



SPIN-GLASS FORMATION IN Co_2RuO_4

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ABSTRACT

Magnetic susceptibility and powder neutron diffraction results are reported on the cubic spinel Co_2RuO_4 . These measurements indicate spin-glass formation in this compound, with a freezing temperature of about 16 K. Magnetic susceptibility results are also reported on ZnCoRuO_4 , a spinel in which only the Ru^{3+} ions are magnetic. No magnetic order was found in ZnCoRuO_4 down to 2 K, indicating extremely weak interactions between the octahedral Ru^{3+} ions in these materials. © 1999 Elsevier Science Ltd

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INTRODUCTION

Aside from perovskites and perovskite-related materials, spinels are probably the most heavily studied class of transition metal oxides. Interest in spinels grew rapidly just after World War II, when Néel explained the magnetism of ferrites [1] and Verwey was studying the metal–insulator transition in Fe_3O_4 that today bears his name [2]. Spinel ferrites, which are good magnetic insulators, are of enormous importance in the electronics industry, and other spinels are important for their catalytic and electrochemical properties. The magnetic

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and electronic transport properties of spinels continue to attract interest. Prior to the emergence of high- T_c superconductivity, the spinel LiTi_2O_4 ($T_c = 14$ K) was noted for having the highest transition temperature of any oxide. Recently, heavy fermion behavior was reported [3] in the spinel LiV_2O_4 , making it the first d -electron material with an effective fermion mass comparable to f -electron materials. Also, if one looks slightly further afield and includes chalcogenide spinels, one finds magnetic semiconductors, such as HgCr_2Se_4 , that show colossal magnetoresistive behavior surpassing that of the manganites [4].

As part of a broad-based effort to study electron correlations in oxides containing second- and third-row transition metals, we have investigated the magnetic properties of the spinel Co_2RuO_4 . Although this compound was first synthesized by Dulac [5] in 1969, little is known about this material except its room temperature resistivity ($7 \Omega \text{ cm}$) [6] and its isomer shift (relative to Ru metal) obtained using Mössbauer spectroscopy [7]. A cation configuration of $\text{Co}^{2+}[\text{Co}^{3+}\text{Ru}^{3+}]\text{O}_4$ was proposed by Gibb *et al.* [7] based on a combination of chemical reasoning and Mössbauer spectroscopy. Here the tetrahedral (A) sites are occupied by Co^{2+} (high-spin, $S = 3/2$) ions, and the octahedral (B) sites are jointly occupied by Co^{3+} (low-spin, $S = 0$) and Ru^{3+} (low-spin, $S = 1/2$) ions. Later Mössbauer measurements on LaRuO_3 by the same group [8] showed that Ru^{3+} has a distinctive isomer shift, thus confirming the cation assignment proposed in ref. 7.

Generally, in spinels, the A–B interaction is much stronger than either the A–A or B–B interaction, and a classical collinear Néel ferrimagnet is produced. Such is the case, for example, in $\text{Co}^{2+}[\text{Co}^{3+}\text{Mn}^{3+}]\text{O}_4$, which orders ferrimagnetically at about 180 K. The magnetic ground state of Co_2RuO_4 , however, is a spin glass. This is somewhat surprising, because the Ru^{3+} $4d$ orbitals are expected to strongly hybridize with the O^{2-} $2p$ orbitals, and strong hybridization is expected to enhance superexchange rather than weaken it. On the other hand, low-spin Ru^{3+} has its t_{2g} manifold practically full, and superexchange interactions involving orbitals that are more than half full are generally weaker than those involving less than half-full orbitals [9] (this rule has exceptions; see Aquino *et al.* [10] for an example of a low spin Ru^{3+} molecular dimer with a superexchange coupling constant greater than 100 K).

Here we present neutron diffraction and ac and dc magnetic susceptibility measurements on Co_2RuO_4 . These measurements show that Co_2RuO_4 undergoes a spin-glass transition at about 16 K. We also present magnetic susceptibility measurements on ZnCoRuO_4 , in which Ru^{3+} is the only magnetic ion present. These measurements indicate that Ru–Ru interactions are weak, and that the likely source of frustration in Co_2RuO_4 is the competition between A–A and A–B interactions.

EXPERIMENTAL

Co_2RuO_4 was originally synthesized by Dulac [5] by combining Co_3O_4 and RuO_2 and heating at 950°C . The result was a cubic spinel with a lattice parameter of 8.241 \AA . Noting the volatility of the higher oxides of Ru, Gibb *et al.* [7] used 25% excess RuO_2 and Co_3O_4 , and heated at 1100°C for 24 h; the result was a cubic spinel with a lattice parameter $a = 8.317 \text{ \AA}$. More recently, Krutzsch and Kemmler-Sack (KK-S) [11] prepared a series of spinels, $\text{Co}_{3-x}\text{Ru}_x\text{O}_4$, and found that the lattice parameter varied from 8.183 \AA for $\text{Co}_{2.6}\text{Ru}_{0.4}\text{O}_4$ to 8.344 \AA for Co_2RuO_4 . The KK-S method starts with the metals rather than the oxides, and involves many regrindings and comparatively brief periods in the furnace. For

Co_2RuO_4 , for example, the KK-S method calls for six 30-min firings at 1100°C, with intermediate regrindings, followed by three 5-min firings at 1200°C, again with intermediate regrindings. Our approach was to combine stoichiometric proportions of Co_3O_4 (Johnson Matthey Puratronic, 99.9985%), Ru powder (Johnson Matthey, -325 mesh, 99.95%), and RuO_2 (synthesized from the Ru powder), ball mill thoroughly, and seal the powder in a Pt tube. The tube was then heated at 1200°C overnight and allowed to cool in the furnace. The result was single-phase according to X-ray diffraction, with a lattice parameter of 8.33 Å obtained by indexing a few high-angle reflections. Powder neutron diffraction, however, yielded a refined lattice parameter of 8.310 Å and revealed the presence of a small amount of RuO_2 in the synthesized powder. Our sample was, therefore, slightly Ru deficient. It is unlikely that this deficiency will affect the present results, however, because measurements of the magnetic susceptibility on all our Co_2RuO_4 samples, synthesized using several different techniques and having a wide spread of lattice parameters, are all in qualitative agreement, and show only extremely minor quantitative differences. The magnetic properties of Co_2RuO_4 , therefore, do not appear to be sensitive to deviations of the Ru stoichiometry at the level of a few percent.

The ac and dc susceptibility measurements reported here were performed using a Quantum Design PPMS coil-extraction magnetometer on a 425-mg sample. Neutron diffraction data were collected using the HB4 high-resolution powder diffractometer at the High Flux Isotope Reactor at ORNL. This instrument has a Ge (115) monochromator which, when 2-theta = 87°, selects an incident neutron wavelength of 1.5 Å. The neutron wavelength was determined more precisely to be 1.4993(2) Å on the basis of unit cell refinements for a silicon standard. Soller slit collimators of 12' and 20' are positioned before and after the monochromator crystal, respectively. An array of 32 equally spaced (2.7°) 3He detectors, each with a 6' mylar foil collimator, can be step-scanned over a range of up to 40° for scattering angles between 11° and 135°. The sample was placed in a vanadium can (9 mm i.d. by 5 cm) held in a closed-cycle He refrigerator for data collection at 300, 25, and 4 K over the 2-theta range of 11° to 135° in steps of 0.05°. For these data collections, the detector array was scanned in two segments to overlap up to eight detectors in the middle of the pattern. Overlapping detectors for a given step serves to average the counting efficiency of each detector. Input for the Rietveld refinement program was prepared by interpolating a constant step-size data set from the raw data, because the spacing between the detectors is not exactly the same. The data were also corrected for the variation in detector efficiencies, which were determined using a vanadium standard. Rietveld refinements were made using the GSAS software [12], and the coherent scattering lengths used were 2.53 (Co), 7.21 (Ru), and 5.81 (O) fm [13].

RESULTS AND DISCUSSION

Rietveld refinement of the 300 K neutron powder diffraction data allowed the cation distribution to be well determined because of the large scattering length difference between Ru and Co. The resulting cation distribution was found to be $\text{Co}[\text{Ru}_{0.892}\text{Co}_{1.108}]_4\text{O}_4$. RuO_2 was included as a second phase in the refinements and was determined to be present 3.6% by weight. The results of the refinements appear in Table 1. For the spinel phase, going from high to low temperature causes the A–O distances to lengthen slightly and the B–O distances to shorten. Using a structural model with nuclear scattering gives equally good fits for the low temperature data; thus, additional scattering due to magnetic ordering is not evident. In the

TABLE 1
Crystal Structure Data for Co[RuCo]O₄ Spinel, *Fd3m* (No. 227, Origin Choice 2) $Z = 8$

Temperature	4 K	25 K	296 K
Cell a (Å)	8.2817(2)	8.28187(9)	8.3095(1)
ρ_{calc} (g/cm ³)	6.510	6.510	6.445
Reflections	41	41	41
R_p	0.0784	0.0700	0.0669
R_{wp}	0.0637	0.0576	0.0544
Goodness of fit, χ^2	1.706	1.885	1.740
$U_{\text{iso}}(\text{A})$ (Å ²) Co	0.011(1)	0.0095(9)	0.014(1)
$U_{\text{iso}}(\text{B})$ (Å ²) 0.554(9)Co:0.446Ru	0.0088(4)	0.0081(4)	0.0095(6)
$x(\text{O})$	0.26187(7)	0.26179(7)	0.26131(7)
$U_{\text{iso}}(\text{O})$ (Å ²)	0.0101(3)	0.0099(3)	0.0124(4)
B–O (Å)	1.963(1)	1.9622(9)	1.9878(5)
A–O (Å)	1.9770(5)	1.9776(5)	1.961(1)

Atom positions: A: $8a$ 1/8,1/8,1/8; B: $16d$ 1/2,1/2,1/2; O: $32e$ x,x,x

spinel, the A . . A , B . . B, and A . . B distances are determined by the lattice parameter, $\sqrt{3}a/4$, $\sqrt{2}a/4$, and $\sqrt{11}a/8$, respectively, so A . . A > A . . B > B . . B. The interpolyhedral angles depend on both the lattice parameter and the oxygen coordinate; for the 300 K structure the A–O–A, A–O–B, and B–O–B angles are 77.3°, 121.4°, and 95.2°, respectively.

The zero-field-cooled (ZFC) magnetic susceptibility of Co₂RuO₄ appears in the main panel of Figure 1. A sharp peak at about 16 K suggests an antiferromagnetic transition, but the divergence of the ZFC and FC curves below 12 K (inset Fig. 1) is not consistent with a classical Néel antiferromagnet. A conventional ferrimagnetic transition is also unlikely, because in that case domain motion would lead to an even greater difference between the FC and ZFC curves. In Figure 2 we plot a magnetization loop taken at 5 K, which shows a small amount of hysteresis. There was no hysteresis in a magnetization loop taken at 25 K, clearly indicating that a magnetic transition occurs between 4 and 25 K.

The most plausible explanation of the data is the formation of a spin glass below a freezing temperature of $T_f = 16$ K. The ac susceptibility results shown in Figure 3 support this conclusion, in that the behavior of χ' and χ'' strongly resembles that of insulating spin-glass systems such as Eu_{0.2}Sr_{0.8}S [14]. In such systems the peak in both χ' and χ'' moves to higher temperatures with increasing frequency. Also, the peak amplitude of χ' decreases with increasing frequency, whereas the peak amplitude of χ'' increases with increasing frequency. This is precisely the behavior observed in Figure 3.

The time dependence of the isothermal remanent magnetization is also consistent with spin-glass formation. After cooling the sample in a field of 20 kOe, the field was switched off and the magnetization was measured as a function of time. The results are plotted in Figure 4. Although the precise functional dependence of the remanent magnetization varies from system to system [15], the qualitative behavior shown in Figure 4 strongly resembles that of classical spin-glass systems.

Powder neutron diffraction measurements were performed above and below the spin freezing temperature in an attempt to look for long range magnetic order. The results appear in Figure 5. If a conventional collinear ferrimagnetic state were to be formed such as occurs in Co²⁺[Co³⁺Mn³⁺]O₄, we would expect to see a strong enhancement of several of the low

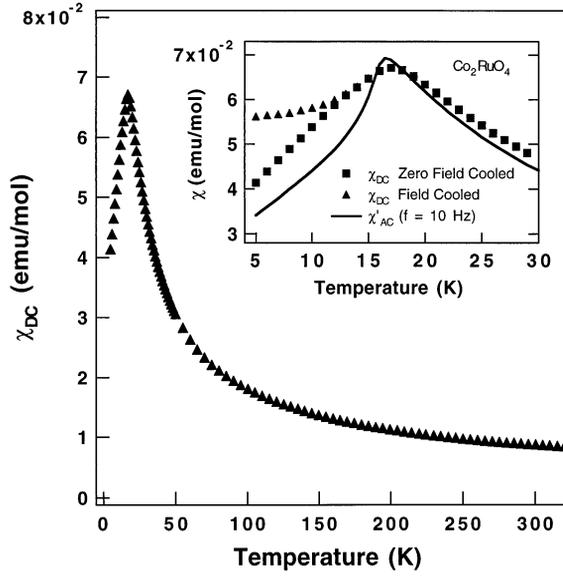


FIG. 1

Main panel: zero-field-cooled dc susceptibility of Co_2RuO_4 vs. temperature obtained on a 440 mg sample in a field of 5000 Oe. Inset: low-temperature zero-field-cooled and field-cooled χ_{DC} on Co_2RuO_4 . The real part of the ac susceptibility χ'_{AC} is shown for comparison.

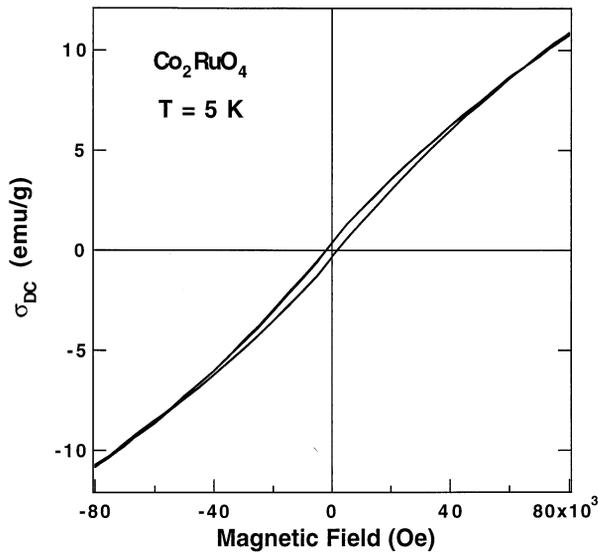


FIG. 2

M vs. H loop obtained on Co_2RuO_4 at 5 K.

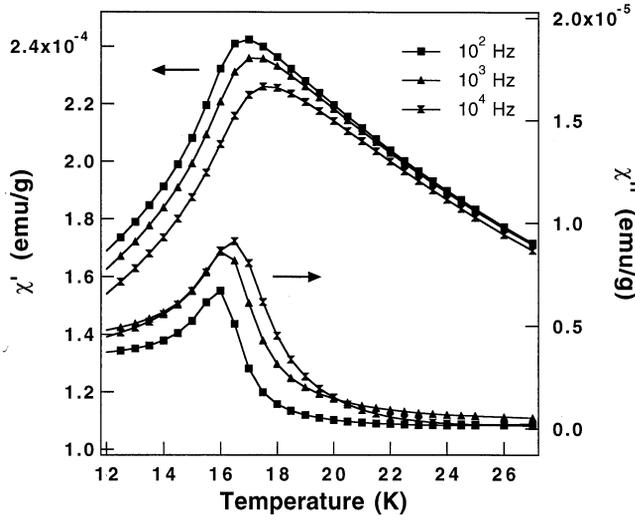


FIG. 3

Real (χ') and imaginary (χ'') part of the ac susceptibility of Co_2RuO_4 vs. temperature at the indicated frequencies.

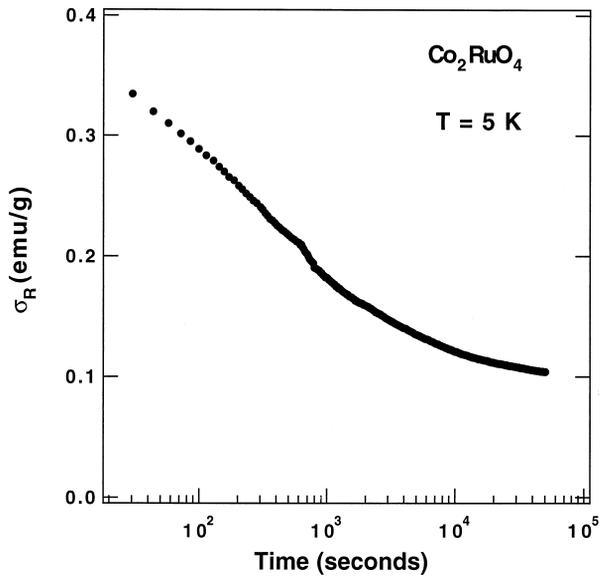


FIG. 4

Time dependence of the isothermal remanent magnetization of Co_2RuO_4 . The sample was cooled in a 20 kOe field, the field was switched off, and the magnetization was measured as a function of time.

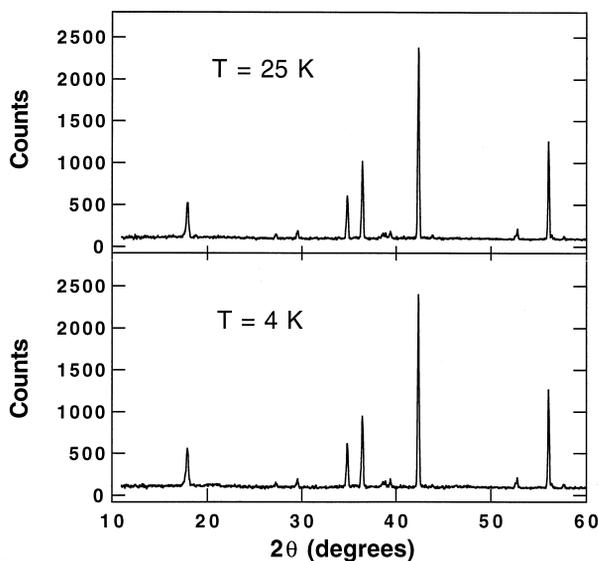


FIG. 5

Neutron diffraction patterns of Co_2RuO_4 obtained at 25 K and at 5 K. There is no indication of long-range magnetic order in the diffraction pattern.

angle reflections such as (111) and (220), and weaker enhancements at higher angles [16,17]. As Figure 5 makes clear, there is no evidence of long-range magnetic order in Co_2RuO_4 ; this is again consistent with spin-glass formation.

In Figure 6 we plot the reciprocal susceptibility $1/\chi_{\text{mol}}$ vs. temperature for Co_2RuO_4 . It is apparent from the nonlinearity of the curve that the data do not obey a Curie–Weiss law over any well-defined region. This makes interpretation of the data difficult, because there may be several different contributions to the magnetism and there is simply not enough information to sort them all out. Below we use the simplest approach that is able to effectively model the data: a Curie–Weiss term plus a temperature-independent paramagnetic term. Although this approach is reasonable and gives reasonable results, especially for ZnCoRuO_4 , it must be kept in mind that this model may, in fact, be too simple, and a healthy skepticism should be maintained regarding the physical content of the fitting parameters.

Although interactions between magnetic sublattices can cause a deviation from Curie–Weiss behavior, a more straightforward explanation of the data involves a temperature-independent Van Vleck term. Such terms are expected in Co-containing materials because of low-lying crystal field levels. In tetrahedrally coordinated Co^{2+} , for example, $\Delta = 3700 \text{ cm}^{-1}$, and in octahedrally coordinated Co^{3+} $\Delta = 19,000 \text{ cm}^{-1}$ [18]. These splittings yield calculated free-ion temperature-independent paramagnetic terms of $0.57 \times 10^{-3} \text{ emu/g-atom}$ and $0.25 \times 10^{-3} \text{ emu/g-atom}$ for Co^{2+} and Co^{3+} , respectively [19]. If we fit the susceptibility data to the equation $\chi(T) = \alpha + C/(T - \theta)$, an excellent fit is obtained with $\alpha = 0.004 \text{ emu/mol}$, $C = 1.44 \text{ emu-K/mol}$, and $\theta = -4.0 \text{ K}$. Although α is considerably larger than the theoretically predicted free-ion value of 0.00082 emu/mol , susceptibility measurements (discussed below) on ZnCoRuO_4 , a material in which only the Ru^{3+} ions are magnetic, show that the temperature-independent paramagnetic term is indeed large in this class of materials

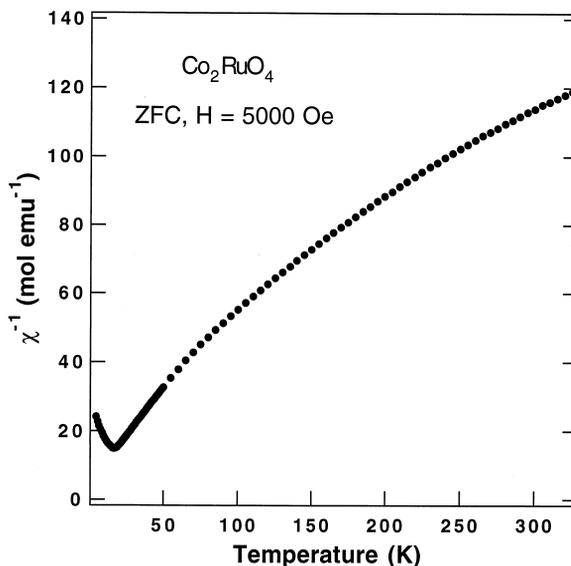


FIG. 6
Reciprocal susceptibility of Co_2RuO_4 vs. temperature.

and that the non-Curie–Weiss behavior is not due to an interaction between magnetic sublattices. The Curie constant resulting from the fit is considerably smaller than the $C = 2.25$ emu-K/mol expected from the spin-only values of the magnetic ions, especially since the orbital part should add for Co^{2+} which has a more than half-filled d shell. A possible explanation of this behavior is that short range antiferromagnetic order is present above T_f that tends to reduce the value of the effective moment. Similar behavior was observed by Battle *et al.* [20] in the Ruddlesden–Popper phase $\text{Sr}_3\text{FeRuO}_7$. Like Co_2RuO_4 , the magnetic ground state of $\text{Sr}_3\text{FeRuO}_7$ is also a spin glass. Finally, the fitted Weiss constant θ is small; this is consistent with competing interactions and spin-glass behavior.

Disorder and competing interactions are both required for spin-glass formation. In Co_2RuO_4 , the disorder is provided by the random occupation of the octahedral sites by Co^{3+} and Ru^{3+} ions. It is not obvious, however, which interactions are in competition. Generally, in spinels, the A–B interaction is dominant, and a collinear ferrimagnetic ground state is favored. This is the case, for example, in Co_2MnO_4 . In cobaltite spinels, however, for reasons that are not completely clear, the A–A interaction is unusually strong. In $\text{Co}^{2+}[\text{Co}^{3+}\text{Co}^{3+}]\text{O}_4$, for example, the A sites order antiferromagnetically at 40 K, and no moment is found on the B sites [19]. Another example is $\text{Co}^{2+}[\text{Co}^{2+}\text{Ti}^{4+}]\text{O}_4$, which has a ground state consisting of a ferrimagnetic longitudinal component and a spin-glass transverse component [21].

In order to cast some light on this question, we prepared $\text{Zn}^{2+}[\text{Co}^{3+}\text{Ru}^{3+}]\text{O}_4$. In this compound only the Ru^{3+} ions are magnetic, which allowed us to study the B–B interaction. The magnetic susceptibility of ZnCoRuO_4 appears in Figure 7. The susceptibility is paramagnetic and shows no sign of magnetic ordering down to 2 K. This is a clear indication that the B–B interaction is extremely weak in these materials. Also shown in Figure 7 is a fit to the modified Curie–Weiss function used above. The parameters in this case are $\alpha = 0.0024$

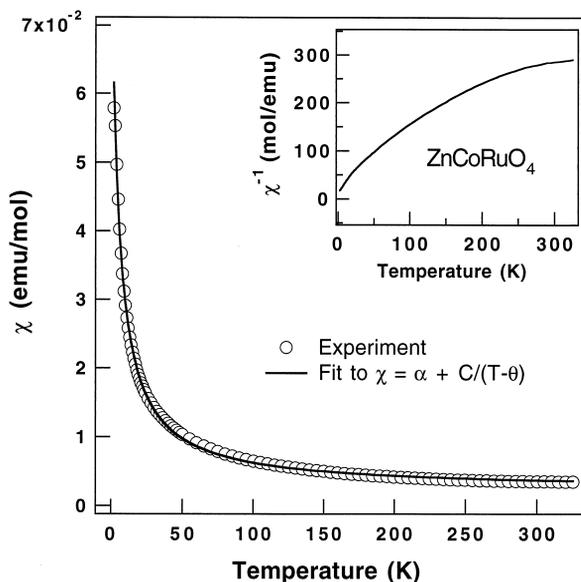


FIG. 7

Main panel: dc magnetic susceptibility vs. temperature for a 465 mg sample of ZnCoRuO_4 . Inset: reciprocal magnetic susceptibility of ZnCoRuO_4 .

emu/mol, $C = 0.41$ emu-K/mol, and $\theta = -4.9$ K. This gives an effective moment of $p = 1.8 \mu_B$ in excellent agreement with the $p = 1.73 \mu_B$ expected from the spin-only value of the $S = 1/2 \text{ Ru}^{3+}$ ions. The large value of α should be noted. Since this large value was observed in a system of weakly interacting paramagnetic moments, it tends to support the interpretation of the susceptibility of Co_2RuO_4 given above.

If the B–B interaction is negligible, we are left with competing A–A and A–B interactions. In light of the reduced value of the effective moment found above, it is likely that both of these interactions are antiferromagnetic.

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