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Antiferromagnetism and Spin Reorientation in “$PbCrO_3$”

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The perovskite “$PbCrO_3$” was synthesized at high pressure and high temperature. Its magnetic properties have been investigated by means of magnetization, specific heat, and resistivity measurements. Earlier workers had concluded it to have a G-type antiferromagnetic structure. However, our measurements suggest a rather more complex situation: first, a weak ferromagnetic transition of the Cr(IV) spins occurs at 245 K; this is followed by a temperature-driven spin reorientation starting at 185 K and ending at 62 K. Since zero-magnetic-field spin reorientation in the “$PbCrO_3$” perovskite should not be expected, an intrinsic “magnetoelectric effect”, associated with the lone-pair Pb electrons, seems to be responsible for the observed smooth rotation of the Cr-spins.

Introduction

ABO_3-perovskite-like compounds have been widely studied because of their rich electronic and magnetic behavior.[1] Among them, perovskites synthesized at high pressures and high temperatures represent a large, although so far less explored, store of very interesting compounds. In particular, the chromium(IV) perovskite oxides require high pressure and high temperature conditions to be synthesized so as to place Cr^{4+} ions in octahedral sites.[2−6] Recently, however, there has been a renewed interest on them, propitiated by their intriguing transport and magnetic properties.[7−11] On the other hand, perovskites containing Bi^{3+} and Pb^{2+} at the A positions are permanently interesting in view of their potential or real useful properties such as ferroelectricity.[12−15] This is mainly due to either the stereochemical effect of the $6s^2$ lone-pair electrons or the covalent A-O bonds (A = Bi and Pb) that stabilize distorted acentric structures.[16,17] Taking these observations into account, the preparation and study of perovskite materials that have both, a cation containing lone-pair electrons as well as a magnetic ion located at the A and B perovskite sites, respectively, are important, and this has led to a revival of multiferroic materials, such as $BiCrO_3$.[18,19] In fact, this compound also presents a temperature-driven spin reorientation clearly observed by powder neutron diffraction (see Figure 7 on ref 20).

The $PbCrO_3$ perovskite was first synthesized by Roth and DeVries in the late 1960s.[4] Concerning the structural characterization, single-crystal and powder X-ray diffraction (XRD) studies at room temperature then showed a cubic structure. In the 1970s, Chamberland and Moeller also

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synthesized $PbCrO_3$, and their structural results were in agreement with the previously published ones. However, it is interesting to note that these authors noticed an unusual broadening on the XRD maxima, even using "monochromatic $CuK_{\alpha1}$ radiation".[5] In both studies, neither atomic stoichiometry control nor microstructural studies were performed. Recently, a structural and microstructural study of $PbCrO_3$ by XRD, SAED, and HREM has revealed that the lead chromate "$PbCrO_3$" perovskite has a Pb deficiency which results in an orthorhombic compositionally modulated structure ($a_p \times 3a_p \times (\sim 14-18)a_p$, where a_p is the cubic perovskite cell parameter) within a complex microdomain texture.[21] From now on, we will refer to the lead chromate perovskite as "$PbCrO_3$" which is in fact $Pb_{1-x}CrO_{3-x}$ ($x \approx 0.09$).[21]

Upon examining the magnetic and transport properties of this compound, Roth and DeVries, by means of neutron diffraction studies, reported an antiferromagnetic (AFM) G-type structure ($a_{mag} = 2a_{nucl}$) with a magnetic moment of $\sim 1.9\ \mu_B$ per chromium atom and with a Néel temperature (T_N) of about 240 K. Yet, in their susceptibility measurements, they did not observe any clear maximum indicative of a massive transition from paramagnetic to a long-range AFM ordering. Surprisingly, Chamberland and Moeller reported a different $T_N \sim 160$ K. Moreover, both works mentioned a possible parasitic ferromagnetic component existing below their T_N that they ascribed to some canted spin arrangement, to ferromagnetic impurities, or, even, to the possibility of Cr^{4+} dissociation into ions with different valences which would develop the ferromagnetic order by virtual double exchange.[22]

We describe in this paper a re-examination of the magnetic and electrical properties of "$PbCrO_3$". Three magnetic transitions have been observed by direct current (DC) susceptibility measurements. The first one, at ~245 K, also detected in the resistivity measurements, supporting the previous neutron diffraction studies.[4] The other two transitions are apparent at low temperature in the susceptibility plots and confirmed by specific heat measurements. Hysteresis loops suggest weak ferromagnetism (WFM) at low temperature. The characteristic parameters of the hysteresis cycles, that is, remanence and coercive field, progressively vanish as the temperature rises to room temperature. Moreover, AC susceptibility measurements do not present any signal which could indicate a possible glassy behavior. The most realistic magnetic behavior for "$PbCrO_3$" that accounts for the results presented here, is a zero field spin-reorientation (SR) of the Cr^{4+} spins which takes place below the Néel temperature.

Experimental Section

"$PbCrO_3$" was synthesized under high pressure and high temperature conditions. Although it can be obtained at 50 kbar and 1073 K, the compound can be prepared nearly as a single phase at the same temperature but at pressures as high as 80 kbar; above 100 kbar the phase is not formed. Experimental synthesis details, structural and microstructural characterization can be found in already published work.[21]

Magnetic susceptibility measurements were performed over the temperature range 1.9−300 K, using a Squid Quantum Design XL-MPMS magnetometer under zero-field-cooling (ZFC) and field-cooling (FC) conditions. Resistivity and specific heat measurements were performed using a Quantum Design PPMS.

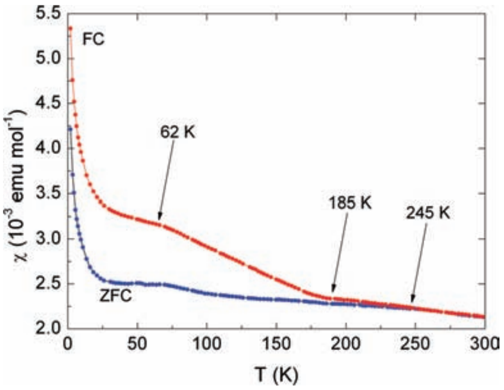

Figure 1. Magnetic susceptibility measured in a 100 Oe field.

Results

Figure 1 shows the temperature dependence of the magnetic susceptibility for "$PbCrO_3$" from 300 down to 2 K measured at ZFC and FC modes at 100 Oe. It is important to mention in here that we are dealing with a high pressure synthesis and, usually, samples contain a certain amount of impurities. Nevertheless, although the sample is not completely single phase, the small amount of other phases present have no influence on the magnetic measurements of the "$PbCrO_3$" compound since, from the assayed impurities, both PbO (2.4%) and Pb_5CrO_8 (5.1%) are non-magnetic compounds, and Cr_2O_3 (5.3%) orders antiferromagnetically at $T_N = 308$ K.[23−25]

The beginning of the divergence of the temperature dependence between the ZFC and FC magnetization curves in Figure 1 indicates a magnetic transition at ~245 K. A further temperature decrease shows noticeable differences between both curves at ~185 K with a marked slope increase in the FC curve. In addition, a broad maximum is observed around ~62 K.

Magnetization versus field measurements (Figure 2) were performed from −9 to 9 T at temperatures of 5, 70, 150, and 250 K. A characteristic hysteresis cycle for a weak ferromagnetic material is obtained at 5 K, with a remanence as low as 0.002 μ_B and a coercive field of 300 Oe. These parameters vanish as the temperature increases, and the cycle disappears completely at 250 K, that is, the compound behaves then as a paramagnet. From the linear fit of the magnetization plot at this temperature, an effective magnetic moment of 2.51 μ_B can be extracted. This value is rather close to the theoretical Cr^{4+} ($^3F_2$) spin-only magnetic moment having an outer $3d^2$ shell, $\sim 2.83\ \mu_B$.

The electrical resistivity data, Figure 3, suggest semiconducting behavior in the temperature range $210 < T < 395$ K. An electrical transport anomaly, observed in the Arrhenius plot at ~236 K, suggests some transition in this region. This seems to be a reflection of the incipient magnetic order observed in the susceptibility at about the same temperature (~245 K). Below 200 K, the resistivity becomes too high for a reliable measurement with our PPMS device.

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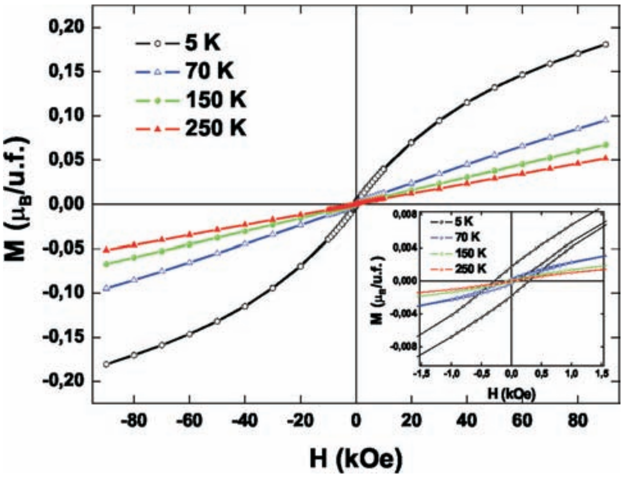

Figure 2. Magnetic hysteresis loops for "PbCrO3" at 5, 70, 150, and 250 K. The inset shows a characteristic hysteresis loop corresponding to a WFM material.

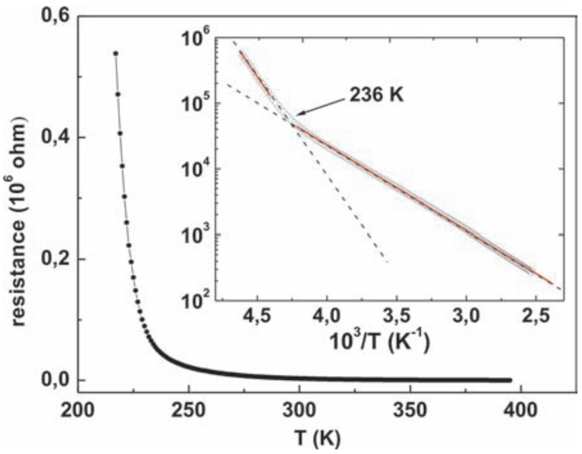

Figure 3. Electrical resistance variation for "PbCrO$_3$" with temperature. Inset: Arrhenius plot indicating the presence two activation energies ranges with 0.11 and 0.26 eV.

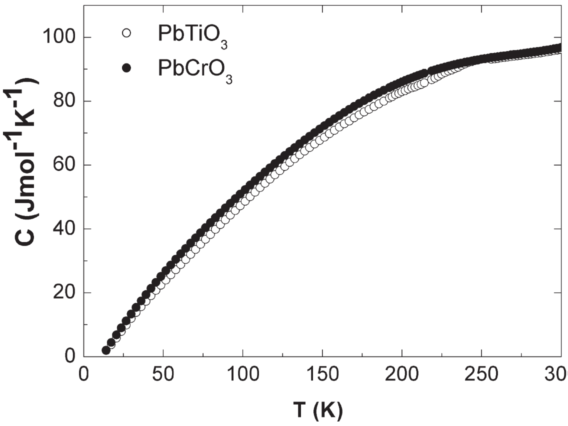

Figure 4. Total specific heat for "PbCrO$_3$" and the PbTiO$_3$ reference compound. Both phonon spectra are similar in these compounds.

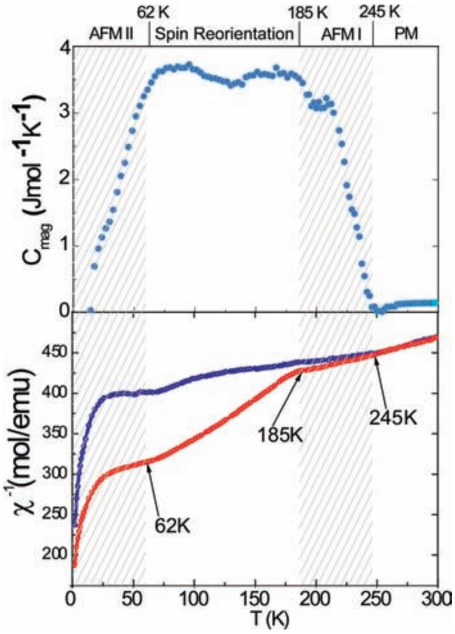

Figure 5. Top: Magnetic specific heat for "PbCrO$_3$" after the subtraction of the lattice contribution from the PbTiO$_3$ reference compound. Bottom: Inverse susceptibility plots included for comparison.

Although the total heat capacity of the sample, Figure 4, does not show any evident transition, the specific heat associated with the magnetic transitions can be extracted from the "PbCrO$_3$" data by subtracting the phonon contribution corresponding to the analogous, and non-magnetic, PbTiO$_3$, that is, [$Cp_{mag} = Cp_{\text{"PbCrO3"}} - Cp_{PbTiO3}$]. It is worth noting that, although both PbTiO$_3$ (c/a = 1.06) and PbVO$_3$ (c/a = 1.22)[26] are tetragonally distorted perovskites, while "PbCrO$_3$" is, on average, cubic, the c/a ratio of the former is closer to that of "PbCrO$_3$" than that of the latter. It is then a fair assumption to accept that their lattice contributions to the specific heat are comparable. In fact, as depicted in Figure 4, there are no crossings between the PbTiO$_3$ and "PbCrO$_3$" total specific heat plots at any temperature (we use the molar weight of the real composition: $Pb_{0.9}CrO_{2.9}$).[21] The data in Figure 5 (top) confirm the three different anomalies that were previously observed in the magnetic susceptibility data. The reciprocal susceptibility temperature profile has also been included for comparison (bottom). A broad steep upward in the magnetic specific heat data occurs at about 245 K finishing at T_N~210 K. The spin-reorientation region extends between T_1 ~ 185 K and T_2 ~ 62 K and is followed by a marked slope change.

a. General Discussion. In the light of these results it appears that, in contrast to what was suggested in earlier studies,[4,5] the cubic "PbCrO$_3$" perovskite displays three magnetic transitions. The first one, at high temperature T ~ 245 K (also deduced from the change in the activation energy from 0.11 to 0.26 eV in the Arrhenius plot of resistivity as a function of temperature (inset Figure 3)) fits rather well with the G-type AFM transition observed by Roth and DeVries[4] using neutron diffraction techniques. It is worth noting that we have been able to show, for the first time, this transition by susceptibility measurements. It can be seen, in Figures 1 and 5(bottom), that both ZFC and FC branches start to diverge at T_N~245 K, which is a clear indication of a weak ferromagnetic interaction (WFM). A further decrease of the temperature shows two additional magnetic transitions below T_N; these indicate subtle changes in the magnetic ordering of the Cr^{4+} ions. At ~185 K, the magnetic irreversibility

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between the ZFC and FC branches is more evident and can be attributed to an increase in the coercivity at low temperature. However, the remanence obtained from the hysteresis loop at 150 K (Figure 2) has the value of 0.2×10^{-3} μ_B, and the coercive field is as low as 85 Oe. A possible interpretation for this transition could be that it corresponds to spin-glass-like behavior.[27] To check for this, temperature dependent AC susceptibility measurements were also performed at different frequencies (Supporting Information). There was no evidence of spin relaxation time nor the presence of any cusps commonly observed in canonical spin-glasses at any temperature.

In the light of all this information, we suggest that "$PbCrO_3$" displays a non-collinear AFM transition ($T_N \sim 245$ K) with a temperature-driven spin reorientation at $T_1 \sim 185$ K extending to $T_2 \sim 62$ K. Such behavior is commonly found in compounds with competing spin anisotropies from different structural positions, for example, some rare earth (RE = Yb, Er, and Tm) orthoferrites exhibit a competition between the crystal field anisotropy at the RE site and an itinerant contribution at the iron positions.[28] Spin-reorientations can also be magnetic-field-induced, as happens in $YCrO_3$ and $YFeO_3$.[29] However, in "$PbCrO_3$" there is only one magnetic site, and its magnetic properties are not magnetic-field-induced. Another possible explanation of the spin-reorientation could be the coexistence of itinerant and localized Cr spins, as observed in other chromium compounds with a unique magnetic site (e.g., $LaCrSb_3$).[30] Moreover it should be noted that, according to resistivity measurements, "$PbCrO_3$" is a semiconductor. Furthermore, early calculations carried out using the Linear Muffin Tin Orbital method with the Hubbard parameter (LMTO + U) were in good agreement with a semiconducting/AFM behavior in $PbCrO_3$,[31] so coexisting itinerant plus localized d-electron behavior are not compatible with this material.

b. Origin of the Spin-Reorientation in "$PbCrO_3$". It is well-known, since the discovery of the Magnetoelectric Effect (ME) by Pierre Curie,[32] that an electric-field-induced magnetization and vice versa, a magnetic-field-induced polarization phenomena, are found in different compounds (see, e.g., ref 33 and references therein). Therefore, we propose that a possible solution to this unconventional magnetism can be found in this effect. In fact, a prerequisite for spin rotation is the presence of anisotropy;[29] thus it is relevant to query whether the anisotropy is an intrinsic property of the Cr sublattice or whether it results principally from the Pb−Cr interaction. Contrary to what happens in RE orthoferrites with non-diamagnetic RE cations where this anisotropy arises indirectly from induced RE ion polarization, the anisotropy in"$PbCrO_3$" must arise from the Pb−Cr interactions since Pb is a diamagnetic cation and the spin reorientation is not magnetic field-induced, as happens in $YCrO_3$ or $YFeO_3$ perovskites containing also a diamagnetic RE cation.[29] Then, the 6s Pb lone-pairs, which often produce a polar structure, in addition to the complex microstructure observed in the perovskite that arises from a compositional modulation of Pb atoms,[21] could induce a change of the anisotropy leading, via spin−lattice interactions, to a reorientation of the spins.[34−37]

Spin reorientations correspond to second-order phase transitions. In view of this, we have performed further specific heat measurements at zero magnetic fields. No singularities are apparent at either the $PbTiO_3$-reference or the "$PbCrO_3$" total specific heat plots (Figure 4). Nevertheless, the specific heat associated with the spin-reorientation transitions in the "$PbCrO_3$" perovskite was obtained by subtracting the phonon contribution from the non-magnetic $PbTiO_3$-reference. Figure 5 (top) shows the magnetic specific heat of the "$PbCrO_3$" perovskite once the phonon contribution is subtracted. Four different magnetic zones are observed: The region named as PM, in the top of Figure 5, corresponds to the beginning of the paramagnetic state in the "$PbCrO_3$" perovskite that extends from 250 K to higher temperatures. The AFM I region starts at 250 K with a Néel temperature $T_N \sim 210$ K down to the spin reorientation temperature transition, $T_1 \sim 185$ K. The spin reorientation regime ranges between T_1 and $T_2 \sim 62$ K, where the spins stop their reorientation. These AFM structures have to be confirmed by neutron diffraction techniques. Some non-collinear spin structures (e.g., helical spin structures) can be determined by powder neutron diffraction;[38] however, the previously powder collected data in $PbCrO_3$ did not show any evidence for spin-reorientation transitions and only noticed the already mentioned G-type AFM structure at high temperature. Yet, those authors did mentioned that "a small ferromagnetic component could easily have escaped detection" in their neutron experiments.[4] In "$PbCrO_3$", the WFM is less than 0.002 μ_B at 5 K, so its contribution to the reflected neutron intensities is negligible compared to the contribution from the 2.51 μ_B of the antiferromagnetic axis. Consequently, inelastic neutron diffraction experiments or neutron diffraction using a single crystal will be mandatory to solve the spin reorientation structures in "$PbCrO_3$".

Conclusions

The spin reorientation as a function of temperature, observed in "$PbCrO_3$" perovskite, seems to be related to the compositional modulation observed in the material by means of HREM-SAED via the Pb(II) lone pair. This reorientation starts from the previously observed AFM

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ordering of the chromium moments at $T_N \sim 245$ K but with a small canting of the spins through a spin-reorientation at $T_1 \sim 185$ K that ends at $T_2 \sim 62$ K. Although we show evidence of the spin reorientation by susceptibility and hysteresis measurements, as well as by resistivity and specific heat techniques, the magnetic structures corresponding to the different spin-reorientation areas should be confirmed by neutron diffraction experiments. This is not an easy task, though, since "$PbCrO_3$" is a high pressure phase and a single crystal big enough for neutron diffraction experiments so as to determine its complex magnetic structure will not be simple to obtain.

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.