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$CaRuO_3$ is not a paramagnetic material

I. Felner and I. Nowik
The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

I. Bradaric
''Vinca'' Institute of Nuclear Sciences, Laboratory for Theoretical and Condensed Matter Physics, P.O. Box 522, Belgrade 11001, Yugoslavia

M. Gospodinov
Bulgarian Academy of Sciences, Institute of Solid State Physics, 72 Tzarigradsko Chaussee Boulevard, Sofia 1784, Bulgaria

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Magnetic studies of ceramic and single crystal $CaRuO_3$ samples demonstrate that irreversibility appears in the zero-field-cooled field-cooled curves only when measured at low applied magnetic fields. A small hysteresis loop opens at low temperatures, and the remanent magnetization decreases with temperature and disappears at ~90 and 71 K for the ceramic and crystal samples, respectively. The easy axis for the magnetization is in the [001]. Mössbauer studies of 1% ^{57}Fe doped in $CaRuO_3$ show a magnetic sextet at 4.1 K which disappears at 90 K. It is proposed that $CaRuO_3$ is not paramagnetic, but rather shows the characteristics of short range magnetic interactions, possibly as spin-glass-like behavior. ^{57}Fe ions experience an exchange field from their magnetic Ru neighbors and also become magnetically ordered.

Ternary ruthenates exhibit a wide range of electronic and magnetic properties, ranging from superconductivity to ferromagnetism.[1–12] One class of oxides that has attracted renewed interest are the orthorhombic perovskite MRuO$_3$ (M = Ca and Sr) compounds,[3] due to their unusual magnetic properties. Both compounds have the same orthorhombic crystal structure and show metal-like conductivity. $SrRuO_3$ is an itinerant ferromagnetic metal with a Curie temperature $T_c \sim 160$ K, whereas the magnetic ground state of $CaRuO_3$ is little more controversial. Recent papers indicate *paramagnetic* behavior (or exchange enhanced paramagnetism) down to 30 mK, which is also supported by the single line shape of a ^{99}Ru Mossbauer spectrum measured at 4.1 K.[13] On the other hand, based on the deviation from linearity of the reciprocal susceptibility, an antiferromagnetic (AFM) ground state was suggested, with a Néel temperature $T_N \sim 110$ K.[1] This finding is consistent with the AFM ordering found in $Ca_3Ru_2O_7$ and Ca_2RuO_4 single crystals at $T_N = 56$ and 110 K respectively.[14,15] The high and low (temperature) resistivity results indicate that $CaRuO_3$ is a non-Fermi liquid metal.[11]

The stark contrast between $SrRuO_3$ and $CaRuO_3$ is surprising because (a) the two compounds are closely related both chemically and structurally and (b) the closed shell *s*-like character of Sr and Ca do not contribute to the density of states at the Fermi surface and therefore, should not be the origin for the different magnetic ground states of these two compounds. It is therefore assumed, that the different magnetic states of $SrRuO_3$ and $CaRuO_3$ are due to different structural distortions in these materials, most significantly it is the large oxygen octahedra rotation in the Ca compound.[2]

The nature of the magnetic and transport properties of oxide ruthenates with narrow 4 d bands strongly depend on the degree of band filling and bandwidth. $CaRuO_3$ is believed to have a narrow itinerant 4 d-band width (narrower than for $SrRuO_3$), composed of Ru t_{2g} and oxygen $2p$, which is too narrow for magnetic ordering, but not so narrow as to cause $CaRuO_3$ to be nonmetallic.[6] It means that $CaRuO_3$ is on the verge of magnetic ordering and readily evolves into a magnetically ordered phase. Indeed, 5 at. % of Sr, or Na substitution for Ca induces anti-ferromagnetic or spin glass ordering at $T = 10$ and 55 K, respectively,[6,8] and for 4–10% of Sn, the system becomes metallic and exhibits a spin frustration or a spin-glass behavior.[16]

We show here a comprehensive study of the magnetic properties of $CaRuO_3$ measured on single crystal and ceramic samples. We demonstrate that irreversibility appears in the zero-field-cooled (ZFC) field-cooled (FC) curves only when measured at low applied magnetic fields. At high applied fields the $M(H)/T$ curves exhibit typical paramagnetic features. To ensure that this effect is intrinsic and not sample dependent, we compare measurements performed on three ceramic samples prepared at different laboratories under various conditions. We have also studied the magnetic anisotropy of $CaRuO_3$ single crystal, and show that the easy axis for the magnetization is in the [001] direction, in contrast to [100] direction found for $SrRuO_3$. It is proposed that $CaRuO_3$ *is not paramagnetic*, but rather shows the characteristics of either long-range magnetic interactions (similar to $SrRuO_3$ and $Ca_3Ru_2O_7$ and Ca_2RuO_4), or (at least) short range interactions, possibly as spin-glass-like behavior.

Ceramic $CaRuO_3$ samples were prepared in Belgrade (sample 1) and in Jerusalem (sample 2) by mixing $CaCO_3$, and RuO_2 (or Ru), and preheating the pressed pellets at 1000 °C for 24 h, and then sintering at 1200 °C for 72 h in air (sample 1) or under oxygen (sample 2). Powder x-ray diffraction (XRD) measurements confirmed the purity of the compounds. Single crystals were grown in Pt crucibles, from a self-flux using a mixture of ground $CaRuO_3$ and $CaCl_2$

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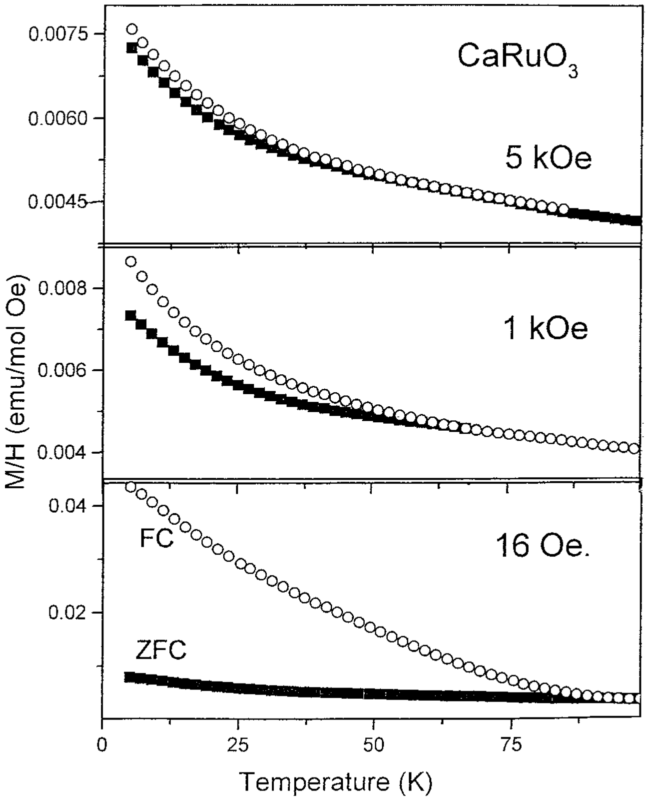

FIG. 1. ZFC and FC susceptibility studies at various applied fields of ceramic $CaRuO_3$.

(ratio 1:30), which was heated to 1260 °C and maintained for homogenization for 48 h, and then cooled at a rate 2 °C/h to 1000 °C, and quenched to room temperatures. Energy-dispersive x-ray analysis (EDAX), scanning electron microscopy (SEM), and XRD were used to determine composition and phase integrity. The crystals tend to form in almost square planar shapes with sizes around $0.4\times 0.4\times 0.02$ mm with the short dimension along the *c* direction [001]. There is no evidence of twinning in the *ab* planes of the crystals down to a scale of ~1–2 μm, and the EDAX analysis confirms the Ru/Ca ratio as 1:1. Magnetic dc measurements were performed in a Quantum Design superconducting quantum interference device magnetometer (SQUID). Mössbauer studies of ceramic samples containing 1% ^{57}Fe (doped for Ru) were performed at 4.1, 90, and 300 K, using a conventional constant acceleration drive and a 50 mCi ^{57}Co:Rh source.

The XRD studies confirm the orthorhombic structure (space-group Pnma), with no secondary phases detected. The lattice parameters for the ceramic samples (1 and 2) and for the $CaRuO_3$ single crystals are $a=5.522(2)$ and 5.526(3) Å, $b=5.360(2)$ and 5.366(4) Å, and $c=7.66(1)$ and 7.662(4) Å, respectively. Within the limits of uncertainty, these lattice parameters, are in excellent agreement with Refs. 3 and 6.

ZFC and FC magnetic $\chi(T)$ curves ($\chi=M/H$), measured up to 5 kOe for sample 1, are shown in Fig. 1. The two branches measured at $H=16$ Oe, merge at $T_{\mathrm{irr}}\sim 90$ K (is it the magnetic ordering temperature). As the field is increased, T_{ir} is shifted to 65 and 55 K for $H=1$ and 5 kOe, respectively, and washes out for $H=10$ kOe. No other anomalies were observed at higher temperatures. All the FC curves (even at low fields) have the typical paramagnetic shape and adhere closely to the Curie-Weiss (CW) law: $\chi=\chi_0+C/(T-\theta)$, where χ_0 is the temperature independent part of χ, C is the Curie constant, and θ is the CW temperature. The extracted values depend strongly on the temperature range of the fitting. A fit of the CW law in the range of $5<T<250$ K yields $\chi_0=2\times 10^{-3}$ emu/mol Oe, $\theta=-36(1)$ K, and an effective moment $P_{\mathrm{eff}}=1.46\mu_B$. However, a fit in the range $120<T<250$ K (above T_{irr} yields $\chi_0=5\times 10^{-4}$ emu/mol Oe, $\theta=-138(1)$ K, and $P_{\mathrm{eff}}=2.66\mu_B$, which is close to the expected $2.83\mu_B$ according to Hund's rule for $Ru^{4+}(4d^4)$ in the low spin ($S=1$) state. Probably, this behavior has led in the past to the conclusion that $CaRuO_3$ is paramagnetic.

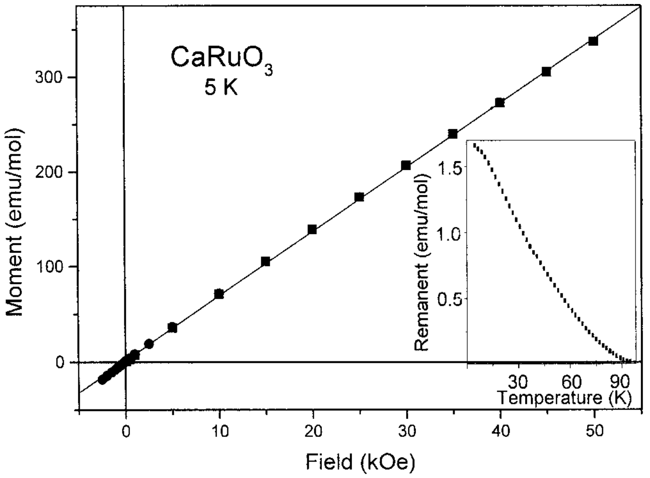

FIG. 2. Isothermal magnetization at 5 K for ceramic CaRuO, and the temperature dependence of the remanent magnetization (inset).

Figure 2 displays the linear isothermal magnetization at 5 K, which is consistent with the data presented in Ref. 6. However, on an expanded scale, a small hysteresis loop is discernible, with (a) a coercive field of ~100 Oe and (b) a remanent moment of 1.6 emu/mol, which disappears around 90 K (Fig. 2, inset). The smooth zero-field specific heat curve for this sample (up to 200 K), is identical to the plot shown in Ref. 5, and no anomaly is visible at any temperature. The linearity of the $C(T)/T$ vs T^2 behavior in the range of $6<T<18$ K, yields the electronic specific heat coefficient $\gamma=77.5$ mJ/mol K^2 and a Debye temperature of 555 (5) K. These values agree perfectly with the published[6] values for $CaRuO_3$ single crystal.

For the sake of brevity, Figs. 1 and 2 present only the data accumulated on sample 1. The same magnetic features have been observed for two different samples prepared in Jerusalem, for a fourth sample prepared and measured at Stores University[17] and for the 1% ^{57}Fe doped sample prepared for our Mossbauer studies. This indicates clearly that the irreversibility observed in $CaRuO_3$ is intrinsic and not sample dependent, and that $CaRuO_3$ is not paramagnetic.[3–9] The possibility that this irreversibility is caused by a magnetic impurity phase not detectable in XRD and/or EDAX, is ruled out for the following reasons. (a) The four ceramic samples have been prepared from different batches of starting materials at different laboratories. (b) The big difference observed in the ZFC and FC branches at low applied fields cannot be accounted for by a minor phase. (c) The data on the single

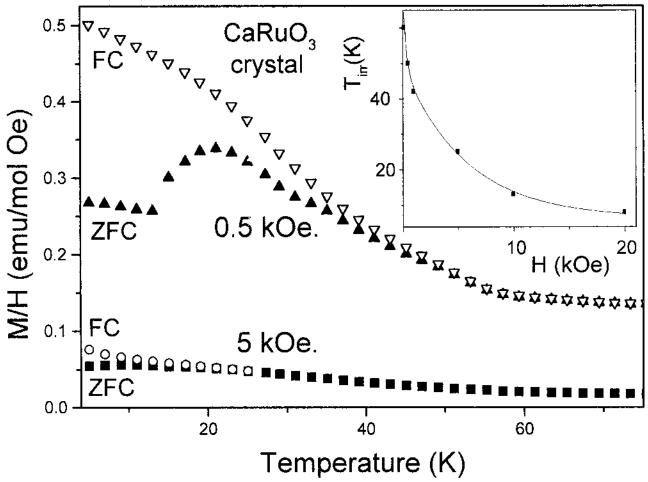

FIG. 3. In-plane ZFC and FC magnetic susceptibility curves measured at 0.5 and 5 kOe for CaRuO$_3$. Single crystal, and the $T_{\mathrm{irr}}(H)$ curve (inset).

crystal sample shown below. One can tentatively argue that pure CaRuO$_3$ is paramagnetic, on the verge of magnetic ordering. The irreversibility shown here, evolves from tiny amounts of impurities (such as Fe and Mn, etc., in the ppm level) which alter the magnetic coupling and give rise to a new magnetically ordered phase. However, the similarity in the magnetic behavior of the four undoped ceramic samples to the 1% Fe doped sample casts some doubt on this interpretation.

The in-plane irreversibility in the ZFC and FC branches measured at 0.5 and 5 kOe for CaRuO$_3$ single crystal, is exhibited in Fig. 3. Note, the broad peak around 25 K in the ZFC curve at 0.5 kOe. At $H=50\,\mathrm{Oe}$, the two curves merge at $T_{\mathrm{irr}}\sim 69\,\mathrm{K}$ (not shown), and the irreversibility remains up to $20\,\mathrm{kOe}(T_{\mathrm{irr}}=8\,\mathrm{K})$. The variation of T_{irr} with the applied field is shown in Fig. 3 (inset). The solid line is a fit to a linear relation between T_{irr} and $\ln H$. The extracted paramagnetic values in the range of $120<T<250\,\mathrm{K}$ yield $\chi_0=9.5\times 10^{-3}\,\mathrm{emu/mol\,Oe}$, $\theta=-36(1)\,\mathrm{K}$, and $P_{\mathrm{eff}}=2.33\mu_B$.

ZFC magnetization $M(H)$ isotherms at 5 K, for an almost square planar shaped CaRuO$_3$ single crystal for H along the ab [100] and the short dimension c planes [001] are shown in Fig. 4 (demagnetization effects are not included). The anisotropy of the magnetization indicates, that the easy axis is along the [001] direction, which is consistent with the out of plane easy axis observed for mixed Ca$_x$Sr$_{1-x}$RuO$_3$ crystals,[6] but in contrast to the in-plane easy axis observed in the FM SrRuO$_3$. Figure 4 also presents the $M(H)$ curve of a number of randomly oriented single crystals, which show intermediate average behavior. Small hysteresis loops are readily observed (in an extended scale) with the same coercive field ($H_C\sim 400\,\mathrm{Oe}$) for both directions. However, the remanent moments along the easy axis are somewhat higher than for the [100] direction, and both disappear at 70(1) K.

Mössbauer studies of dilute iron in CaRuO$_3$ measured at 4.1 and 90 K are shown in Fig. 5. The spectra at 300 and 90 K are identical, and display a single quadrupole doublet (splitting 0.24 mm/sec) of nonmagnetically ordered Fe^{3+} ions in a single site. On the other hand, at 4.1 K two subspectra are observed. A nonmagnetic doublet (~40%), similar to that at 90 K, and a sextet (~60%), with a distribution

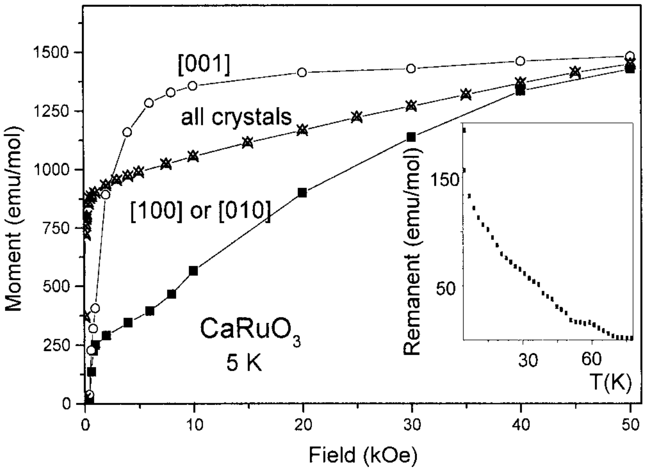

FIG. 4. Isothermal magnetization at 5 K of single crystal CaRuO$_3$ measured along the principal directions, and the $M(H)$ curve for a collection of several crystals, and the temperature dependence of the remanent magnetization (inset).

of the magnetic hyperfine fields with an average value of $H_{\mathrm{eff}}=462\,\mathrm{kOe}$, representing magnetically ordered iron ions. The same isomer shift $(\mathrm{IS})=0.51\,\mathrm{mm/sec}$ (relative to iron metal at 300 K) is obtained for the two subspectra, indicates that all iron ions reside in one crystallographic site.

This magnetic sextet is our supporting evidence that CaRuO$_3$ is magnetically ordered at 4.1 K. The two subspectra are probably due to interexchange of some Ca and Ru ions (caused by Fe doping) in their crystallographic positions. The sextet results from those Fe^{3+} ions which presumably reside in the mixed Ru/Ca sites, and experience an exchange field from their *magnetic* Ru^{4+} neighbors and become also magnetically ordered. The nonmagnetic iron ions are those which sense the *nonmagnetic* Ca^{2+} ions as first nearest neighbors, and therefore experience a reduced exchange field. The large fraction (40%) for the nonmagnetic doublet is probably caused by the fact that the dilute Fe^{3+} ions are more attracted to Ca^{2+} than to the Ru^{4+} in the same crystallographic sites.

We provide here magnetic measurements on ceramic and CaRuO$_3$ single crystal materials, which show definitely many of the features reflecting either to long-range or short-range and/or spin-glass ordering. In particular, (i) the irreversibility below 90 K at low applied field, (ii) the magnetic ^{57}Fe Mössbauer subspectrum at 4.1 K, (iii) the hysteresis loops at 5 K, and (iv) the temperature dependence of the remanent magnetization, reinforce this statement, and exclude CaRuO$_3$ from being characterized as a *paramagnetic* material. Thus, the Ru moments are magnetically correlated without additives such as Sr, Sn, and/or Na.[6,8,16] It that sense, CaRuO$_3$ behaves in a way similar to its homologue SrRuO$_3$ and to Ca$_3$Ru$_2$O$_7$ (Ref. 14) and Ca$_2$RuO$_4$,[15] in which the long-range magnetic state is well accepted. Our results are consistent with the temperature dependence of the T_c and θ phase diagram of Ca$_{1-x}$Sr$_x$RuO$_3$, except that for the paramagnetic $x=0$ sample.[6] We speculate, that the *paramagnetic* determination[3–11] for CaRuO$_3$ in the past was based on magnetic $\chi(T)$ measurements performed under conditions where the curves adhere closely to the CW law, namely, either at high applied field (above 5 kOe) where irreversibility is not

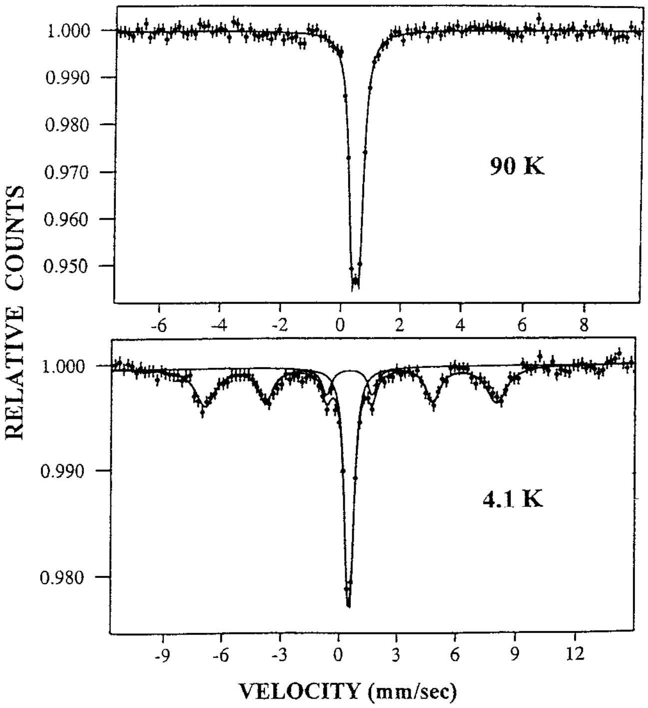

FIG. 5. Mössbauer spectra at 4.1 and 90 K for 1% ^{57}Fe dilute in CaRuO$_3$. Note the magnetic sextet at 4.1 K.

visible, or at low applied fields in the FC process.

Qualitatively speaking, the irreversibility phenomenon appears in both ceramic and CaRuO$_3$ single crystal materials. We are aware of some differences in the magnetic features of the two forms. The irreversibility for the ceramics samples starts at ~18 K higher than for the single crystal, and the linear behavior of $M(H)$ curve at 5 K for ceramic samples differ significantly from FM-like behavior observed for the CaRuO$_3$ single crystal, in both *ab* and *c* orientations (Figs. 2 and 4). These differences might be a result of some intrinsic properties such as (i) a variation in oxygen content and/or (ii) to some interexchange of the Ca and Ru ions in their crystallographic positions (supported by our Mössbauer studies), and/or (iii) to both irregularities in the structure all of which are caused by the preparation procedure. This picture may account for our preferable model of a spin-glass state,[16] which is more pronounced in the ceramic samples, than in the single crystal On the other hand, it is possible that particle size effect, namely, the ceramic sintered materials which consists of many microscopically small single crystals, shows an averaged behavior of phenomena observed in macroscopic single crystal. Regardless of these differences, the fact that CaRuO$_3$ is not paramagnetic, stands alone as the most significant feature of this study. Our finding is consistent with the time-dependent percolation model of the conductivity, proposed in Refs. 18,19, which argues that crystal distortions may determine the sign of the magnetic interaction in CaRuO$_3$. Finally, our T_{irr} values roughly coincide with Hall-effect measurements which show a sign change from negative to positive at ~50 K (Ref. 19) invoking again the spin-dependent scattering[20] mechanism for this sign change.

Our results (see Fig. 5) oppose the single line shape at 4.1 K of ^{99}Ru Mössbauer spectrum obtained in the early 1970's.[13] Note that the 4.1 K spectrum is somewhat broader than the 77 K one.[13] It is possible that the three contributions to H_{eff} acting on the Ru^{4+}S state ions, which differ in their signs, namely, (a) core polarization, (b) polarization of conduction electrons by the ion itself, and (c) polarization of electrons by magnetic neighbors accidentally cancel each other, and the total H_{eff} value is almost zero. The possible spin glass (see also Ref. 16) type magnetism of CaRuO$_3$ deserves more extensive investigations. We recommend additional low applied magnetic field experimental studies, and theoretical reconsideration of the magnetic state of CaRuO$_3$.

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