Magnetic frustration in a stoichiometric spin-chain compound, Ca_3CoIrO_6

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The temperature dependent ac and dc magnetization and heat capacity data of Ca_3CoIrO_6, a spin-chain compound crystallizing in a K_4CdCl_6-derived rhombohedral structure, show the features due to magnetic ordering of a frustrated-type below about 30 K, however without exhibiting the signatures of the so-called "partially disordered antiferromagnetic structure" encountered in the isostructural compounds, $Ca_3Co_2O_6$ and Ca_3CoRhO_6. This class of compounds thus provides a variety for probing the consequences of magnetic frustration due to topological reasons in stoichiometric spin-chain materials, presumably arising from subtle differences in the interchain and intrachain magnetic coupling strengths. This compound presents additional interesting situations in the sense that, ac susceptibility exhibits a large frequency dependence in the vicinity of 30 K uncharacteristic of conventional spin-glasses, with this frustrated magnetic state being robust to the application of external magnetic fields.

PACS numbers: 75.50.Lk, 75.50.-y; 75.30.Cr; 75.30.Kz

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Conventionally, the phenomenon of spin glass freezing has been associated with the randomness of exchange interactions, mainly due to random distribution of magnetic impurities in a non-magnetic matrix and/or due to crystallographic disorder. In stoichiometric compounds, one can in principle encounter spin-glass-like magnetic frustration anomalies due to certain topological reasons, for instance, due to antiferromagnetic coupling among the magnetic moments in a triangular lattice. Thus, the investigation of glassy effects due to geometric frustration is one of the most interesting topics in magnetism and, in this regard, kagome (2D) or pyrochlore (3D) lattices remain at the centrestage of this direction of research.[1] In this article, we bring out that the spin-chain compounds of the type, $(Sr, Ca)_3ABO_6$ (A, B= a metallic ion, magnetic or nonmagnetic), crystallizing in the K_4CdCl_6 (rhomhohedral) derived structure (space group $R\bar{3}c$) [See, for instance, Refs. 2 and 3] need an attention in this regard. The structure is characterized by the presence of chains of A and B ions running along c-direction arranged hexagonally *forming a triangular lattice.* These chains are separated by Sr (or Ca) ions. Within the chains, alternating AO_6 trigonal prism and BO_6 octahedra share one of the faces. It is generally found that the interchain interaction is antiferromagnetic and therefore triangular arrangement of magnetic ions in the a-b plane may result in magnetic frustration.[4] This, coupled with the tunability of the relative magnitudes of interchain and intrachain magnetic coupling strengths as one varies A and/or B, should provide an opportunity to observe a variety of magnetic anomalies among this class of compounds.

A survey of the very limited literature suggests that this class of compounds is indeed characterized by a host of novel behavior (see, for instance, Refs. 2 - 14). In particular, the observation of '$CsCoCl_3$-like[15] partially disordered antiferromagnetic (PDA) structure', in $Ca_3Co_2O_6$ (Ref. 4) and Ca_3CoRhO_6 (Ref. 9) is quite fascinating; in the PDA structure, 2/3 of the magnetic chains order antiferromagnetically with each other and the remaining 1/3 are left incoherent in an intermediate T range; however, the magnetism of the latter compounds are *unique* in the sense that the intra-chain coupling is *ferromagnetic* unlike in $CsCoCl_3$ in which case this coupling is also antiferromagnetic; in addition, the spins in the incoherent chains are randomly frozen at a lower temperature, while in the Cs compound a ferrimagnetic ordering is observed. In light of these interesting anomalies in Co-based oxides, we considered it worthwhile to subject the sister compound, Ca_3CoIrO_6, which has been previously reported[3] to undergo antiferromagnetic ordering below 30 K, for a reinvestigation. The present results reveal that there is only one magnetic transition at about 30 K, which is actually of a spin-glass-like frustrated type, however without the PDA structural characteristics in the sense described above for Ca_3CoRhO_6 and $Ca_3Co_2O_6$.

Polycrystalline Ca_3CoIrO_6 was prepared by a conventional solid state method. The stoichiometric amounts of high purity (> 99.9%) $CaCO_3$, Co_3O_4 and Ir were thoroughly mixed in an agate mortar and calcined in air at 1173 K for one day. Then the preheated powder was reground, pelletized and heated in air for 10 days at 1273 K with intermediate grindings as per the procedure in Ref. 3 and the specimen thus prepared contained an extra line in the x-ray diffraction pattern. Subsequently, the specimen was subjected to an additional heat treatment at a higher temperature of 1423 K for 2 days with an intermediate grinding. The sample thus prepared was found to be single phase and therefore, under our synthetic conditions, we require a temperature higher than that mentioned in Ref. 3 to synthesize the single phase material. The x-ray diffraction pattern is found to be in excellent agreement with that reported in Ref. 3 establishing ordered arrangement of Co and Ir ions. The lattice parameters are: a= 9.160 $\AA$ and c= 10.890 $\AA$. Dc χ measurements (1.8 - 300 K) in the presence of various magnetic fields and isothermal M measurements at several temperatures were performed employing a superconducting quantum interference device (Quantum Design). The same magnetometer was employed to measure ac χ (2-200 K) in a frequency (ν) range 1 - 1000 Hz in an ac field of 1 Oe, in the presence of different dc magnetic fields (H= 0, 5 and 40 kOe). The C measurements (2 - 60 K) were performed by semi-adiabatic heat-pulse method employing a home-built calorimeter.

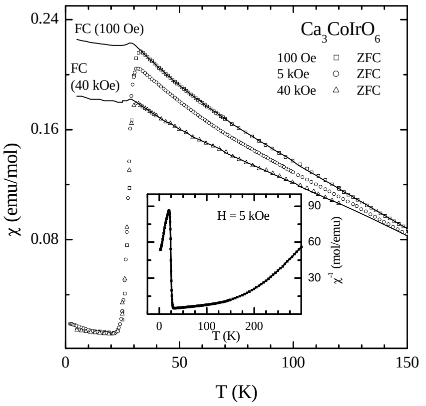

FIG. 1. Dc magnetic susceptibility (χ) as a function of temperature (T) for Ca_3CoIrO_6 measured in the presence of an external magnetic field (H) of 100 Oe, 5 kOe and 40 kOe. The data points represent zero-field-cooled (ZFC) data, whereas the continuous lines correspond to field-cooled (FC) state of the specimen. The FC data for H= 5 kOe bifurcates from the ZFC curve at the peak (similar to the curve for other two fields) and for the sake of clarity this curve is omitted. Inset shows the T-dependence of inverse χ (ZFC) for H= 5 kOe.

The results of dc χ measurements are shown in Fig. 1 and are found to be in broad agreement with those reported in Ref. 3. χ monotonously increases with decreasing T down to 30 K. The Curie-Weiss law is obeyed only above 250 K; there is a continuous change in the slope of the plot of inverse χ versus T (see, Fig. 1 inset) down to about 125 K, below which (for T > 30 K) there is a negligible variation in slope. From the high T linear region, the effective moment is found to be 4.40 μ_B per formula unit, which is very close to the theoretical value of 4.24 μ_B under the assumption that Co is in 2+ state (S= 3/2, high spin) and Ir is in 4+ state (S= 1/2). The paramagnetic Curie temperature (θ_p) is found to be 168 K and the positive sign with a large magnitude suggests the existence of strong ferromagnetic correlations. As the T is lowered below 30 K, the ZFC χ exhibits a sharp fall, attaining a nearly T-independent value at lower temperatures for all values of H. The field-cooled (FC) χ curves measured at various fields bifurcate from respective ZFC curves at 30 K; this, though sometimes observed in long range magnetically ordered systems, is a characteristic feature of spin glasses.

In order to resolve whether the 30K-feature is due to long range magnetic ordering, we have performed ac χ measurements, the results of which are shown in Fig. 2. We first discuss the data taken in zero dc magnetic field. *Looking at the curves for ν= 1 Hz*, there is a distinct drop in the real part ($\chi\prime$) of ac χ as well below the peak temperature of 42 K. There is also a sharp upturn in the imaginary part ($\chi\prime\prime$) below 45 K and there is a distinct peak at about 35 K and the plots of ac χ versus T move to a higher temperature with increasing frequency; these findings are sufficient enough[16] to conclude that there is a spin-glass-like behavior taking place in this T range in this compound. However, the peak temperature in $\chi\prime$ as well as the T-range (32-40 K) where the decreasing part of $\chi\prime$ is sharp do not coincide with the corresponding temperatures in dc χ (30 K and 25-30 K respectively), but shifted to a higher temperature by about 12 K in $\chi\prime$. It is also important to note that the peak temperatures in $\chi\prime$ and $\chi\prime\prime$ do not agree. Similar features were observed[17] also in pyrochlores with magnetic frustration (due to topological reasons) and this implies strong frequency dependence of susceptibility arising from slow magnetic dynamics. Further evidence for this explanation comes from the *large frequency dependence* of ac χ peaks; for instance, the curve shifts upwards by as much as 15 K for a change of frequency from 1 Hz to 1 kHz. Such a large shift corresponds to a value beyond 0.1 for the factor,[15] $\Delta T_f/T_f\Delta(\log\nu)$, which is much larger than that known for conventional spin glasses. In this sense the dynamics of magnetic frustration is quite unusual. It may be recalled that a large frequency dependence of ac χ has been recently reported for $Ca_3Co_2O_6$ and Ca_3CoRhO_6 (Refs. 7 and 10). But the magnitude of the discrepancy between the peak temperatures of dc χ(T) and $\chi\prime$(T) is relatively smaller (about 2 K) for $Ca_3Co_2O_6$ (Refs. 7 and 14).

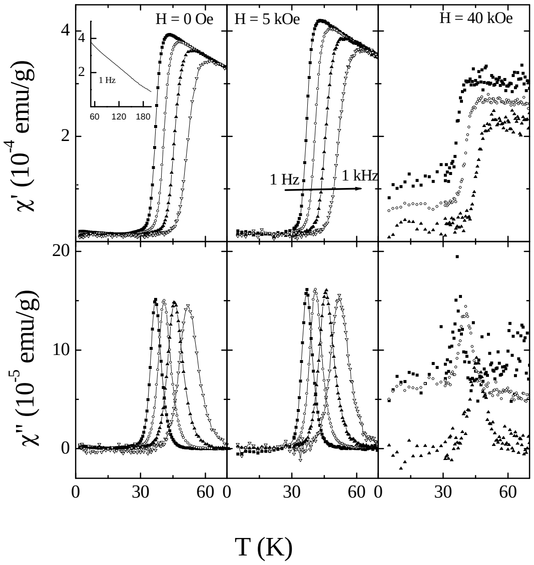

FIG. 2. Ac susceptibility as a function of temperature for various frequencies (1, 10, 100, and 1000 Hz) in the absence and in the presence of external dc magnetic fields for Ca_3CoIrO_6. $\chi\prime$ and $\chi\prime\prime$ refer to real and imaginary parts. The curves shift to higher temperatures with increasing frequency as marked by an arrow. Gradual and linear variation of the $\chi\prime$ with T in the range 50 - 250 K is typically shown in the inset (ν= 1 Hz).

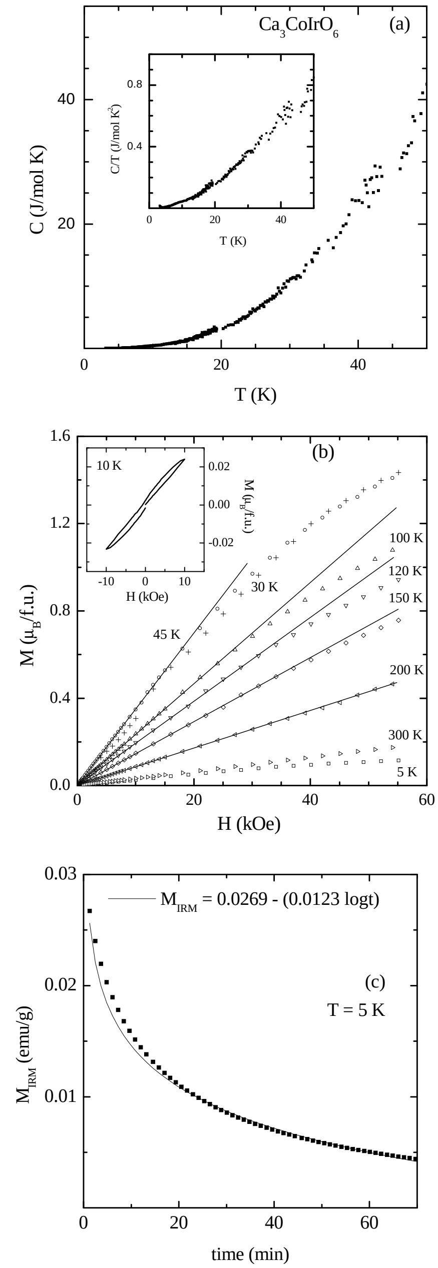

FIG. 3. (a) Heat capacity (C) as a function of temperature (T); inset shows C/T as a function of at various temperatures; continuous lines in some cases are drawn to highlight low-field linear region; the data for 30 (symbol: +) and 45 K (circles) K; and (c) Isothermal remanent magnetization as a function of time (obtained as described in the text), for Ca_3CoIrO_6.

Further evidence for spin-glass-like frustration is offered by the C data. It is obvious from Fig. 3a that C increases monotonously with T without any evidence for a well-defined peak characterizing long range magnetic ordering around 30 K. The peak is so washed out that there is no clear-cut anomaly even in the plot of C/T (Fig. 3a, inset). It may be recalled[11] that an intense peak in C could be seen at 19 K in Sr_3ZnIrO_6 due to antiferromagnetic ordering from Ir ions (S= 1/2), with a magnitude of C jump of about 4J/molK. Therefore, the absence of a noticeable jump in C around 30 K in the present compound conclusively establishes randomness of magnetic interactions. Consistent with this, isothermal M below 30 K, say at 10 K (see Fig. 3b, inset) is found to be hysteretic with a sluggish variation of M with H in the field range of measurement. We have also performed isothermal remanent magnetization (M_{IRM}) measurements at 5, 45 and 150 K in the following way: The sample was cooled from 200 K to the desired T in zero field, then a magnetic field of 5 kOe was switched on for 5 mins and the magnetization, M_{IRM}, was measured as a function of time immediately after the field was switched off. While the M attained a very small value (close to the detection limit of the magnetometer) at 45 and 150 K, M_{IRM} at 5 K is found to undergo a slow relaxation with time, decreasing exponentially for initial periods followed by logarithmic variation after waiting for 20 mins (Fig. 3c). This slow relaxation of M is also consistent with spin-glass-like freezing.

We have also measured ac χ in the presence of external dc magnetic fields (see Fig. 2). It is fascinating to see that the ac χ features described above, not only frequency dependence but also the order of magnitude of ac χ, are not significantly affected by the field. (The plots are found to be noisy for H= 40 kOe and it is so bad for ν = 1 kHz that it is not shown in the figure). This situation is completely different from that observed for the Rh (for Ir) analogue[10] in the sense that the zero-field features are completely suppressed by a field of, say, 30 kOe. Thus, the magnetic frustration phenomenon in this compound is unique in the sense that it is quite robust to the application of H. This difference can be correlated to isothermal M behaviour: It may be recalled[10] that isothermal M as a function of H in the range 30 - 100 K exhibits a plateau in the Rh compound, whereas, in the Ir case, M varies linearly for initial applications of H followed by a curvature towards saturation at higher values of H without exhibiting a plateau (see Fig. 3b). This holds true even in the vicinity of magnetic transition temperature (see the data for 30 K in Fig. 3b). Thus, it appears that the zero-field magnetic state undergoes dramatic modification with H in the Rh case.

A further comparison of M behavior of these two compounds in the intermediate T range (30 - 300 K) is quite revealing. For instance, for Ca_3CoIrO_6, in Fig. 1, the bifurcation of ZFC-FC χ sets in at the peak (close to 30 K) irrespective of the field, whereas for the Rh analogue, the bifurcation occurs at a noticeably higher temperature depending upon the magnitude of external H; also, the $\chi\prime$ exhibits a distinct upturn below 100 K for the Rh compound as though there is a magnetic phase transition below 100 K, whereas $\chi\prime$ surprisingly exhibits a linear decrease with increasing temperature up to the highest T measured (see, Fig. 2, inset, for a typical variation). There is a slow decay of M_{IRM}, say at 62 K as at 5 K in the Rh compound, whereas, in the present case, no magnetic relaxation could be observed above 30 K. However, there is a clear evidence for magnetic relaxation at 5 K in the present case as well, as described earlier (see above); it is to be noted that the coefficient of the logarithmic term is larger (about 5 times) compared to that in Ca_3CoRhO_6, which could mean stronger glassy-effects in the former case. Though dc χ is field dependent above 30 K for both the compounds, this sets in at a *well-defined* temperature (close to 100 K, corresponding to the onset of PDA structure) for the Rh compound, whereas this field-dependence vanishes in a sluggish way persisting over a wide temperature range for the Ir compound. Apparently, the T-range over which this field-dependence persists may be sample-dependent, as in our case this tendency persists till about 150 K, whereas in Fig. 6 in Ref. 3, this feature appears to terminate around 70 K. Though exact origin of this sample-dependence is not clear, we believe that the T-range over which ferromagnetic correlations (described below) persist may sensitively depend on sample preparative conditions.

From the above discussion, one can infer that presumably short range ferromagnetic correlations persist, say, till about 150 K in the Ir compound without any evidence for glassy features in the intermediate T range, whereas in the Rh analogue, the signatures of the existence of 'first' long range magnetic ordering (arising from intrachain interaction) and glassy behaviour set in at a well-defined temperature near 100 K. Interestingly, the plots of inverse χ versus T above 30 K for both look similar in the sense that there is not much change in the slope below about 150 K for both. Also, the sign (positive) and the magnitude of θ_p (close to 170 K) are practically the same for both, as though both should have similar magnetic characteristics. It is therefore interesting that the present compound does not apparently show PDA characteristics as in the case of the Rh compound. The fact that there is no well-defined C jump at 30 K in the Ir case implies that the even the 30K-transition is *purely* glassy-like in its character, rather than originating from simultaneous long range ordering from 2/3 of the chains. It looks as though this difference between these two compounds lies in the elongation of magnetic chain of the Ir compound (c= 10.890$\mathring{A}$) with respect to the Rh compound (c= 10.730$\mathring{A}$) as the basal plane parameters are nearly equal. The c/a ratio for the three compounds, $Ca_3Co_2O_6$, Ca_3CoRhO_6, and Ca_3CoIrO_6 are 1.143, 1.166 and 1.189 respectively and it appears that the magnetic behavior critically depends on relative strengths of interchain and intrachain coupling determined by c/a ratio in some fashion.

To conclude, we have identified a stoichiometric spin-chain compound, Ca_3CoIrO_6, undergoing a glassy-type of magnetic ordering below 30 K. We have compared and contrasted the observed magnetic behavior with those of isostructural compounds, $Ca_3Co_2O_6$ and Ca_3CoRhO_6. It is particularly notable that the title compound does not exhibit PDA structural characteristics unlike the other two compounds. It may also be added that the behavior of this compound (glassy magnetic transition with a single magnetic transition temperature, which is also robust to the application of magnetic field) is unique among this class of quasi-one-dimensional magnetic oxides. The results sufficiently demonstrate that this class of compounds provide an avenue to probe the consequences of geometric frustration in psuedo-one-dimensional magnetic compounds, presumably resulting from the relative strengths of interchain versus intrachain magnetic coupling.

The authors would like to thank K.K. Iyer for his help while performing the experiments.

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