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The influence of Cu substitution for Ru on the magnetic behaviour of a weak ferromagnet, Ca_3LiRuO_6

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Abstract. The influences of gradual Cu substitution for Ru on the magnetic characteristics of a weak ferromagnet, Ca_3LiRuO_6 (with a magnetic ordering temperature of 113 K), are reported as obtained by magnetization studies. We find that single-phase compounds could be formed only until $x = 0.3$ in $Ca_3LiRu_{1-x}Cu_xO_6$. We do not find evidence for superconductivity in the temperature range of the investigation (2–300 K). The onset of magnetic ordering is depressed only marginally with Cu substitution (to about 90 K for $x = 0.3$), which indicates that the magnetic interaction along the chain is not predominantly of a long-range type, but rather of a short-range (superexchange?) type. There are notable changes in the magnetic field/temperature dependence of the magnetization, as if there are dramatic changes in the magnetic structure.

The topic of one-dimensional magnetism has regained its importance in recent years following the observations of the spin–Peierls transition in $CuGeO_3$, such studies however being mostly focused on 3d spin-1/2 systems (Cu) in the current literature [1, 2]. It is of interest to identify such magnetic materials among 4d/5d transition metal systems (particularly with spin greater than 1/2) and to subject these to detailed magnetic investigations, which may eventually contribute to the systematic theoretical understanding of this topic. In this regard, the oxides of the type $A_3A'TO_6$ (A = Ca, Sr; A′ = Li, Na; T = Ru, Pt, Ir), adopting K_4CdCl_6-type rhombohedral structure [3], are of considerable interest, as this structure consists of infinite chains of alternating $A'O_6$ trigonal prisms and TO_6 octahedra, which are separated by Ca/Sr ions. Among these, the compound Ca_3LiRuO_6 shows magnetic behaviour that is especially noteworthy, as this is one of the very few Ru-based oxides exhibiting an onset of magnetic ordering at a fairly large temperature ($T_o = 113$ K). The behaviour of the magnetization (M) of this material is quite fascinating [3, 4] in the following sense: while the dependence on the temperature (T) of the magnetic susceptibility (χ) for the field-cooled (FC) state of the specimen tends to saturate as $T \rightarrow 0$ following a sharp rise at 113 K as if the material is ferromagnetic, the observed value of the magnetic moment (less than 0.02 μ_B) is too small to be attributable to strong ferromagnetism. Considering that this material is insulating, the small moment cannot be attributed to itinerant ferromagnetism. In addition, the isothermal M below T_o varies linearly at higher fields (however with a hysteresis loop at low fields) and also the paramagnetic Curie temperature (Θ_p) is negative with a magnitude much larger than T_o, as if the material is antiferromagnetic. In view of the fact that neutron diffraction data [3] show strong features due to magnetic ordering, the observed ferromagnetic component cannot be associated with impurities. A way to reconcile these experimental findings is to

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propose that the material is a weak ferromagnet with the compensation of the moment arising from strong intra-chain or inter-chain antiferromagnetic coupling. (Due to the presence of both of these types of magnetic interaction, we prefer to use the notation T_o to denote the onset of the magnetic ordering temperature, rather than using T_N or T_C.) In addition, the magnetic moment in the magnetically ordered state gets locked along the direction of the applied magnetic field ($\boldsymbol{H}$) [4], as if the ferromagnetism is of a very soft type. The gradual introduction of carriers by Y substitution for Ca does not result in metallicity and T_o undergoes only a marginal reduction with this substitution with the M-features otherwise remaining the same as those of the parent compound [4]. This finding signals that the magnetic chains are decoupled by intervening Ca ions, an observation taken to infer a one-dimensional nature of the magnetism. However, considering that a broad peak in χ above T_o characterizing one-dimensionality of the magnetism [5] is not observed in these materials, this inference remains tentative. We consider it important to subject this interesting material to more investigations. In this article, we report the influence of a substitution at the Ru site, namely that of Cu. This substitutional study is partly motivated by the observation of high-temperature superconductivity induced by Cu substitution in an antiferromagnetic insulator, YSr_2RuO_6 (see reference [6]).

The compounds, $Ca_3LiRu_{1-x}Cu_xO_6$ ($x = 0.0$, 0.1, 0.3 and 0.5), were prepared by the solid-state method as suggested in reference [3]. Initially, $CaRuO_3$ was prepared by heating in air appropriate amounts of high-purity $CaCO_3$ and RuO_2 at 750 °C for 24 hours and then heating for eight days at 1100 °C in air. The samples were then prepared by reaction of $CaRuO_3$, Li_2CO_3 and CuO at 550 °C for 24 hours, at 800 °C for 24 hours and at 950 °C for two weeks with intermediate grindings. All of the preparations were carried out under a flow of oxygen. The samples were subsequently characterized by x-ray diffraction (Cu K_α) and we notice that for the $x = 0.5$ sample there are strong additional lines, thereby establishing that, among the compositions studied, the single-phase solid-solution range is restricted to a maximum of $x = 0.3$. The hysteresis loops were obtained at 5, 70 and 120 K for the zero-field-cooled (ZFC) state of the specimens, employing a vibrating-sample magnetometer up to a value of H of 60 kOe. The T-dependence of χ was probed in a field of 2 kOe for the FC and ZFC states of the specimens.

The T-dependence of χ and the hysteresis loops are shown in figures 1 and 2 respectively for all the three compositions. The features to be noted are:

(i) The value of T_o only undergoes a reduction from 113 K for $x = 0.0$ to about 105 and 95 K for $x = 0.1$ and 0.3 respectively. The magnitude of this reduction is large compared to that for Y substitution (for Ca) to a comparable fraction. Thus, for instance, the replacement of about one third of Ca with Y results in a T_o of 106 K [4]. This may imply that the magnetic interaction is stronger along the chain, compared to the inter-chain interaction. However, the magnitude of the reduction is still small, as the value of T_o does not scale with the concentration of magnetic Ru ions. This conclusion of course assumes that Cu does not possess any magnetic moment, for which one gains support from the paramagnetic χ-data. On the basis of this observation, we infer that the magnetic coupling is not of a long-range type, but rather predominantly of a short-range type (superexchange?)

(ii) FC and ZFC χ-data tend to diverge at T_o; this divergence arises due to the 'locking effect' of H mentioned in the introduction; however, looking at the shapes of the plots, the locking effect gets modified for other compositions. The data were collected even in the presence of a low field H (200 Oe) and the features are qualitatively the same, except that the divergence at T_o for $x = 0.3$ could be more distinctly seen.

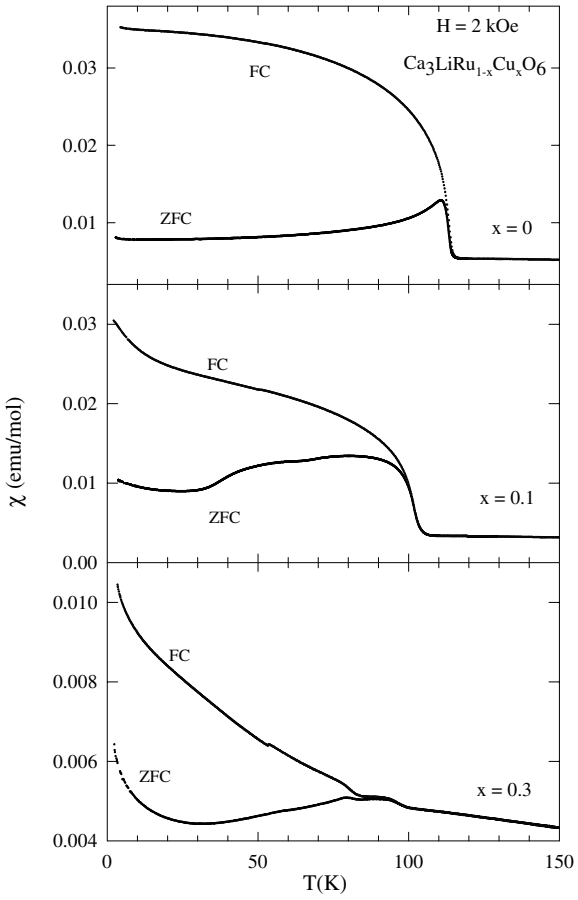

Figure 1. The temperature dependence of the magnetic susceptibility for the oxides $Ca_3LiRu_{1-x}Cu_xO_6$ ($x = 0.0$, 0.1 and 0.3), taken in a field of 2 kOe for the field-cooled and zero-field-cooled states of the specimens.

(iii) Unlike the case for Y substitutional effects [4], there are marked differences in the shapes of the plots of χ versus T. While χ tends to saturate as $T \rightarrow 0$ for $x = 0.0$, there is an upward curvature for Cu-substituted samples. In addition, there are additional peaks in the plots for ZFC data below T_o.

These findings suggest qualitative changes in the magnetic structure brought about by Cu substitution as regards Y substitution. Further indications for this conclusion can be obtained from figure 2. The hysteresis loops (measured at 5 and 70 K) are rather narrower for $x = 0.1$ compared to those of the parent compound. The loop is practically absent for $x = 0.3$, as if the ferromagnetic component vanished for this composition; presumably, this composition is an antiferromagnet at these temperatures. The plot of M versus H is linear at 120 K, as expected for a paramagnet (and hence is not shown in the figure). Finally, it may be added that, in the paramagnetic state, the effective moment is close to 4 μ_B per Ru, which suggests that Ru remains in a pentavalent state and that Cu does not possess a magnetic moment.

In conclusion, Cu substitution for Ru brings out notable changes in the magnetic behaviour of the weak ferromagnet Ca_3LiRuO_6, in contrast to the substitution at the Ca site. The results also rule out the possibility of superconductivity in these compositions. It may be mentioned that, subsequent to our report [4], M-behaviour similar to that of the present parent compound has been noted for $BaCu_2Ge_2O_7$ (see reference [2]), a system classified as a spin-1/2 quasi-one-dimensional weak ferromagnet. If future studies can throw more light on the dimensionality

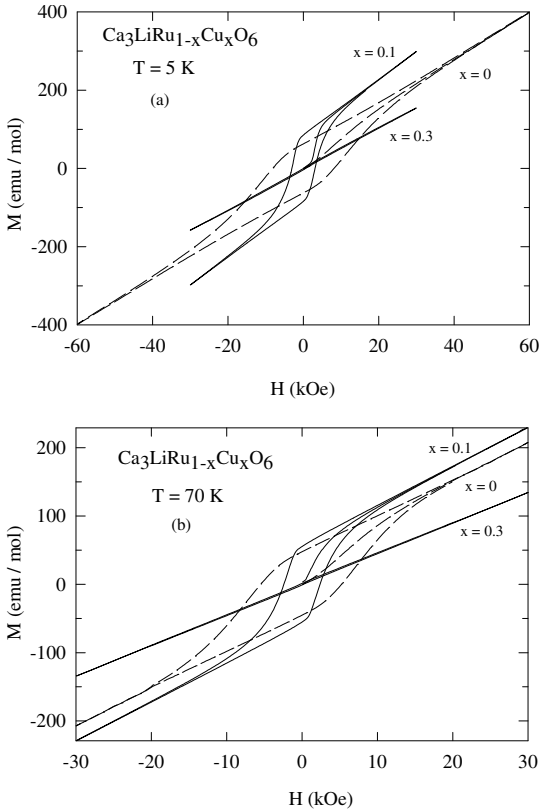

Figure 2. Hysteresis loops for $Ca_3LiRu_{1-x}Cu_xO_6$ ($x = 0.0$, 0.1 and 0.3) at (a) 5 and (b) 70 K.

of magnetic ordering and establish one-dimensionality in the material under discussion, then this material could be an example showing this phenomenon among 4d metal systems with spin greater than 1/2.

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