Stability of the geometrically frustrated magnetic state of Ca_3CoRhO_6 to applications of positive and negative pressure

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Abstract
The influence of negative chemical pressure induced by gradual replacement of Ca by Sr as well as of external pressure (up to 10 kbar) on the magnetism of Ca_3CoRhO_6 has been investigated by magnetization studies. It is found that the solid solution, $Ca_{3-x}Sr_xCoRhO_6$, exists at least until about $x = 1.0$ without any change in the crystal structure. Apart from insensitivity of the spin–chain feature to volume expansion, the characteristic features of geometrical frustration interestingly appear at the same temperatures for all compositions, in sharp contrast to the response to Y substitution for Ca (reported previously). Interestingly, the huge frequency dependence of ac susceptibility known for the parent compound persists for all compositions. We do not find a change in the properties under external pressure. The stability of the magnetic anomalies of this compound to volume change (about 4%) is puzzling.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The compounds crystallizing in the K_4CdCl_6-type rhombohedral structures have started attracting considerable attention in recent years, as, in this family, one observes several manifestations of interplay between spin–chain behavior and topologically frustrated magnetism due to triangular arrangement of (antiferromagnetically coupled) magnetic chains [1]. Among these, the Co-based compounds, Ca_3CoRhO_6 and (to a larger extent) $Ca_3Co_2O_6$, have been of special interest to the community due to their interesting magnetic behavior [2, 3]. As the temperature is lowered, following short-range correlation features over a wide temperature range arising from the spin–chains, one observes two magnetic transitions (which we label as T_1 and T_2). At T_1, two of the three chains at the corners of the triangle undergo magnetic ordering with an intrachain fer-

romagnetic interaction and interchain antiferromagnetic coupling, while the third one is left incoherent, leading to a not-so-common 'partially disordered antiferromagnetic (PDA) structure' (see articles cited in [3] and [4] for a few more examples of PDA structure, $CsCoCl_3$ and $CsCoCl_3$). At a lower temperature, T_2, a complex glassy phase evolves, which results in an unusually large frequency dependence of ac susceptibility (χ), revealing interesting spin-dynamics [4, 5]. Though the values of T_1 and T_2 are widely different for these two compounds (near 24 and 10 K for $Ca_3Co_2O_6$ and 90 and 30 K for Ca_3CoRhO_6), the dc χ curves, if plotted as a function T/T_1, are found to be similar [6]. While large values of T_1 and T_2 for the latter could be explained through local spin density approximation (LSDA) calculations including Coulomb interaction and spin–orbit coupling [7], this similarity among these compounds is quite striking considering that, in the former, one of the two Co sites (running alternately along the c-axis) is non-magnetic, whereas, for the latter, the consensus is that there is

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a magnetic moment at both Co and Rh sites (Co^{2+}, $3d^7$ high spin; Rh^{4+}, $4d^5$ low spin) [7–9].

In this paper, we investigate whether the behavior of Ca_3CoRhO_6 can be modified by chemical and external pressure effects. It is commonly known that the anomalies associated with the geometrically frustrated magnetic state are quite sensitive to any perturbation or lattice distortion, and that one can even attain (long-range magnetic) order by (chemical) disorder. Even for this family, order-by-disorder has been demonstrated, for example, for $Ca_3Co_{1-x}Mn_xO_6$ [10] and Ca_3CuMnO_6 [11]. In fact, even in the case of Ca_3CoRhO_6, a small substitution (less than 5 atomic per cent) of Y for Ca in Ca_3CoRhO_6 was reported to dramatically depress the high-temperature three-dimensional ordering (occurring at T_1) [12]. In view of this, we undertake this investigation. To simulate lattice expansion, we succeeded in gradual replacement of Ca by Sr, resulting in the formation of the solid solution, $Ca_{3-x}Sr_xCoRhO_6$, without a change in the crystal structure until $x = 1.0$. For contraction, we applied external pressure up to 10 kbar. It is interesting to note that all the characteristic features of the parent compound are retained for all compositions and pressures nearly at the same temperatures as those in the parent compound—in sharp contrast to the observation in Y-substituted Ca_3CoRhO_6. This reveals that the magnetic properties are quite robust to volume changes, but possibly sensitive to electron doping.

2. Experimental details

Attempts were made to synthesize several compositions of the series, $Ca_{3-x}Sr_xCoRhO_6$ ($x = 0.0, 0.1, 0.2, 0.3, 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0) by a conventional solid state route as described in [4] starting from stoichiometric amounts of high purity ($>99.9\%$) $CaCO_3$, $SrCO_3$, CoO and Rh powder. Characterization of the materials was carried out by x-ray diffraction (Cu Kα) and scanning electron microscopy (SEM). It is found that the solid solution in the rhombohedral structure forms up until $x = 1.0$ only, without any other phase, whereas additional weak lines in the x-ray diffraction pattern are seen for higher compositions. For this reason, we restrict our discussions for $x \leqslant 1.0$. Energy dispersive x-ray analysis on several grains confirms homogeneity of the compositions. The dc magnetic susceptibility measurements in the temperature interval 1.8–300 K were performed employing a commercial superconducting quantum interference device (SQUID) (Quantum Design, USA) for zero-field-cooled (ZFC) and field-cooled (FC) conditions of the specimens for two externally applied magnetic fields ($H=$) 100 Oe and 5 kOe. Frequency (ν) dependence of ac χ was obtained in the temperature region of interest with the same SQUID magnetometer. We have also performed isothermal M measurements at 5 and 62 K with a vibrating sample magnetometer (VSM, Oxford Instruments, UK), which enabled us to take the data up to 120 kOe. The magnetization behavior under high pressure for the parent compound was tracked (1.8–300 K) in a hydrostatic pressure medium (daphne oil) up to 10 kbar, employing a pressure cell procured from EasyLab Technologies Ltd (UK) with the help of the SQUID
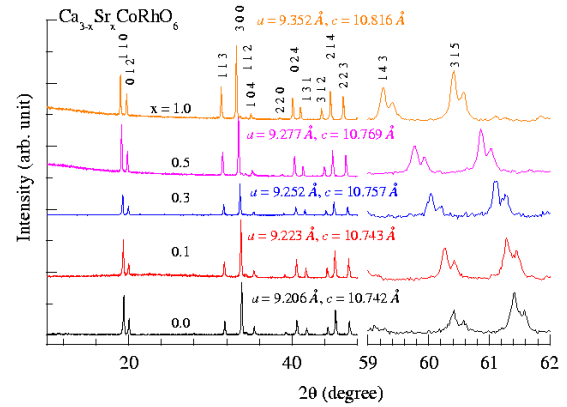

Figure 1. X-ray diffraction patterns (Cu Kα) of solid solution, $Ca_{3-x}Sr_xCoRhO_6$ ($x = 0.0, 0.1, 0.3, 0.5$ and 1.0). The patterns at the higher angle side are shown in an expanded form (and the splitting of the lines is due to slightly different wavelengths of K$\alpha 1$ and K$\alpha 2$). The lattice constants (± 0.004 Å) and the Miller indices are included.

magnetometer. The pressure monitored by measuring the superconducting transition temperature of Sn is the one being mentioned in this paper (at 300 K, the actual pressure is higher by about 2 kbar).
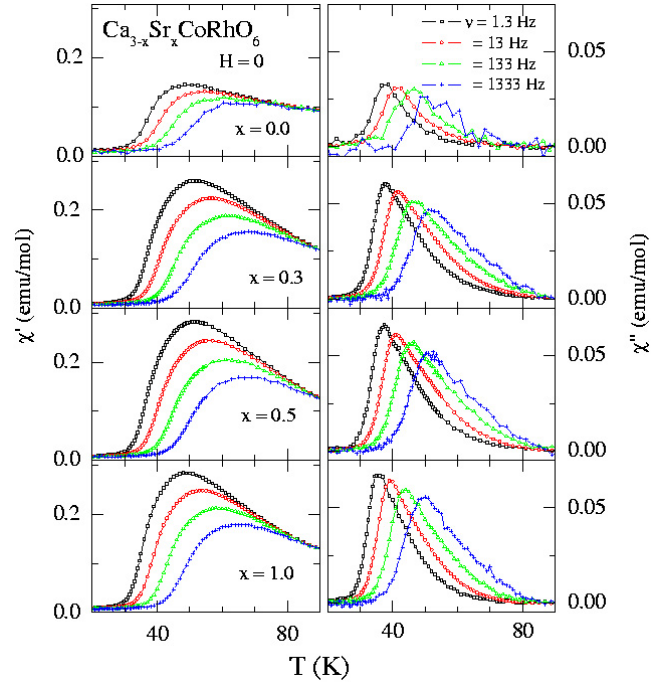
3. Results and discussion

The x-ray diffraction patterns are shown in figure 1 for selected compositions ($x \leqslant 1.0$). It is clear from this figure that all the diffraction lines could be indexed to K_4CdCl_6-type rhombohedral structure. The fact that there is a gradual expansion of the unit-cell with increasing Sr concentration is convincingly demonstrated by showing the data in the higher angle side in an expanded form. This plot also demonstrates that there is a complete formation of the solid solution, as the diffraction pattern for any composition is not a superimposition of the patterns of any other compositions. The lattice constants obtained by least-squares fitting of the lines are included in the figure. Both the cell parameters, a, c, and unit-cell volume (V) increase with x, by about 1.58%, 0.69% and 4.06% respectively as x is varied from 0 to 1.

The results of dc χ measurements are shown in figure 2 in two different ways. For all compositions, we see all the features noted for the parent compound [3]. There is a Curie–Weiss region above 225 K, followed by a broad peak in $\chi(T)$ in the range 100–150 K representative of intrachain interaction strength [13]; there is a sudden increase of χ below 100 K attributable to the onset of three-dimensional ordering [3], followed by a peak in the ZFC $\chi(T)$ curve at 40 K with a bifurcation of ZFC–FC curves as known earlier (see, for example, [4]) due to the onset of second magnetic transition of a glassy type. In the range 30–90 K, M/H is H-dependent known for PDA structure. A visual inspection of the curves itself clearly reveals that the features do not change with Sr substitution. In order to demonstrate more vividly that the T_1 and T_2 do not vary across the solid solution, we have plotted $d\chi/dT$ of $H = 100$ Oe data as well in figure 2. It is clear that the plots for all compositions overlap and, in
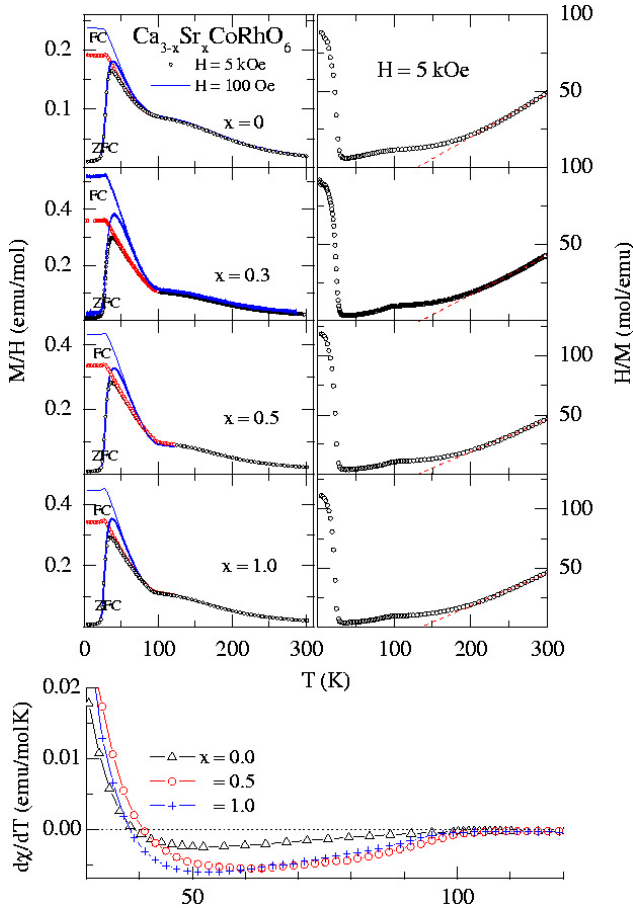
Figure 2. Right: dc magnetization (*M*) divided by magnetic field (*H*) as a function of temperature for the solid solution, $Ca_{3-x}Sr_xCoRhO_6$ ($x \leqslant 1.0$), for the zero-field-cooled and field-cooled conditions of the specimens, in the presence of 100 Oe and 5 kOe. Left: ZFC H/M as a function of temperature. A discontinuous line is drawn through the high-temperature linear region. Bottom: the temperature derivative of magnetic susceptibility (ZFC, $H = 100$ Oe) as a function of temperature in the vicinity of two magnetic transitions for three selected compositions.

Figure 3. Real (χ') and imaginary (χ'') parts of ac susceptibility for $Ca_{3-x}Sr_xCoRhO_6$ measured with different frequencies and an ac field of 1 Oe. The curves move towards higher temperatures with increasing frequency (ν). The lines through the data points serve as a guide to the eyes.

particular, there is a sudden change in the value of $d\chi/dT$ at the same temperatures. This establishes that these transition temperatures remain the same for all *x*. (From this derivative plot, we infer that T_1 could be actually 100 K and not 90 K as proposed in the literature.) It is therefore evident that interchain coupling is not sensitive to Sr substitution. The sign and magnitude of the paramagnetic Curie temperature ($\theta_p = 136 \pm 2$ K) obtained from the Curie–Weiss region (225–300 K) also do not vary with *x*. Since the sign of θ_p is positive, this parameter can be directly correlated to intrachain ferromagnetic exchange coupling in these oxides. Incidentally, the magnitude of θ_p falls in a temperature range where $\chi(T)$ exhibits a maximum. Taking these observations into consideration, we conclude that the intrachain coupling strengths also are unaffected by lattice expansion. Finally, the magnitude of the effective moment ($5.3\pm0.1\ \mu_B$/f.u.) obtained from the high-temperature Curie–Weiss region is the same for all the compositions within the limits of experimental error, which establishes that the spin/valence states of Co and Rh do not change with *x*.

We address whether the 'superparamagnetic-like' ac χ response [4] is modified across the series. The real (χ') and imaginary (χ'') parts of ac χ as a function of temperature are shown in figure 3 for $H = 0$. As known earlier [4], for the parent compound, there is a peak in χ' and χ'' at about 50 and 38 K respectively for $\nu = 1.3$ Hz, and these peak temperatures undergo a dramatic upward shift (by about 12 K) as ν is increased to 1.333 kHz. These features interestingly persist for all compositions, as though the spin-dynamics also is not influenced at all by lattice expansion. Since the peak in χ'' is rather sharp compared to that in χ', it is more straightforward to infer the trends in the *x*-independence of characteristic temperatures from the peak position in χ''. We have also performed ac χ measurements in the presence of high magnetic fields (not shown here) and the features are not different from those noted for $x = 0.0$ [4].

In order to investigate whether positive pressure induces a change in the magnetic behavior, we have performed high pressure dc magnetization studies at 2, 6 and 10 kbar. The observation of emphasis is that the features are unaffected by compression of the lattice caused by the external pressure as well (see figure 4). The fact that there is no observable variation in T_1 and T_2 is established by the fact that the curves of $d\chi/dT$ lie one over the other for all pressures, as demonstrated in an inset of figure 4.

In this connection, it is worthwhile recalling that Martinez *et al* [14] investigated the influence of high pressure on the magnetic anomalies of $Ca_3Co_2O_6$. It was found that there is a small upward shift of magnetic ordering temperature (T_1) and magnetic field, H_{SF}, at which the spin reorientation
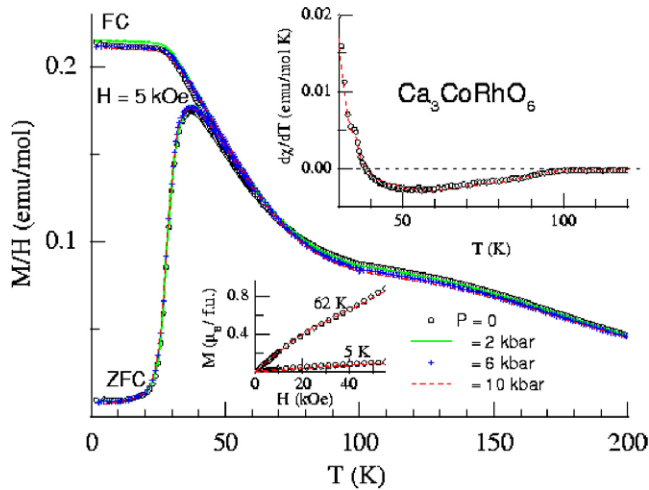
Figure 4. Dc magnetization (*M*) divided by magnetic field (1.8–200 K) under pressure for the solid solution, Ca$_3$CoRhO$_6$, for the zero-field-cooled and field-cooled conditions of the specimens, in the presence of 5 kOe. The data above 200 K also overlap for all pressures, and hence are not shown. In the top inset, the temperature derivatives of magnetic susceptibility in the range 30–120 K are plotted for zero pressure and 10 kbar. In the bottom inset, for the same pressures, isothermal magnetization data (ZFC condition) at 5 and 62 K are plotted.

effect occurs, as inferred from the isothermal *M* data in the PDA regime. These authors used the values of H_{SF} as a measure of interchain coupling and hence of magnetic ordering temperatures. H_{SF} was assumed [15] to be related to the compressibility modulus. Therefore, following [14],

$$\frac{\mathrm{d}\ln T_N}{\mathrm{d}P} \approx \frac{\mathrm{d}\ln H_{SF}}{\mathrm{d}P} = -\frac{n}{l}\frac{\mathrm{d}l}{\mathrm{d}P}$$

where *l* is the interchain distance and the value of *n* is typically 12. Interestingly, a quantitative agreement between the experimentally observed variations in transition temperatures and those derived from H_{SF} was found with the help of this relationship. The pressure derivative of magnetic ordering temperature was found to be 0.073 K kbar^{-1}. In the compound under investigation, Ca$_3$CoRhO$_6$, the value of H_{SF} is about 55 kOe which is the extreme limit of the magnetic field in the high pressure experiments; hence it was not possible for us to track an increase of H_{SF} with external pressure. Therefore, we used isothermal *M* data (figure 5) obtained up to 120 kOe (with VSM) for the Sr-substituted oxides, which allows us to draw some conclusions with the knowledge of the influence of negative pressure. Though all the 5K-plots overlap for all Sr-substituted specimens (see inset of figure 5), the value of H_{SF} varies with *x* significantly in the PDA region, say at 62 K: ∼55, 52, 51, 45 and 40 kOe for *x* = 0.0, 0.1, 0.3, 0.5 and 1.0 respectively. In the absence of compressibility data for this compound, we use the value employed in [14] for this property. Then, the value of *c* for −10 kbar corresponds to a composition close to *x* = 1.0. This means that, for this compound, d ln H_{SF}/d*P* = 0.027 kbar^{-1}. Following the above-mentioned relationship between ordering temperature and H_{SF}, one should have observed a depression
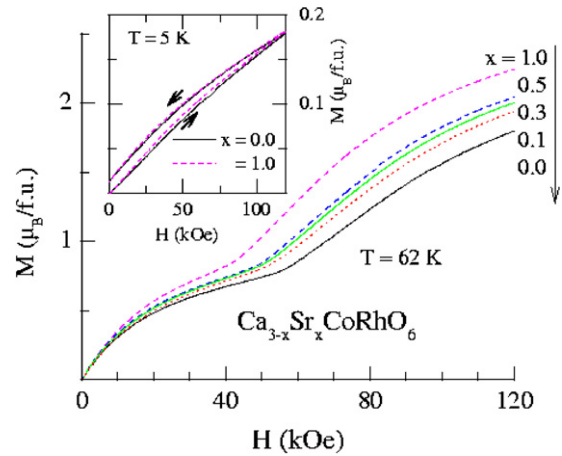
Figure 5. Isothermal magnetization at 5 (in the inset) and 62 K for Ca$_{3-x}$Sr$_x$CoRhO6 ($x \leqslant 1.0$) for the zero-field-cooled conditions of the specimens under ambient pressure. The curves at 62 K are nonhysteretic.

of about 25 K for T_1 as *x* varies from 0.0 to 1.0. This is not found to be the case experimentally. (A more straightforward comparison of the behavior of Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$ can be made by noting that, for the former, as shown in figure 3a of [14], dH_{SF}/d*P* falls in the range of 135–150 Oe kbar^{-1}, whereas in the latter, it appears to be about 10 times larger, as inferred from the data for Sr samples.) Clearly, this line of argument leads us to propose that the observed insensitivity of magnetism to positive and negative pressure resulting in a volume change of at least 4% (which is of significant magnitude) is intriguing.

4. Conclusion

Positive and negative pressure, resulting in a significant unit-cell volume change of at least 4%, does not influence the features attributable to geometrical frustration and spin–chain interaction as well as the characteristic magnetic transition temperatures in the compound, Ca$_3$CoRhO$_6$. This is despite the fact that the temperatures governing intrachain and interchain interactions appear to be about three times larger than in Ca$_3$Co$_2$O$_6$, in which case an observable variation in the properties has been reported in the literature. The extreme robustness of the properties of the former is noteworthy. A different behavior of Y-substituted systems [12] could then be attributed to sensitivity to electron doping. It is notable that possible randomness of interatomic distances or local strain induced by chemical disorder in the Sr-based solid solution does not lift frustration effects in favor of long-range magnetic order. We emphasize that unusually large frequency dependence of the peak in ac susceptibility in the parent compound, which is not influenced by chemical doping, is an issue that requires urgent theoretical attention.

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