

The electronic properties of non-stoichiometric barium iridate, $\text{BaIrO}_{3-\delta}$

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Abstract

Polycrystalline single-phase samples of $\text{BaIrO}_{2.73}$ and $\text{BaIrO}_{2.96}$ were successfully prepared. Superconducting quantum interference device data indicate the magnetic susceptibility of both samples is low and only weakly temperature dependent in the range $180 \text{ K} < T < 296 \text{ K}$, demonstrating the presence of delocalized electrons. The materials exhibit high electrical conductivity which is dependent on the oxygen stoichiometry. In addition, magnetic susceptibility data for both compositions show that a transition to a ferromagnetically ordered state occurs at 180 K. It is proposed that this ferromagnetism arises from a difference in the relative populations of the α and β spin bands and not from localized electrons.

1. Introduction

In recent years, much of our research effort has been focused on the electronic properties of cations of metals from the second transition series. In particular, we have investigated a wide range of mixed ruthenium oxides with perovskite or perovskite-related structures [1, 2]. The increased width of the 4d band over that of the 3d band, together with the large correlation energy associated with octahedral Ru(V) (t_{2g}^3), makes such systems interesting for a study of the competition between itinerant and localized electron behaviour. In order to investigate the effect on this competition of moving to the third transition series, and because of the many parallels that exist between the chemistries of ruthenium and iridium, we have recently extended our study to encompass the mixed oxides of iridium.

The solid state chemistry of iridium oxides is dominated by the 4+ oxidation state (d^5), although Ir(V) is present in KIrO_3 [3] and $\text{Ba}_{0.5}\text{IrO}_3$ [4], and mixed valency has been reported in the oxide $\text{La}_3\text{Ir}_3\text{O}_{11}$ [5]. Of the mixed oxides containing Ir(IV), those with the alkaline earth oxides have been extensively studied [6]. They adopt a wide range of structures, many of which are related to the hexagonal BaTiO_3 structure. However, the existence of a number of polytypes for compounds of a given stoichiometry prepared under different experimental conditions had led to considerable confusion in the literature, particularly in the case of BaIrO_3 .

Early reports [7] stressed the similarity of its powder X-ray diffraction pattern to that of 9-R BaRuO_3 with which it was assumed to be isostructural. At the same time other workers [8] suggested that the structure was of the 18-R type with a c axis of 44.5 Å. A later study by high-resolution electron microscopy [9] concluded that the structure was that of a novel 9-H perovskite although a second 4-H polytype was detected. This confusion has been resolved by a recent X-ray single-crystal structure determination [10] which has shown that the structure is in fact a monoclinic distortion of the nine-layer BaRuO_3 structure. In the latter structure, three face-sharing RuO_6 octahedra form Ru_3O_{12} clusters which are vertex-linked to form columns parallel to the c axis [11]. The monoclinic distortion in BaIrO_3 produces a shifting and tilting of the columns relative to each other as shown in Fig. 1.

During the course of our investigations into the properties of barium iridates, a recent paper [12] describing the electronic properties of BaIrO_3 came to our attention. This paper presented magnetic susceptibility data in the range 77–298 K, together with two-probe electronic conductivity data. These data were not entirely in agreement with an earlier report [13]. Furthermore, it was reported [14] that attempts to prepare non-stoichiometric iridates had been unsuccessful. We therefore thought it timely to present the results of our own susceptibility and conductivity measurements for polycrystalline samples of $\text{BaIrO}_{3-\delta}$ which have been prepared at lower temperatures than those used previously.

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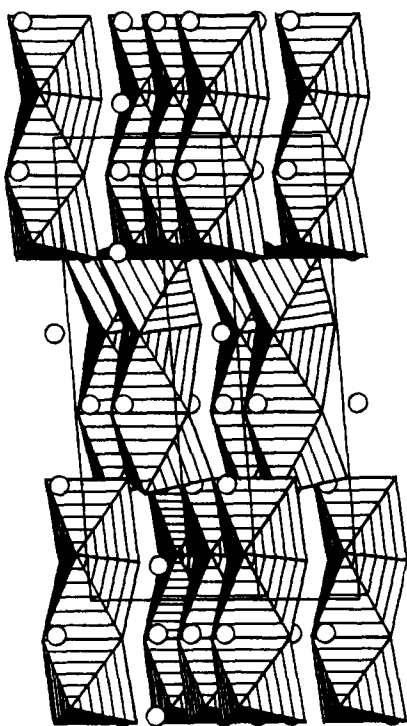


Fig. 1. Crystal structure of BaIrO₃.

2. Experimental details

Stoichiometric amounts of BaCO₃ and IrO₂ (Matthey Catalogue Sales) were ground in an agate mortar and fired in an alumina crucible for an initial period of 3 days at 973 K (with one intermediate regrinding). This was followed by successive 2-day firings in air at 1013, 1073 and 1223 K, the sample being reground between each firing. The course of the reaction was monitored by powder X-ray diffraction on a Philips PW1710 powder diffractometer. After the final firing, the products were either quenched rapidly to room temperature by removal from the furnace or were allowed to cool to room temperature over a period of approximately 8 h. Oxygen contents were determined thermogravimetrically by reduction in flowing hydrogen and by oxidation in flowing oxygen. Magnetic susceptibility measurements on a powdered sample were made using a Cryogenic Consultants SCU500 superconducting quantum interference device (SQUID) susceptometer. Samples were loaded at room temperature and measurements were taken in the temperature range 6–296 K after cooling the sample in zero field and after cooling in a measuring field of 1 kG. The sample was then re-cooled to 6 K in the measuring field and the magnetization was measured as a function of applied field in the range 1–30 kG. The measurements as a function of temperature were repeated following rapid initial cooling of the sample by loading at 6 K in 0.0 kG. Ingots (approximately 7

mm×3 mm×1.5 mm) were cut from sintered pellets of the oxides and four contacts were attached using colloidal silver paint. Their d.c. resistivities were then measured by a four-probe method at 298 K and 77 K using an HP3478A autoranging multimeter. The distance between the measuring probes was approximately 3 mm.

3. Results and discussion

Thermogravimetric analysis by hydrogen reduction to a mixture of barium oxide and iridium metal indicated that the material which had been subjected to rapid cooling was deficient in oxygen. This was confirmed by thermogravimetric oxidation to BaIrO₃ in flowing oxygen, followed by reduction of the product in hydrogen. The weight changes in these experiments were consistent with the composition BaIrO_{2.73±0.04}. The material which had been cooled slowly to room temperature was almost ideally stoichiometric with a composition of BaIrO_{2.96±0.04}. This observation of non-stoichiometry in BaIrO₃ is remarkable in view of the recent unsuccessful attempts by Wiley and Poeppelmeier [14] to prepare oxygen-deficient perovskites containing 4d and 5d transition metals. However, these workers, in attempting to abstract oxygen from stoichiometric BaIrO₃, state that they were unable to prepare a pure phase of the latter; other groups have experienced similar difficulties in preparing pure, polycrystalline BaIrO₃ [9]. We believe that the use of relatively low temperatures during the early stages of synthesis allowed us to prepare single-phase samples; Wiley and Poeppelmeier [14] used higher initial temperatures (1273 K). It would appear that once a pure phase of BaIrO_{3-δ} is formed at these lower reaction temperatures, its oxygen content is then determined by the conditions under which it is cooled.

Powder X-ray diffraction patterns of both materials were almost identical (Fig. 2). This is not surprising as the diffraction pattern is dominated by the scattering from the heavy elements barium and iridium and is relatively insensitive to changes in oxygen stoichiometry. Both patterns could be completely indexed on the unit cell proposed by Siegrist and Chamberland [10]. It is apparent that the positions of the heavy metals are undisturbed by the presence of vacancies on the anion sublattice. Refinement of the data resulted in the cell parameters $a = 10.015(7)$, $b = 5.752(2)$, $c = 15.187(9)$ Å, $\beta = 103.27(4)^\circ$ for BaIrO_{2.73} and $a = 10.009(6)$, $b = 5.753(3)$, $c = 15.181(15)$ Å, $\beta = 103.27(4)^\circ$ for BaIrO_{2.96}. In both cases the agreement with the lattice parameters determined in the single-crystal study of BaIrO₃ is excellent. Utilizing the atomic coordinates determined in the aforementioned study, the LAZY PULVERIX [15] program was used to calculate the relative

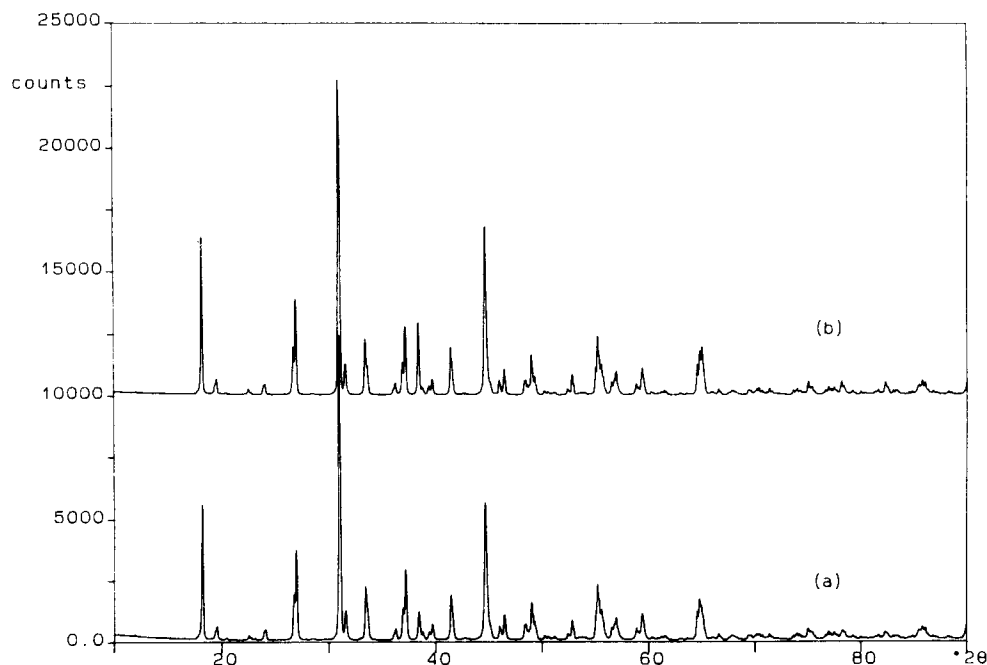


Fig. 2. Powder X-ray diffraction patterns for BaIrO_{2.73} (a) and BaIrO_{2.96} (b); peaks from the Al sample holder are marked.

intensities for all of the allowed reflections for BaIrO₃. These are presented together with the corresponding observed intensities for BaIrO_{2.73} in Table 1. The good agreement between the two sets of data, coupled with the nearly identical nature of the powder diffraction patterns for BaIrO_{2.73} and BaIrO_{2.96}, confirms these samples to be monophasic with an arrangement of heavy atoms identical with the single-crystal sample characterized by Siegrist and Chamberland [10].

Four-probe resistivity measurements on BaIrO_{2.96} gave the following values: at 77 K $\rho = 2 \times 10^{-2} \Omega \text{ cm}$ and at 298 K $\rho = 0.60 \Omega \text{ cm}$. The corresponding values for BaIrO_{2.73} were 0.15 $\Omega \text{ cm}$ and 0.73 $\Omega \text{ cm}$ respectively. The low room-temperature resistivities measured for both samples are incompatible with the presence of localized electrons and suggest that a band description is more appropriate for these materials. The dependence of the resistivity on the oxygen stoichiometry is consistent with such a picture. The 5d orbitals of iridium are split by an octahedral crystal field into a t_{2g} set and an e_g set which in a solid are broadened into bands. As the crystal field splitting for a third-transition-series element is greater than the band broadening, discrete t_{2g} and e_g bands exist. The iridium in BaIrO_{2.96} is present almost exclusively as iridium(IV): $5d^5$. These electrons occupy the t_{2g} band giving the configuration t_{2g}^5 . The resulting holes in the t_{2g} conduction band give rise to the high electronic conductivity that is observed. In the oxygen-deficient BaIrO_{2.73} some of the iridium(IV) has been reduced to Ir(III); the material may be conveniently formulated as BaIr^{III}_{0.54}Ir^{IV}_{0.46}O_{2.73}, with the extra electrons accommodated in the t_{2g} band, thus reducing the

density of states at the Fermi level and causing a significant decrease in the conductivity.

Unfortunately, Chamberland does not quote resistivities in his study of BaIrO₃ [12], merely resistances. Whilst a value of 20 Ω at liquid nitrogen temperature is not incompatible, for a sample of typical dimensions, with our resistivity for BaIrO_{2.96}, we feel sure that the value of 10 Ω observed at room temperature would lead to a much higher resistivity than is observed in this study and may simply be a consequence of the use of a two-probe measuring technique which is generally unsuitable for the measurement of low resistances. Further experimental support for a low resistivity for BaIrO_{2.96} is provided by Schaller *et al.* [13] who quote resistivities for BaIrO₃ of 0.7 and 0.63 $\Omega \text{ cm}$ at 298 and 77 K respectively and conclude that the material is metallic over a wide temperature range.

The measured magnetic susceptibilities were corrected for core diamagnetism. The magnetic susceptibility *vs.* temperature curves were very similar for both compositions (Figs. 3 and 4). The curves measured after cooling in zero field (zfc) and after cooling in the measuring field (fc) overlie each other almost completely at higher temperatures (greater than 240 K). Above this temperature, the susceptibility is almost independent of temperature. Fitting the reciprocal susceptibility in this region to a Curie-Weiss law results in very large, negative Weiss constants (approximately -1200 K) and an effective magnetic moment of 2.5 μ_B . This effective moment is much greater than that resulting from a low-spin octahedral Ir(IV) (d^5) ion. This, together with the weak temperature dependence

TABLE 1. Powder X-ray diffraction data for $\text{BaIrO}_{2.73}$ (space group: $C2/m$, $Z=12$; $a=10.015(7)$, $b=5.752(2)$, $c=15.187(9)$ Å, $\beta=103.27(4)^\circ$)

d_{obs} (Å)	$(I/I_0)_{\text{obs}}$	d_{calc} (Å)	$(I/I_0)_{\text{calc}}$	$h k l$
4.868	0.54	4.874	0.16	2 0 0
		4.871	0.27	-1 1 1
4.539	0.06	4.540	0.04	1 1 1
3.943	0.03	3.948	0.03	-2 0 3
3.701	0.04	3.697	0.03	2 0 2
		3.695	0.01	0 0 4
3.328	0.14	3.336	0.15	-2 0 4
3.304	0.29	3.306	0.26	1 1 3
2.881	1.00	2.887	0.64	-3 1 1
		2.876	0.36	0 2 0
2.831	0.10	2.838	0.05	-3 1 2
		2.832	0.01	-2 0 5
		2.829	0.04	3 1 0
2.676	0.17	2.680	0.16	-1 1 5
2.477	0.04	2.477	0.02	2 2 0
2.430	0.09	2.435	0.09	-2 0 6
2.415	0.23	2.418	0.20	1 1 5
2.318	0.03	2.321	0.02	4 0 1
2.284	0.03	2.290	0.01	-4 0 4
		2.285	0.01	-3 1 5
2.268	0.06	2.270	0.02	2 2 2
		2.270	0.01	0 2 4
		2.266	0.01	3 1 3
2.176	0.15	2.178	0.11	-2 2 4
		2.171	0.03	4 0 2
1.971	0.05	1.974	0.04	-4 0 6
1.954	0.08	1.955	0.08	2 2 4
1.878	0.05	1.883	0.02	-5 1 1
		1.883	0.02	-4 2 2
		1.877	0.02	-1 3 1
1.857	0.12	1.859	0.11	-2 2 6
1.848	0.06	1.849	0.04	4 0 4
1.815	0.02	1.817	0.01	-5 1 4
1.749	0.02	1.746	0.02	-5 1 5
1.732	0.06	1.733	0.03	4 2 2
		1.732	0.04	1 3 3
1.663	0.18	1.663	0.13	-3 3 1
		1.661	0.03	-5 1 6
		1.660	0.02	-6 0 3
1.653	0.10	1.657	0.02	-6 0 1
		1.653	0.01	-3 3 2
		1.653	0.07	2 2 6
		1.651	0.01	3 3 0
1.627	0.04	1.627	0.04	-4 2 6
1.616	0.07	1.620	0.03	-1 3 5
		1.617	0.03	5 1 3
		1.616	0.02	-1 1 9
1.568	0.04	1.569	0.03	-5 1 7
1.555	0.08	1.556	0.05	1 3 5
		1.555	0.04	4 2 4
		1.555	0.01	0 2 8
1.443	0.09	1.444	0.06	-6 2 2
		1.443	0.03	-4 2 8
1.438	0.13	1.438	0.06	0 4 0
		1.438	0.02	-6 2 3
		1.437	0.04	-1 3 7
		1.436	0.03	-6 2 1
1.404	0.02	1.405	0.02	2 2 8
1.353	0.02	1.354	0.01	-4 2 9
		1.353	0.01	7 1 0

Only peaks with $d_{\text{obs}} > 1.65$ Å were used in cell refinement. Peaks with $(I/I_0)_{\text{obs}} < 0.01$, although indexable are not tabulated. All intensities are normalized to the total intensity at $d_{\text{obs}} = 2.881$ Å.

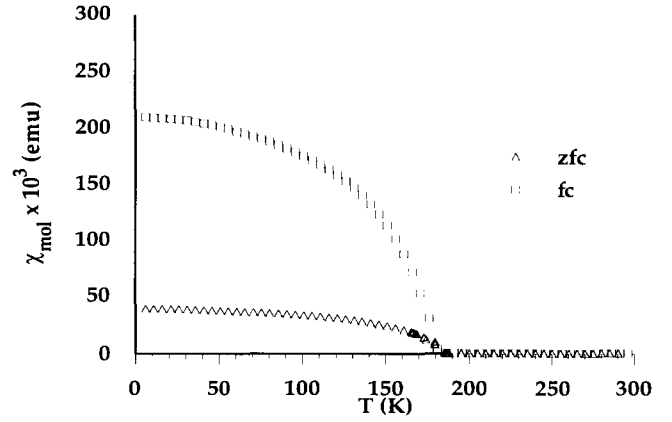


Fig. 3. Variation in magnetic susceptibility (χ) with temperature for $\text{BaIrO}_{2.73}$ after slow cooling in zero applied field (zfc) and in the measuring field (fc).

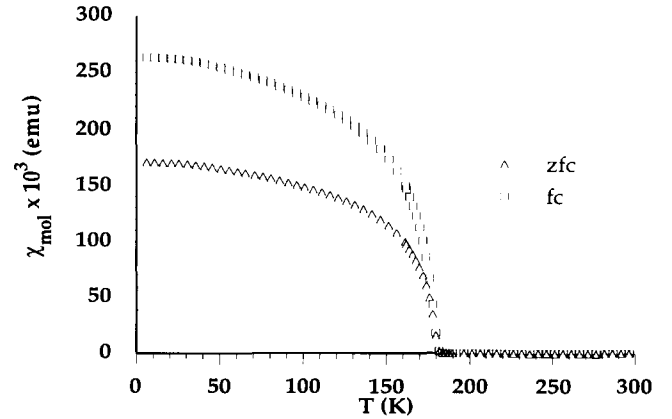


Fig. 4. Variation in magnetic susceptibility (χ) with temperature for $\text{BaIrO}_{2.96}$ after slow cooling in zero applied field (zfc) and in the measuring field (fc).

of the susceptibility in the high-temperature regime, suggests that it is inappropriate to apply the localized electron Curie-Weiss law to $\text{BaIrO}_{3-\delta}$ and reinforces the view that a description based on delocalized electrons is more appropriate. The measured susceptibility may then be attributed to Pauli paramagnetism. Similar behaviour has been observed in metallic iridium-containing pyrochlores $\text{A}_2\text{Ir}_2\text{O}_7$ [16].

A sharp increase in susceptibility is observed for zfc and fc curves for both materials in the range $150 \text{ K} < T < 180 \text{ K}$. Below about 150 K χ increases more slowly with decreasing temperature. The striking feature is that the zfc and fc curves, although taking the same form, no longer overlap each other; the fc curve lies above that obtained on zero-field cooling. This is understandable if the transition is to a ferromagnetically ordered state since, in a polycrystalline ferromagnet, the ferromagnetic domains will be randomly oriented on cooling in the absence of an applied field but will, when cooled in a field, align themselves in the direction of the field resulting in a higher susceptibility. The

magnetization (σ) *vs.* applied field measurements for BaIrO_{2.73} demonstrate that although σ increases almost linearly with applied field at 6 K, the value of $d\sigma/dH$ is very low (approximately $1.5 \times 10^{-3} \mu_B \text{ kG}^{-1}$). The variation in the magnetic moment as a function of field is shown in Fig. 5; a moment of $0.047 \mu_B$ per Ir ion is observed at 30 kG. A similar field dependence was observed for BaIrO_{2.96} leading to a moment of $0.038 \mu_B$ per Ir ion at 30 kG. A spin-only atomic moment for a low-spin Ir(IV) ion (d^5) with localized electrons would be $1.0 \mu_B$ per molecule. This would be increased by any orbital contribution. It is apparent that the moments for BaIrO_{3-δ}, although not saturated, are greatly reduced from their expected values. There are a number of ways in which this may arise, including spin canting. However, we believe, in view of the metallic nature of the materials, as shown by their high electronic conductivities, that BaIrO_{2.96} and BaIrO_{2.73} are band ferromagnets in which there are holes in both the α and β spin bands. The net overall moment then results from the unequal population of the two sub-bands. Although the absolute number of holes is greater in BaIrO_{2.96} than in BaIrO_{2.73}, the changes in the population differences of the α and β spin bands will be less marked. Hence the magnetic behaviour of the two samples does not vary to the same degree as the electronic conductivities. The extremely low values of $d\sigma/dH$ are a consequence of changes in the relative populations of the α and β spin bands with increasing field similar to that observed in metallic iron. Such behaviour has been observed previously in the case of the regular perovskite SrRuO₃ [17]. The difference in populations of the α and β spin bands in BaIrO_{3-δ} is smaller than in the latter compound where the reduction in moment was less marked (from $2.0 \mu_B$ to $0.8 \mu_B$). The perovskite structure adopted by SrRuO₃ particularly favours π overlap between cation t_{2g} orbitals and oxygen p orbitals enabling formation of π and π^* bands. In

a pseudo-hexagonal perovskite, such as BaIrO_{3-δ} face-linked octahedra are present in addition to the vertex-linked octahedra of the cubic perovskite structure. Therefore, in order to promote band formation, an interaction has to occur across the face-shared octahedra. If the metal–metal distance across the face is sufficiently short, direct overlap of Ir t_{2g} orbitals may take place thereby allowing itinerant electron behaviour to occur. In BaIrO₃ two crystallographically distinct Ir clusters are present with Ir–Ir distances of 2.62 and 2.63 Å. These are considerably shorter than the separation of 2.72 Å found in metallic iridium, providing support for a band description of the material. The χ *vs.* T curves obtained after quenching at 6 K show a rather different behaviour (Fig. 6). Rapid cooling in zero field appears to freeze in the room-temperature form of the material which shows a correspondingly low molar susceptibility in the region 6–170 K. As the material is warmed and the transition temperature of the material is approached, enough thermal energy is acquired to undergo the transition to the ferromagnetic state and the susceptibility begins to rise. At the transition temperature, the material transforms to its room-temperature metallic form and the susceptibility falls again.

The data presented here for polycrystalline samples of BaIrO_{3-δ} demonstrate that the materials are metallic at room temperature. On cooling, long-range ferromagnetic ordering occurs at 180 K. The low observed moment and slow approach to saturation with applied field in the ferromagnetically ordered state indicate that delocalized behaviour persists below the transition temperature. If the observed properties do not arise from a change from delocalized to localized electron behaviour, then another process must be occurring at the transition temperature. The sharpness of the magnetic transition, together with the retention of the room-

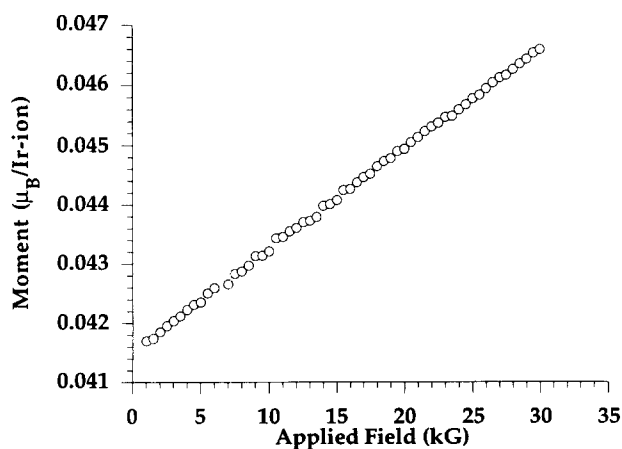


Fig. 5. Variation in the magnetic moment per Ir ion for BaIrO_{2.73} as a function of applied magnetic field.

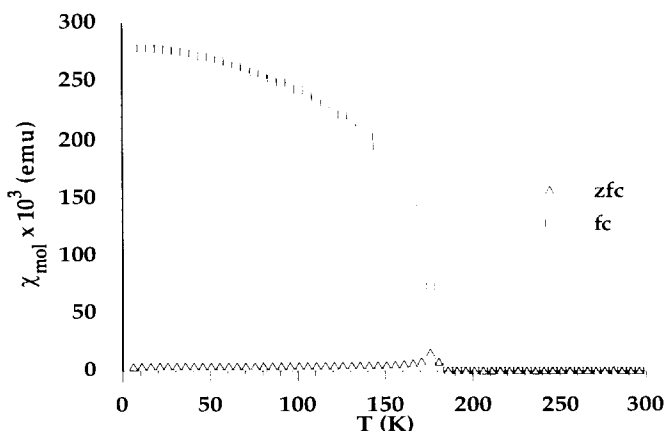


Fig. 6. Variation in magnetic susceptibility (χ) with temperature for BaIrO_{2.96} after rapid cooling in zero applied field (zfc) and then slow cooling in the measuring field (fc).

temperature phase on rapid cooling, may be indicators that the origin lies in a structural phase change. Such a process is not unreasonable in view of the well-documented polytypic nature of BaIrO₃, for which a number of closely related structures have been reported. By analogy with other materials which show polytypism, relatively subtle structural distortions are likely to relate these other structures to that of the pseudo-9-R polytype adopted by our samples at room temperature. Such distortions would cause corresponding changes in the local coordination geometry of iridium and alter the overlap of cation orbitals. This may be sufficient to alter the band structure and cause the splitting of the two spin sub-bands necessary for the observed ferromagnetism. Clearly, further work needs to be carried out on structure-property relations within the BaIrO_{3-δ} system. In particular, detailed structural investigations need to be performed below the transition temperature.

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