at the trigonal prisms move slightly away within the basal plane from its original position thereby attaining pseudo-square-planar oxygen coordination.[1] An interplay of this distortion and defects makes the magnetism inhomogeneous[12] with the magnetic behavior being sensitive to sample preparative conditions.[13,14] One would therefore expect that such distortions should not result in long-range magnetic ordering. Therefore we carried out magnetic studies on another Cu containing compound, Ca_3CuMnO_6, which has been recently synthesized[18] and found to undergo further distortion to a triclinic structure (space group, P-1). The results reveal that this compound actually undergoes antiferromagnetic ordering close to 5.6 K, in contrast to the inhomogeneous, spin-glass behavior seen for Sr_3CuIrO_6, thereby presenting another interesting situation among this class of compounds. In addition, interestingly, there is one more magnetic transition below 3.6 K, a feature uncommon among other classes of quasi-low-dimensional magnetic materials.

The title compound was prepared by a conventional solid-state route from high-purity (>99.9%) $CaCO_3$, MnO_2, and CuO. Required amounts of these were thoroughly mixed, pressed into pellets, and annealed at 1130 °C for 48 h. The pellets were ground finely, pelletized and heat treated in an atmosphere of oxygen at 1000 °C for 4 h, after which it was slow cooled. The samples were characterized by x-ray diffraction and the pattern (see Fig. 1) confirms single phase nature of the specimen. The dc magnetic measurements were performed by commercial superconducting quantum interference device (Quantum Design) and vibrating sample (Oxford Instruments) magnetometers, whereas ac susceptibility (χ) data were obtained with the former. Heat-capacity (C) data (1.8–40 K) were obtained by a semiadiabatic heat-pulse method.

The results of dc χ measurements recorded in the presence of a magnetic field (H) of 5 kOe is shown in Fig. 2(a).

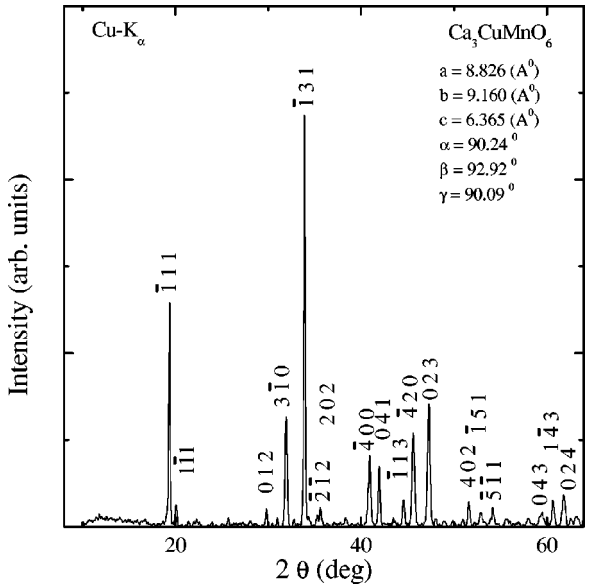

FIG. 1. X-ray-diffraction pattern (Cu K_α) of Ca_3CuMnO_6 at room temperature. Intense peaks are indexed. The lattice parameters and Miller indices are also included in the figure.

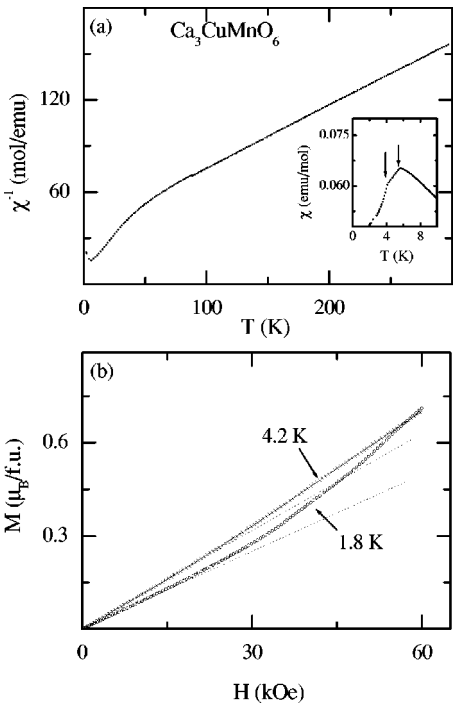

FIG. 2. (a) Inverse susceptibility (χ) as a function of temperature measured in a magnetic field of 5 kOe for Ca_3CuMnO_6. Inset shows the low-temperature χ data in an expanded form to highlight the features due to magnetic ordering. Vertical arrows mark the two transitions. (b) Isothermal magnetization at selected temperatures and the linear lines extrapolated from low-field data are also shown.

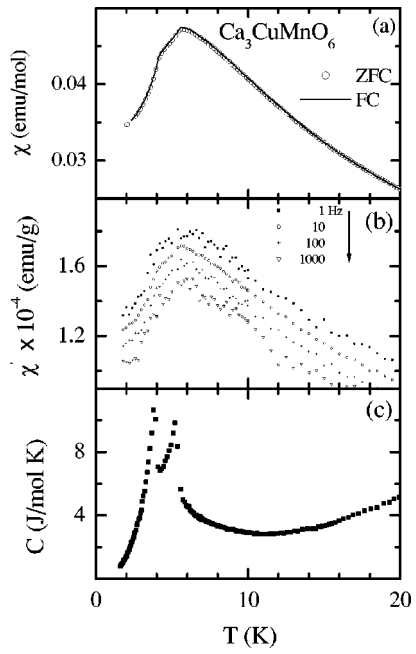

FIG. 3. (a) Low-temperature magnetic susceptibility (χ) behavior measured in 100 Oe for Ca_3CuMnO_6. Zero-field-cooled data are shown by points, whereas the continuous line represents the data for the field-cooled state. (b) Real part of ac χ measured at various frequencies. The curves for all the frequencies overlap and hence are shifted downwards with increasing frequency for the sake of clarity. (c) Heat-capacity as a function of temperature.

The $\chi(T)$ follows Curie-Weiss behavior above 50 K. The paramagnetic Curie temperature (θ_p) obtained from this plot turns out to be about -85 K with the negative sign indicating the existence of antiferromagnetic correlations. The effective moment is found to be $4.4\mu_B$, which is close to the value obtained assuming Cu and Mn are $2+$ and $4+$ states, respectively. As the temperature is lowered below 50 K, there is a deviation of inverse $\chi(T)$ curve from high-temperature linear behavior, presumably due to short-range magnetic correlations, leading to magnetic ordering close to 5.7 K as evidenced by the appearance of a distinct peak at 5 K. There is an additional shoulder at 3.6 K as though there is another magnetic transition. In order to understand the nature of the magnetic ordering, we have performed χ measurements at low temperatures (2–20 K) in the presence of a H of 100 Oe, both for field-cooled (FC) and zero-field-cooled (ZFC) conditions of the specimen, as well as isothermal magnetization (M) measurements. It is clear from Fig. 3(a) that there is a distinct peak at 5.7 K. The $\chi(T)$ plots for both ZFC and FC states merge and this is sufficient enough to establish that both the magnetic transitions are of a long-range type, presumably of an antiferromagnetic type judged by the appearance of a peak in the $\chi(T)$ plot at the onset of magnetic ordering. Further evidence for this conclusion is obtained from the data shown in Fig. 2(b). At 1.8 K, M varies linearly with H till about 30 kOe, which is followed by a curvature of the plot of $M(H)$ at higher fields to a higher M value compared to the one obtained from the linear extrapolation of the low-field data as though there is a spin reorientation. There is no evidence for saturation until the highest field applied and the plot is nonhysteretic. Similar features are seen at 4.2 K, but not at 10 K (not shown in the figure). These features establish that both the transitions are of an antiferromagnetic type. It is at present not clear whether both Cu and Mn ions contribute to these magnetic transitions.

Further evidence for the absence of spin-glass freezing is obtained from the ac χ data (1.8–20 K), recorded at various frequencies ($\nu = 1$, 10, 100, and 1000 Hz). In the real part (χ') of ac χ, there is a broad peak close to 5.7 K, in addition to a weak shoulder at about 3.6 K, as clearly seen in the data for $\nu = 10$ Hz (in which case the data are less noisy), consistent with the two magnetic transitions inferred above [Fig. 3(b)]. It is to be noted that the peak temperature is not frequency dependent. In addition, the imaginary part of ac χ is completely featureless in the temperature range of investigation (and hence not shown in the form of a figure). These findings conclusively establish that both the magnetic orderings are not of a spin-glass type. We have also measured C as a function of temperature [Fig. 3(c)]. There are two prominent peaks in $C(T)$ plot, one at 3.7 K and the other at 5.2 K; the huge jumps at the transitions establish that both the transitions are of bulk nature thereby ruling out a role of magnetic impurities (not detectable by x-ray diffraction) on the origin of either of the two transitions. The sharpness of both the transitions in this plot is consistent with long-range magnetic order, but not with random freezing of the spins. If the spins undergo spin-glass freezing, then the peak in C should be broader without λ anomaly; in addition, the peak in C should appear[19] at a temperature which is higher by about

20% compared to the transition temperature, given by, say the peak temperature in ac χ, and C should vary linearly with T well below magnetic transition temperature, in sharp contrast to the observations. Therefore spin-glass freezing is completely ruled out.

Thus the results presented above conclusively establish that this compound exhibits antiferromagnetic ordering close to (T_N) 5.7 K. A careful look at the crystallographic features[18] indicates that this finding is intriguing. In contrast to Sr_3CuIrO_6, there is a partial replacement of Cu sites (to the extent of 10%) by X ions (in this case Mn), however, maintaining the characteristic coordination $(4 + 2)$ for all the Cu ions. As a result of this atomic disorder, the Jahn-Teller effect is partially suppressed for this fraction of Cu, which means that there is an increase of Cu-O mean distances for four-coordination, though still all the six Cu-O bond distances are totally different. This means that the positions of these Cu ions are more towards the center of the trigonal prism, compared to the rest of Cu ions, which remain closer to a face of trigonal prism (that is, pseudo-square-planar coordination) as in the case of Sr_3CuIrO_6. The mean four-coordination Cu-O distances for the latter case are thus reduced to 2.026 Å compared to that (2.122 Å) of former Cu ions. In the same way, there are multiple Ca-O and Cu-Mn distances. Thus, in spite of randomness of Cu-O and Mn-O bond distances and Cu-Mn disorder, it is fascinating that this compound does not exhibit a corresponding frustration in the magnetic structure. The only role of frustration presumably is to reduce the magnetic ordering temperature, considering that the value of θ_p is comparatively larger. Therefore the observation of long-range magnetic ordering implies that the site exchange takes place in an ordered fashion. Thus this compound serves as a nice example for ''order in disorder'' phenomena. In this respect, it is worthwhile to carry out crystal structure studies at low temperatures in order to ensure that there is no change in crystal symmetry in the vicinity of magnetic ordering temperature.

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