Evidence for the coexistence of low-dimensional magnetism and long-range order in Ca$_3$CoRhO$_6$

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Abstract. – We report the results of neutron powder diffraction studies on the spin-chain compound Ca$_3$CoRhO$_6$ in the temperature range from 3 to 293 K. Bragg peaks due to magnetic ordering start appearing below about 100 K. The most interesting observation is that there is a diffuse magnetic peak superimposed over the strongest magnetic Bragg peak. The diffuse magnetic intensity is observed below as well as above 100 K. This finding provides a new insight into the physics of this compound as though the low-dimensional magnetic interaction coexists with long-range magnetic order—a novel situation among quasi–one-dimensional oxides.

Introduction. – The pseudo low-dimensional insulators have been of constant interest among physicists and chemists [1] for the past few decades as the interplay between intra-chain and inter-chain interactions has been found to result in novel magnetic anomalies [2]. Till to-date, in all such compounds, the presence of weak inter-chain magnetic coupling results in eventual loss of the identity of the chains, thereby paving the way for three-dimensional magnetic ordering at low temperatures. In this article, we report the temperature-dependent neutron diffraction data for a quasi–one-dimensional compound, Ca$_3$CoRhO$_6$, which apparently has the signatures of the correlations within a chain coexisting with long-range magnetic order, thereby providing a novel situation in this direction of research. The compound under investigation crystallizes in the K$_4$CdCl$_6$-type rhombohedral structure (space group R3c). This class of compounds, (Sr, Ca)$_3$MXO$_6$ (M, X = a metallic ion, magnetic or non-magnetic), have started attracting attention in recent years due to the presence of spin-chains (M–X) separated by Sr/Ca ions (see refs. [3–16] and references cited therein) and the magnetic chains form a triangular lattice (with an inter-chain spacing of 5.313 Å in the present compound). In this structure, there is face-sharing of octahedra of X ions and trigonal prisms of M ions. Of these, the title compound is of special interest. On the basis of previous neutron diffraction
data [16], it was inferred that this compound can be classified as a “Partially Disordered Antiferromagnet (PDA)” —a novel magnetic structure very rarely encountered [16] in magnetism. In this magnetic structure, there is a temperature range (below the paramagnetic state) in which the chains at the apices of the hexagon are antiferromagnetically coupled to each other, whereas the one at the center of the hexagon is left incoherent; as the temperature is lowered further, the incoherent chains can undergo spin-glass freezing (as proposed for the present case [16]) or couple ferrimagnetically with other chains. It has been found that the dc magnetic susceptibility ($\chi$) exhibits a complex behavior at temperatures below 300 K (refs. [14,15]), reflecting the existence of different temperature regions: there is a broad maximum in the plot of $\chi$ vs. $T$ around 100 to 150 K, with an isothermal magnetization behavior highly non-linear with the magnetic field in the intermediate $T$-range (40–90 K), but tending to a constant (zero-field–cooled) $\chi$ at still lower temperatures. However, ac susceptibility exhibits a broad feature in the range 40–70 K with an unusually strong frequency dependence, implying a more exotic magnetic behavior of this compound, thereby warranting further investigations for better understanding [15]. Motivated by this situation, we have subjected this compound to more careful neutron diffraction investigations as compared to those reported in ref. [16], the new results of which are reported in this article. It is worthwhile stating that, in sharp contrast to the situation in this material, the analogous Fe compound exhibits a simple magnetic behavior [14] with a magnetic ordering temperature around 15 K.

Sample preparation. – The polycrystalline specimen of Ca$_3$CoRhO$_6$ was synthesized by a conventional 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. The pre-reacted powder was then 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 was single phase. Neutron powder diffraction measurements were performed at the constant wavelength thermal neutron instrument SV7 at the DIDO research reactor in the Forschungszentrum Jülich [17] using the diffractometers SV7-a and SV7-b with neutron wavelengths of 1.095 Å and 2.332 Å, respectively. Both instruments are equipped with JULIOS-type linear scintillation detectors. The sample was contained in a vanadium cylinder of 8 mm diameter and 30 mm height and inserted in a helium refrigerator cryostat equipped with vanadium windows. Full-long-term diffraction patterns were collected at 293, 100, and 3 K in the short-wavelength configuration (λ = 1.095 Å) and at 4 K and 293 K using the long wavelength of 2.332 Å. Short-term runs were performed in the temperature regime between 3 K to 250 K for both wavelengths.

Results and discussion. – We show in fig. 1 the temperature dependence of the raw diffraction patterns in the low-angle region with the long wavelength. We have carried out a crystal structure data analysis by full-pattern Rietveld refinements using Fullprof [18]. A two-step data handling was applied to the magnetic structure analysis using 1) a modified version of the program Profan [19] and 2) the full-matrix least-squares program IC-POWLS [20]. Profan fits pre-selectable profile functions, e.g. Gaussian or Lorentzian, into measured peaks or peak clusters and individually refines sets of three profile parameters each for peak position 2Θ, half-width FWHM, and peak height $H$. This procedure permits the separation of broad diffuse magnetic scattering contributions from the pure Bragg peaks and thus the separation of disorder and long-range order effects, respectively. The refined profile parameters are used for the calculation of integrated peak intensities. IC-POWLS uses these intensities as observations for magnetic structure refinement calculations. With our analysis, we confirm that Ca$_3$CoRhO$_6$ crystallizes in the rhombohedral space group $R\bar{3}c$ with the lattice constants, $a = 9.214(2)$ Å and $c = 10.742(2)$ Å at 293 K, in good agreement with those from X-ray
Fig. 1 – Temperature dependence of diffraction patterns of Ca$_3$CoRhO$_6$ measured with a neutron wavelength of 2.332 Å.

diffraction [15]. The atomic site occupations are Ca in 18e $(x, 0, 1/4)$, Co in 6a $(0, 0, 1/4)$, Rh in 6b $(0, 0, 0)$ and O in 36f $(x, y, z)$. As the temperature is lowered below 100 K, a prominent new line appears in the pattern around 15.5 degrees scattering angle attributable [16] to the onset of long-range magnetic ordering. The parameters characterizing the long-range magnetic order obtained from our analysis of the diffraction data at 4.2 K are tabulated in table I. We obtain a moment value of 3.7(4) $\mu_B$ parallel to $c$ per antiferromagnetically ordered Co-ion (4 out of 6 in the unit cell) in fair agreement with the value of 4$\mu_B$ for Co-ions in a trivalent state and with high-field magnetization data at 4.2 K and no moment on Rh, in accordance with [16].

We now turn to the point of central importance. A careful look at our raw diffraction patterns shown in fig. 1 indicated to us that there is in addition to the magnetic Bragg peak a broad weak peak ("magnetic short-range-order–like") that is present at all investigated temperatures, both above and below the long-range magnetic ordering temperature. We have

Table I – Parameters of the antiferromagnetic structure of Ca$_3$CoRhO$_6$ at 4.2 K.

| Magnetic atom | Position in chemical cell | Moment orientation     | Magnetic moment (µ$_B$) |
|---------------|---------------------------|------------------------|-------------------------|
| Co-1          | 2/3, 1/3, 0.0833          | + (parallel to c)      | 3.7(4)                  |
| Co-2          | 0, 0, 0.25                | − (anti-parallel to c) | 3.7(4)                  |
| Co-3          | 1/3, 2/3, 0.4167          | not ordered             | 0                       |
| Co-4          | 2/3, 1/3, 0.5833          | + (parallel to c)      | 3.7(4)                  |
| Co-5          | 0, 0, 0.75                | − (anti-parallel to c) | 3.7(4)                  |
| Co-6          | 1/3, 2/3, 0.9167          | not ordered             | 0                       |
carefully obtained the patterns at several temperatures for the shorter wavelength (1.095 Å) and the typical patterns obtained are shown in fig. 2 for 3, 100, and 293 K. The strongest magnetic reflection (100) is clearly visible at 2θ = 8 degrees as a superstructure reflection at 3 K and a diffuse intensity enhancement at 100 K (figs. 2 and 3). This is visible even in the diffraction patterns measured with increased resolution using a neutron wavelength of 2.332 Å (fig. 4). It may be noted that in the latter case there is a clear separation of the (110) and (012) Bragg reflections when compared to the low-resolution data of fig. 2 and the strongest magnetic peak at 2θ = 16.5 degrees is superimposed by a broad diffuse share (dotted line) as obtained by peak profile fits using two Gaussian-type curves. In order to highlight the features due to the diffuse part, we have fitted the curves (for short wavelength) around 2θ = 8 degrees to a superposition of two Gaussians with different widths (one of them resolution-limited), as shown in fig. 3.

In figs. 5, 6, and 7 we present the temperature dependence of the relevant parameters (intensity, width and position, respectively) of the diffuse peak, apart from showing the temperature dependence of the intensity related to the long-range magnetic order.

The most remarkable feature is that the diffuse peak intensity persists in the entire temperature range of investigation as though the magnetic ions (Co-3 and Co-6, see table I) responsible for this peak are only weakly coupled to those undergoing long-range magnetic ordering (Co-1, Co-2, Co-4, and Co-5). The only influence of long-range magnetic ordering appears to narrow this peak marginally and to pull out some intensity below 100 K. A closer inspection of the temperature dependence of the intensity of the diffuse peak (fig. 5) is quite revealing. The peak intensity increases as the temperature is lowered below 300 K, attaining a maximum around 100 to 150 K, followed by a decrease at lower temperatures. This qualitatively mimics the behavior of $\chi$ expected for antiferromagnetic correlations in

**Fig. 2**
Comparison of Ca$_3$CoRhO$_6$ diffraction patterns measured at 3 K, 100 K, and 293 K using a neutron wavelength of 1.095 Å. The strongest magnetic reflection (100) is clearly visible as a superstructure reflection at 3 K and as a diffuse intensity enhancement at 100 K.

**Fig. 3**
Magnetic reflection (100) of fig. 2 in an expanded scale according to its appearance in the temperature difference patterns. Profile fits (lines) show that the peak at 3 K is composed of a Gaussian (resolution-limited) Bragg peak resulting from long-range magnetic order and a diffuse share which also exists at 100 K.
Fig. 4 – Comparison of the diffraction patterns of Ca$_3$CoRhO$_6$ measured with increased resolution at 293 K (crystal structure indexing) and at 4 K using a neutron wavelength of 2.332 Å. Note the clear separation of the (110) and (012) Bragg reflections if compared to the low-resolution data of fig. 2. The strongest magnetic peak at 2θ = 16.5 degrees is superimposed by a broad diffuse share (dotted line) as obtained by peak profile fits using two Gaussian-type curves. The temperature difference pattern (4K–293K, bottom) shows the pure long-range magnetic Bragg scattering after subtraction of the diffuse part.

one-dimensional chains [21] and is actually observed in the χ data. The reader may see in fig. 1 of ref. [15] the tendency for the flattening of χ in the range 100–150 K as though there is a Bonner-Fischer–type peak and the fall of χ below 100 K is presumably intercepted by the enhancement of χ due to the onset of long-range magnetic order. Thus, the present neutron

Fig. 5

Fig. 6

Fig. 5 – Temperature dependence of the integrated (100) magnetic Bragg intensity and of the diffuse intensity of Ca$_3$CoRhO$_6$ (measured with λ = 1.095 Å) after subtraction of a constant background assuming Gaussian line shapes for both lines.

Fig. 6 – Temperature dependence of the line width (FWHM) of the diffuse peak of Ca$_3$CoRhO$_6$. 
Fig. 7 – Temperature dependence of the angular position of the diffuse peak of Ca$_3$CoRhO$_6$ assuming a Gaussian line shape.

data is able to distinctly delineate the features due to long-range magnetic ordering and the intra-chain effects. We therefore believe that the so-called “incoherent chains” described in the introduction retain their individuality (“isolated intra-chain interactions”) down to low temperatures. The width of the broad diffuse peak underneath the strongest magnetic Bragg reflection (100) (compare fig. 6) has been used for an estimation of the correlation length at 4 K. The estimation is based on the reciprocal relation between cluster size $D$ (Å) and peak half-width broadening FWHM (degrees) according to

$$D = \frac{\lambda \cdot 57.3}{\cos \Theta \cdot \text{FWHM}}.$$  

By taking the actual experimental parameters (neutron wavelength $\lambda = 1.096$ Å, central diffuse peak position $2\Theta = 7.4$ degrees and FWHM = 2.75 degrees after correction for instrumental resolution), the calculation results in a characteristic value of 23 Å for the linear extension of the antiferromagnetic chain segments that coexist with the long-range magnetic order. In the region without long-range order, i.e. above 100 K, the diffuse peak is somewhat broader, hence the characteristic length for the one-dimensional cluster size is correspondingly smaller (16 Å). Thus, the influence of long-range magnetic order is to increase the correlation length. The position-shift of the diffuse peak with decreasing temperature to larger scattering angles (see fig. 7) indicates the reduction of short-range correlations from larger distances and/or larger numbers of Co atoms (nearest, next-nearest and even more neighbors) to a smaller number and finally to only Co-3 and Co-6 atoms with an inter-atomic distance of 6.415 Å. However, because of the limitation of the diffuse experimental data in Q-space (only one maximum of the scattering function is observed) the data cannot be used for the calculation of a pair-correlation function.

**Conclusion.** – From a detailed neutron diffraction investigation we find direct evidence for the coexistence of isolated intra-chain interactions and long-range magnetic ordering due to inter-chain interactions from the rest of the chains in a spin-chain system, Ca$_3$CoRhO$_6$. This is a fascinating finding in the field of quasi-one-dimensional magnetism.

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