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Magnetic behavior of the $Bi_{2-y}Sr_yIr_2O_7$ pyrochlore solid solution

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ABSTRACT

The temperature dependence of magnetic susceptibility of the $Bi_{2-y}Sr_yIr_2O_7$ system was studied from 2 to 300 K. According to these measurements, the solid solution ($0 \leq y \leq 0.9$) does not show any magnetic transition; however, a noticeable deviation from the Curie–Weiss law occurs and the magnetic behavior of this system can be ascribed to short-range magnetic order that is also present in several geometrically frustrated systems. The Pauli magnetic susceptibility decreases as the Sr content increases, this can be associated with a shift towards Ir^{5+} in samples; also the Ir effective magnetic moment decreases. The estimated Wilson-ratio indicates the presence of strong electron–electron correlations.

1. Introduction

The Iridium α-pyrochlore family of compounds, $A_2Ir_2O_7$, spans a broad spectrum of electrical and magnetic properties that make them prime candidates for the exploration of complex phenomena in solid state chemistry and physics [1]. The crystalline structure of this family is face-centered cubic with space group $Fd\bar{3}m$ (S.G. 227) that can be described as two interpenetrated sublattices, A_2O2 and Ir_2O1_6. In $A_2Ir_2O_7$ the Ir atoms form the 3D equivalent of a Kagome structure. When the A cation is a rare-earth (RE) element, the effective magnetic moment agrees with the expected value for the RE^{3+} ions, indicating its localized nature [2]. All of the $A_2Ir_2O_7$ (A=RE) compounds have Weiss temperatures θ corresponding to an antiferromagnetic (AF) order and none of their moments exhibits magnetic ordering at temperatures well below the θ value (down to 0.3 K) [2]. Systems with a nonmagnetic A-cation have been reported; $Y_2Ir_2O_7$ is a Mott insulator with a small ferromagnetic component below 170 K, as a consequence of either a spin-glass ordering or spin canting [3]. When Y is partially substituted by Bi, $Y_{2-x}Bi_xIr_2O_7$, experimental data of transport properties indicate a metal–insulator transition at $x \sim 0.5$ [4]. In the solid solution $Y_{2-x}Ca_x$-Ir_2O_7, in which Y and Ca are nonmagnetic but have different oxidation states, partial substitution of Y changes the electrical and magnetic properties substantially; a metallic behavior appears when $x \geq 0.3$, also the ferromagnetism (transition temperature at 170 K) disappears [3].

Recently weak magnetic frustration has been proposed to occur in $Eu_2Ir_2O_7$ [5]. This compound presents an interesting case of a magnetic frustrated system, in which Eu^{3+} is a $J=0$ ($L=S$) nonmagnetic cation and only the Ir^{4+} 5d electrons contribute to magnetism in this compound, in which a metal–insulator/AF transition is reported at 120 K [6]. The occurrence of localized magnetic moments and a 5d cation is an unexpected situation, since the Ir^{4+} wave functions should result in a metallic conduction via Ir-derived bands [5]. Poor metals such as $R\,InCu_4$ (R=Gd, Dy, Ho) [7] and the Cd doped system ($R\,In_{1-x}Cd_xCu_4$, R=Gd–Tm) [8] behave as frustrated systems. In the latter system, long-range interactions introduced into the system by the conduction electrons are thought that they reduce the magnetic frustration. In itinerant electron systems the exchange interactions are not restricted to nearest neighbors and magnetic order can occur if the magnetic interactions are large enough; in this situation the mechanism is via the RKKY interaction [9].

The $Bi_2Ir_2O_7$ α-pyrochlore was first reported by Bouchard and Gillon [10] and later structurally analyzed by Kennedy [11]. This is a metallic system in which no magnetic transition has been reported. The temperature dependence of the magnetic susceptibility is Curie–Weiss-like (CW), however, a detailed analysis that explains the magnetic behavior has not been completely done. The metallic character in the $Y_{2-y}Bi_yIr_2O_7$ system shows a Bi-content dependence [4,12], and we recently showed [13] that in this type of compounds the main contributors at the Fermi energy (E_F) are Ir and O1 atoms. In the present work we report the effect of Bi substitution by Sr on the magnetic behavior of $Bi_2Ir_2O_7$ ($Bi_{2-y}Sr_yIr_2O_7$, $0 \leq y \leq 0.9$). This substitution is also accompanied by important changes in the local geometry around Ir [13]. The system studied here shows an enhanced paramagnetism that

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can be described by a modified Curie–Weiss (mCW) equation in which short-range magnetic interactions are taken into account. On the other hand, the Pauli magnetic susceptibility decreases with the Sr content and this should be indicative of a similar tendency of the electronic density of states at the Fermi energy $N(E_F)$.

2. Experimental details

Polycrystalline samples of $Bi_{2-y}Sr_yIr_2O_7$ were prepared by solid state reaction with stoichiometric amounts of IrO_2, Bi_2O_3 and $SrCO_3$ powders. Details of syntheses and structure analysis can be found elsewhere [13]. DC magnetization data were acquired with a SQUID magnetometer (MPMS, Quantum Design) in a temperature range between 2 and 300 K. Field Cooling mode measurements were performed under a magnetic field of 0.1 T for all samples.

3. Results and discussion

In $Bi_{2-y}Sr_yIr_2O_7$ a monotonous increase of the cubic lattice parameter is observed as a function of the strontium content, y, which is in agreement with the difference between the Sr^{2+} and Bi^{3+} ionic radii ($Sr^{2+}=1.26$ Å) and $Bi^{3+}=1.17$ Å, both in 8-coordination [14]. Additionally, a linear reduction of the Ir–O1 bond distance was observed as consequence of the steric effect associated with the increase in the oxidation state of the Ir cation and the repulsive effect due to the larger Sr radius [13]. These structural modifications were earlier predicted by Koo et al. [15] in terms of the coordination environment of the O1 atom.

When a divalent cation is included into the $A_2^{3+}B_2^{4+}O_7$ α-pyrochlore lattice to form an aliovalent solid solution, a charge-compensation process is expected to occur by the appearance of a positive charged lattice defect [16,17]. This charge-compensation can be considered through the Kröger–Vink notation [18]. According to the chemical reaction, in the localized defects scheme, there are three possible consequences resulting from the Bi by Sr substitution:

$$SrO+O_0^x+Ir_{Ir}^x \overset{Bi_2Ir_2O_7}{\rightarrow} Sr_{Ir}''+V_0^{\cdot\cdot}+IrO_2 \quad (1)$$

$$2SrO+O_0^x+2Bi_{Bi}^x \overset{Bi_2Ir_2O_7}{\rightarrow} 2Sr_{Bi}'+V_0^{\cdot\cdot}+Bi_2O_3 \quad (2)$$

$$SrO+Ir_{Ir}^x \overset{Bi_2Ir_2O_7}{\rightarrow} Sr_{Bi}'+O_0^x+Ir_{Ir}^{\cdot} \quad (3)$$

When Sr^{2+} is incorporated into the $Bi_2Ir_2O_7$ lattice it could occupy an Ir^{4+} or Bi^{3+} site, with the consequent generation of an oxygen vacancy and the corresponding metal oxide (IrO_2 and Bi_2O_3, Schottky reactions 1 and 2). An additional effect related with the incorporation of Sr^{2+} at the Bi^{3+} site is associated with a change of the oxidation state of Ir (reaction 3). Considering the oxygen occupation values obtained from the Rietveld analysis [13], it is possible to think that Schottky reactions could happen, however, the corresponding bismuth or iridium oxides were not found in the diffraction patterns as products of such reaction. It should be pointed out that the prolonged time of the solid-state reaction could lead to evaporation and disproportionation of the iridium-oxide, releasing oxygen [19]. On the basis of the experimental results, it is clear that reaction 3 is being preferred but is difficult to accurately determine the oxygen content of samples.

The temperature dependence of the magnetic susceptibility of the $Bi_{2-y}Sr_yIr_2O_7$ compounds with the y-compositions 0.0, 0.1, 0.3, 0.5, 0.7 and 0.9 are shown in Fig. 1. All susceptibility data were corrected for core diamagnetism [20]. As can be observed in this figure, none of the samples showed a magnetic transition, at least down to 2 K, and the magnetic susceptibility diminishes as the Sr content increases. The magnetic susceptibility reduction can be explained in terms of a change in the oxidation state of the Ir atoms, since Ir is the only magnetic cation present in the $Bi_{2-y}Sr_yIr_2O_7$ series.

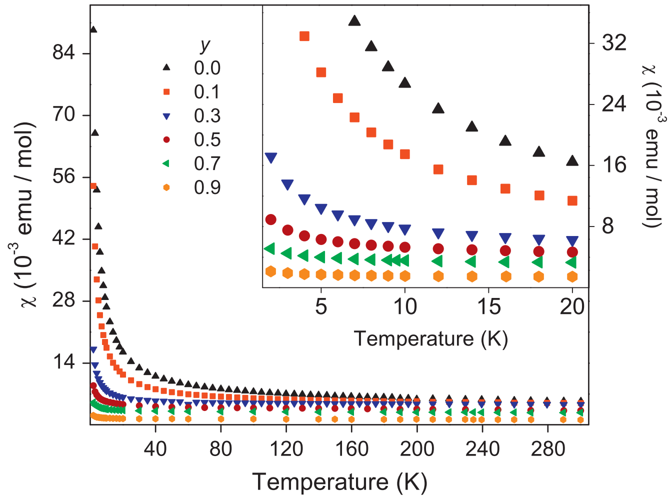

Fig. 1. Magnetic susceptibility as a function of temperature of $Bi_{2-x}Sr_xIr_2O_7$. The inset shows a magnification of the low temperature region.

The coordination environment around the Ir cation in the α-pyrochlore crystal lattice is a distorted octahedron in the form of a trigonal antiprism (TA) [21], that is, the lattice is distorted in the [111] direction. As a consequence, from the $t_{2g}(d_{xy},d_{yz},d_{xz})$ and $e_g(d_{x^2-y^2},d_{z^2})$ regular octahedron splitting, now t_{2g} splits into $e_g'(d_{x'z'},d_{y'z'})$ and $a_{1g}(d_{x'y'})$ [22], where x',y' and z' is a new coordinate system with z' in the [111] direction. On the other hand, the bands are wide [13] and the $e_g'-a_{1g}$ splitting for the studied system is considerably smaller. Thus, in the crystal field scheme, the electron configuration of Ir^{4+} is $[Xe]4f^{14}5d^5 : e_g'^4a_{1g}^1$, with a spin magnetic moment $S=1/2$. In this way the explanation of the magnetic susceptibility reduction as a function of the Sr content is that the inclusion of Sr in trivalent cation positions (Bi), produces a partial oxidation of iridium atoms from Ir^{4+} to Ir^{5+}.

The Ir^{5+} produced to achieve electroneutrality has an electron configuration $[Xe]4f^{14}5d^4 : e_g'^4a_{1g}^0$, with $S=0$, therefore it would not contribute to the magnetic susceptibility [23], and the susceptibility of the compounds is due to the remaining Ir^{4+} [24,25]; consequently, magnetic susceptibility of samples should diminish as is experimentally found. In contrast, in an octahedral crystal field splitting (low spin), Ir^{4+} has $S=1/2$ (the same that for TA splitting), but Ir^{5+} has $S=1$. The experimental measurement of magnetization seems to point the existence of nonmagnetic Ir^{5+}, which increases as a function of the Sr content, see Fig. 1. Several other pyrochlore systems containing Ir^{5+} have previously been reported, in which the Ir valence was stated by X-ray photoemission spectroscopy (XPS) [26] and X-ray absorption near edge spectroscopy (XANES) [27].

In order to explain in detail the magnetic behavior of the $Bi_{2-y}Sr_yIr_2O_7$ system, a first approximation was done fitting the susceptibility data to the CW equation, $\chi(T)=C/(T-\theta)$. This fit was performed for the high temperature region but the C and θ values are not congruent with those expected for a paramagnet.

All samples of the $Bi_{2-y}Sr_yIr_2O_7$ series show metallic behavior, but at a fixed temperature, for a bigger Sr-content corresponds a larger resistivity. The metallic conductivity and non-CW behavior is not exclusive of magnetic compounds crystallizing in the α-pyrochlore structure, this has also been observed in iron pnictides [28] and $La_{2-x}Sr_xCuO_4$ systems [29]. Likewise, short-range magnetic interactions between rare earth ions on the A site of magnetic pyrochlores have been reported in $R_2Ru_2O_7$ (R=Tb, Er and Yb) [30]. Therefore, it is necessary to consider short-range magnetic order and spin fluctuations [31,32] in the interpretation of the magnetic behavior of $Bi_{2-y}Sr_yIr_2O_7$.

Based on the theoretical expressions deduced by Opechowski and Li, in which the short-range magnetic order effects are included in power series of $Jz/2k_BT$ [31,33,34], a mCW equation was tried to fit the observed magnetic susceptibilities. The $Jz/2k_B$ term could be associated with the θ value in the Curie–Weiss model when $S=1/2$, since $\theta=2zJS(S+1)/3k_B$, where J is the exchange integral and z is the spin coordination number. Additionally, a phenomenological linear temperature term αT was included. The modified CW equation is [29,35]

$$\chi=\chi_0+\alpha T+\frac{C}{T\left[1+\left(\frac{\theta}{T}\right)^2-\left(\frac{\theta}{T}\right)^3\right]-\theta} \tag{4}$$

The parameters obtained with the mCW fitting are shown in Table 1. It is worth mentioning here that when an equation such as $\chi=C/(T-\theta)+\alpha T+\chi_0$ was tried, the fitting was not satisfactory, especially in the low temperature region, $T<100$ K. Even though all samples exhibit a paramagnetic behavior in the 2–300 K range, a noticeable deviation from the linearity in χ^{-1} is observed for the low temperature region. This departure goes to lower temperatures as the Sr content increases. The further from Ir^{4+} towards Ir^{5+}, the larger is the fitting range to the CW equation.

The results of the magnetic susceptibility fitting obtained with Eq. (4) show that the α term is small when it is compared with χ_0, but this phenomenological term is necessary to obtain a good adjustment of the experimental data and also permits a suitable interpretation of C and θ.

If the conventional procedure to determine C and θ from magnetic susceptibility data had been used, that is, extrapolating χ^{-1} *vs.* temperature data for the high temperature range, then one obtains very large $-\theta$ values: 470 K ($y=0$); 1020 K ($y=0.1$); 2940 K ($y=0.3$); 1138 K ($y=0.5$); 2687 K ($y=0.7$) and 1577 K ($y=0.9$). From the C values, Ir effective magnetic moments of 5.7, 7.4, 11.18, 7.14, 10.11 and 5.67 Bohr magnetons (μ_B), are obtained, which are unacceptable (for the Ir^{4+} free-ion $\mu_{eff}=1.73\mu_B$ [36]).

The small negative values obtained for θ with Eq. (4) suggest a weak AF coupling in all samples of this solid solution. No magnetic transition was observed, if this transition exists, it might occur at temperature below 2 K. Very recently, Qi et al. reported the magnetic and thermal behavior of $Bi_2Ir_2O_7$ single-crystal. They showed that in the range 0.05–350 K there are no anomalies indicating long-range order, and found that $\chi_0=1.07\times10^{-2}$ (emu/mole), $\theta=-2.3$ K and a $\mu_{eff}=0.10\mu_B$/Ir and the magnetic susceptibility of that sample noticeably differs from that of the CW equation [37].

Table 1
Magnetic parameters obtained from fitting of magnetic susceptibility data of the $Bi_{2-y}Sr_yIr_2O_7$ system using Eq. (4).

y	$\chi_0\times10^{-3}$ (emu/mol)	$\alpha\times10^{-6}$ (emu/K-mol)	C (emu/K-mol)	θ (K)
0.0	5.93	−4.85	0.2148	−0.45
0.1	5.04	−2.08	0.1287	−0.49
0.2	4.70	−0.09	0.0316	−0.43
0.3	4.41	−1.33	0.0151	−0.60
0.4	4.37	−0.30	0.0149	−0.60
0.5	4.00	−2.62	0.0134	−0.56
0.6	4.43	−0.37	0.0124	−0.39
0.7	3.06	−1.04	0.0051	−0.43
0.8	1.98	−0.24	0.0040	−0.41
0.9	1.37	−0.67	0.0018	−0.35

Since the cell-parameter of the $Bi_{2-y}Sr_yIr_2O_7$ solid solution behaves according to the Vegard law, then knowing the ionic radii of Bi^{3+} (1.17 Å, CN=8), Sr^{2+} (1.26 Å, CN=8), Ir^{4+} (0.625 Å, CN=6) and Ir^{5+} (0.57 Å, CN=6) (CN is the coordination number) [14] an approximation of the Ir^{5+} content can be obtained. This procedure is better than that using the Ir–O bond-distances [13], since these values are influenced by the effect of Bi substitution by Sr, mentioned above [15]. Using this approximation the Ir^{4+} atomic fractions, x, in samples were calculated.

The Ir^{4+} atomic fractions reported in this work agree well with the oxygen occupation factors from previous Rietveld refinements results [13]. The difference between the stoichiometric Sr value, y, and the Ir^{5+} content of samples to preserve electroneutrality, can be attributed to the oxygen deficiencies of samples [19].

The C term of Eq. (4) can be interpreted as the effective magnetic moment per magnetic ion, μ_{eff}. According to Eq. (4), and taking into account the remaining Ir^{4+} content, the μ_{eff} values are shown in Fig. 3. For the $y=0.0$ sample, μ_{eff} corresponds to 76% of the expected value for $S=1/2$ in a TA geometry, however, in $Y_2Ir_2O_7$, which is magnetically similar to $Bi_2Ir_2O_7$, Fukazawa et al. [3] report 14% of the expected value with $S=1/2$. This difference could be associated with oxygen or iridium vacancies, because in both compounds the atomic distances Ir–O1 and bond angles Ir–O1–Ir are similar. Moreover, the μ_{eff} values of the $Bi_{2-y}Sr_yIr_2O_7$ system indicate that with increasing the Sr^{2+} content, the effective magnetic moment diminishes until it reaches 8.1% of the expected value, at $y=0.9$.

Ir-μ_{eff} values smaller than the expected value of $1.73\mu_B$ [36] have been reported for several Ir compounds, these values range from 0.13 to $0.69\mu_B$ [38]. One explanation of this small value of μ_{eff} is attributed to the strong spin–orbit coupling of *Ir* cations and the strong exchange interactions that lower the magnetization of samples [38]. In the case of $Eu_2Ir_2O_7$, muon spin rotation and relaxation experiments did not suffice to provide the magnetic structure of such compound, furthermore neutron scattering measurements result prohibitively difficult because of the high neutron absorption cross section of Ir nucleus [5].

As can be observed from Fig. 2, the magnetic measurements of the $Bi_{2-y}Sr_yIr_2O_7$ solid solution, rather than being the result of a type of magnetic alignment of moments under an applied magnetic field (paramagnetic gas), they seem to show the effect of short-range magnetic interactions, which, prevailing at the

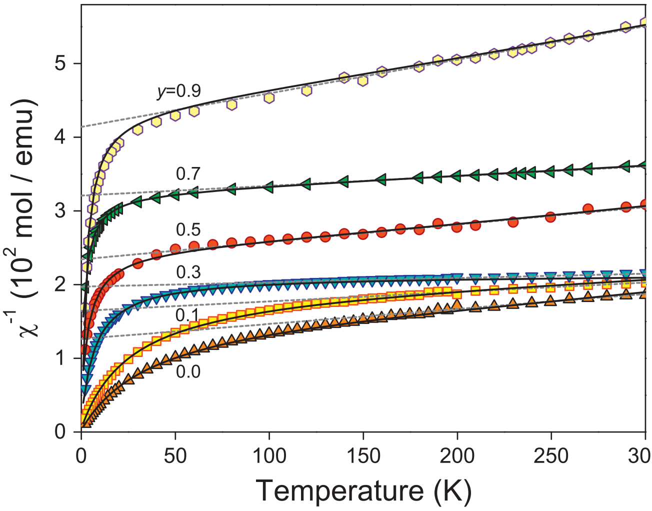

Fig. 2. Inverse of the magnetic susceptibility χ^{-1} of the $Bi_{2-y}Sr_yIr_2O_7$ as a function of temperature. The dashed lines represent a linear fitting of data above 100 K. The continuous lines represent the data fitting using the modified Curie–Weiss equation, see text.

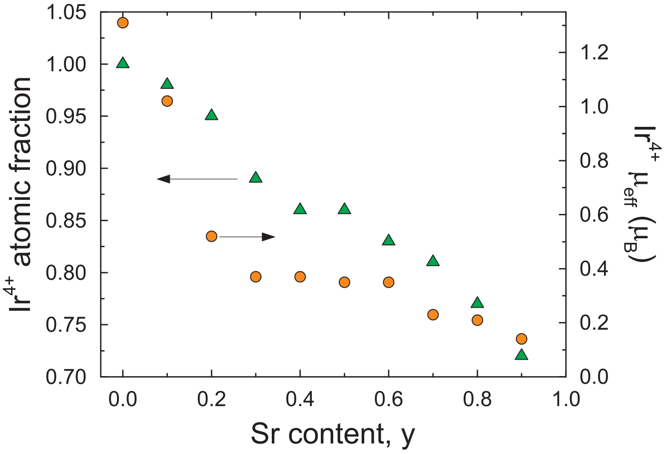

Fig. 3. Ir^{4+} atomic fraction (triangles) and iridium effective magnetic moment, μ_{eff} (circles) in the $Bi_{2-y}Sr_yIr_2O_7$ solid solution as a function of the Sr content. The Ir^{4+} atomic fraction is obtained from the y-dependence of the crystal cell-parameters, and the μ_{eff} from the C value, see Table 1.

whole 2–300 K temperature range, are not capable to condensate into a large-range AF state. In this way, while no noticeable variation of the θ value dependent of the Sr content is observed, there is a clear departure from the CW behavior that can be associated with short-range interactions, especially in the low temperature region.

For $y=0$ and 0.1 the calculated magnetic moments are 1.23 and $1.02\mu_B$, respectively. These values agree well with those reported for Ir^{4+} in $Eu_2Ir_2O_7$ ($1.1\mu_B$) [5]. On the other hand, the independent temperature susceptibility terms, χ_0, obtained are of the order of 10^{-3} emu/mol, and these decrease as the Sr content increases. These χ_0 values are similar to the values obtained for other pyrochlore iridates [2,3] such as $Y_2Ir_2O_7$ and ruthenates, $Pb_2Ru_2O_{6.5}$ [39,40].

The tendency of χ_0 to diminish with the Sr content could have origin in two different processes. On one hand, one could think of a reduction of the $N(E_F)$ associated to the appearance of Ir^{5+}. However, according to previous results [13] of DFT density of states calculation for $Bi_2Ir_2O_7$ and $BiSrIr_2O_7$, these $N(E_F)$ values are practically insensitive to the Sr content. Since in both systems the main contributors to $N(E_F)$ are Ir and O1 (95% in $Bi_2Ir_2O_7$ and 96.5% in $BiSrIr_2O_7$), Ir^{5+} is not expected to be the main responsible for this diminishing in the χ_0 values. On the other hand, it is worth mentioning that, associated to the 5d electronic configuration and the local geometry of Ir^{4+}, a strong spin–orbit coupling (SOC) has been pointed out as responsible of spectacular electronic properties in localized [5,41] and metallic systems [2,42]. The existence of this strong SOC would significantly modify the χ_0 values with respect to those observed in 3d and 4d-transition metal oxides. At this regard the Wilson ratio, R_W, provides an empirical indicator of the strength of the electron–electron correlation.

As the case of the '5M' barium iridiate, $BaIrO_3$, the temperature independent magnetic susceptibility, χ_0, of $Bi_{2-y}Sr_yIr_2O_7$ is in the range of the free electron system [38]. In the free-electron approximation of metals the Pauli susceptibility, χ^P can be calculated from χ_0 by subtracting the diamagnetic Landau contribution, $\chi^P=(3/2)\chi_0$ (where χ_0 is corrected for core diamagnetism), and χ^P is proportional to $N(E_F)$.

For $Bi_2Ir_2O_7$ single-crystal in the low temperature regime ($50\ \text{mK} < T < 4$ K), the heat capacity measurement is well described by $C(T)=\gamma T+\beta T^3$, were $\gamma=16\ \text{mJ mol}^{-1}\ \text{K}^{-2}$ [37]. Considering this γ value for an evaluation of the Wilson ratio, defined as $R_W=(4\pi^2k_B^2\chi^P)/[3(g\mu_B)^2\gamma]$, the R_W value for $Bi_2Ir_2O_7$ is 27.1. Since $R_W=1$ for a non-interacting free electron-system, the R_W obtained is indicative of substantial electron–electron correlation in $Bi_2Ir_2O_7$. As shown in Table 1, χ_0 decreases as the Sr content; as the electrical resistivity value as a function of the Sr content remains in the same order, we can roughly assume that $N(E_F)$ has no noticeable variation and γ has a small dependence with the Sr content. In this way R_W is expected to decrease as χ^P and the electron–electron correlation would decrease as the Sr content. We could suppose that such decrease is associated to the presence of Ir^{5+} and that such electronic correlation can be either originated in the SOC (anticipated for all the 5d electronic systems) or to short-range correlations of magnetic electrons.

Even though 5d orbitals are spatially more extended than 3d and 4d, and the correlations effects are expected to be minimal, there are some iridium-oxide based compounds in which electron correlation seems to play a crucial role in the electronic properties of them. In Sr_2IrO_4 the SOC is assumed responsible for a Mott ground state of spin driven correlated-electron phenomena [43]; a quantum Hall effect has been anticipated in Na_2IrO_3 on the basis of spin–orbit interaction and electron correlation [44] and more strongly in the $Sr_{n+1}Ir_nO_{3n+1}$ series of compounds ($n=1$, 2 and ∞), optical spectroscopy results and first-principles calculations consistently show that large SOC in 5d systems could drastically enhance electron correlation effects [45].

4. Conclusions

Magnetic susceptibility measurements on the $Bi_{2-y}Sr_yIr_2O_7$ system indicate a shift towards nonmagnetic Ir^{5+} in samples with $y>0$. The temperature dependence of the magnetic susceptibility is consistent with a trigonal antiprism crystal field splitting ($S=1/2$ for Ir^{4+} and $S=0$ for Ir^{5+}). In the 2–300 K temperature range a magnetic transition was not observed and the small θ values can be associated with a weak antiferromagnetic coupling in this system. The Bi substitution by Sr in $Bi_{2-y}Sr_yIr_2O_7$, produced a magnetic state whose temperature behavior is not well described by a Curie–Weiss equation. The $Bi_{2-y}Sr_yIr_2O_7$ solid solution is magnetically well described by a modified CW equation in which short-range interaction and magnetic thermal-fluctuations are taken into account. The estimated Wilson-ratio indicates the existence of electron–electron correlations in a paramagnetic state; this correlation seems to extend over the whole range of y-composition but decreases with the Sr content.

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References

[1] J.E. Greedan, J. Mater. Chem. 11 (2001) 37.
[2] D. Yanagishima, Y. Maeno, J. Phys. Soc. Jpn. 70 (2001) 2880.
[3] H. Fukazawa, Y. Maeno, J. Phys. Soc. Jpn. 71 (2002) 2578.
[4] M. Soda, N. Aito, Y. Kurahashi, Y. Kobayashi, M. Sato, Physica B 329–333 (2003) 1071.
[5] S. Zhao, J.M. Mackie, D.E. MacLaughlin, O.O. Bernal, J.J. Ishikawa, Y. Ohta, S. Nakatsuji, Phys. Rev. B 83 (2011) 180402. (R).
[6] K. Matsuhira, M. Wakeshima, R. Nakanishi, T. Yamada, A. Nakamura, W. Kawano, S. Takagi, Y. Hinatsu, J. Phys. Soc. Jpn. 76 (2007) 043706;

K. Matsuhira, M. Wakeshima, Y. Hinatsu, S. Takagi, J. Phys. Soc. Jpn. 80 (2011) 094701.
[7] V. Fritsch, J.D. Thompson, J.L. Sarrao, Phys. Rev. B 71 (2005) 132401.
[8] V. Fritsch, J.D. Thompson, J.L. Serrao, H.-A. Krug von Nidda, R.M. Eremina, A. Loidl, Phys. Rev. B 73 (2006) 094413.
[9] C. Lacroix, J. Phys. Soc. Jpn. 79 (2010) 011008.
[10] R.J. Bouchard, J.L. Gillon, Mater. Res. Bull. 6 (1971) 669.
[11] B.J. Kennedy, J. Solid State Chem. 123 (1996) 14.
[12] N. Aito, M. Soda, Y. Kobayashi, M. Sato, J. Phys. Soc. Jpn. 72 (2003) 1226.
[13] C. Cosio-Castaneda, P. de la Mora, G. Tavizon, J. Solid State Chem. 184 (2011) 1251.
[14] R. Shanno, Acta Crystallogr. A 32 (1976) 751.
[15] H.-J. Koo, M.H. Whangbo, B.J. Kennedy, J. Solid State Chem. 136 (1998) 269.
[16] M. Pirzada, R.W. Grimes, J.F. Maguire, Solid State Ionics 161 (2003) 81.
[17] G.D. Blundred, C.A. Bridges, M.J. Rosseinsky, Angew. Chem. Int. Ed. 43 (2004) 3562.
[18] F.A. Kröger, H.J. Vink, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics, vol. 3, Academic Press, New York, 1956.
[19] D.E. Peterson, Thermodynamics and Transport of Gaseous Iridium Oxide in Multi-Hundred-Watt Thermoelectric Generators. National Technical Information Service. U.S. Department of Commerce. UC-4 & UC-25, May 1976.
[20] G.A. Bain, J.F. Berry, J. Chem. Educ. 85 (2008) 532.
[21] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, Prog. Solid State Chem. 15 (1983) 55.
[22] M. Avdeev, M.K. Haas, J.D. Jorgensen, R.J. Cava, J. Solid State Chem. 169 (2002) 24.
[23] P.D. Battle, J.G. Gore, R.C. Hollyman, A.V. Powell, J. Alloys Compd. 218 (1995) 110.
[24] G. Cao, V. Durairaj, S. Chikara, S. Parkin, P. Schottman, Phys. Rev. B 75 (2007) 134402.
[25] A.V. Powell, J.G. Gore, P.D. Battle, J. Alloys Compd. 201 (1993) 73.
[26] T. Otsubo, S. Takase, Y. Chimizu, ECS Trans. 3 (2006) 263.
[27] K. Sardar, J. Fisher, D. Thompsett, M.R. Lees, G.J. Clarkson, J. Sloan, R.J. Kashtiban, R.I. Walton, Chem. Sci. 2 (2011) 1573.
[28] G.M. Zhang, Y.H. Su, Z.Y. Lu, Z.Y. Weng, D.H. Lee, T. Xiang, Eur. Phys. Lett. 86 (2009) 37006.
[29] T. Nakano, M. Oda, C. Manabe, N. Momono, Y. Miura, M. Ido, Phys. Rev. B 49 (1994) 16000.
[30] N. Taira, M. Wakeshima, Y. Hinatsu, J. Mater. Chem. 12 (2002) 1475.
[31] S. Ebisu, T. Komatsu, N. Wada, T. Hashiguchi, P. Kichambare, S. Nagata, J. Phys. Chem. Solids 59 (1998) 1407.
[32] J.N. Reimers, Phys. Rev. B 45 (1992) 7287.
[33] Y.-Y. Li, Phys. Rev. 84 (1951) 721.
[34] W. Opechowski, Physica 4 (1937) 715.
[35] N. Shannon, Eur. Phys. J. B 27 (2002) 527.
[36] M.W. Lufaso, H.-C. Zur Loye, Inorg. Chem. 44 (2005) 9143.
[37] T.F. Qi, O.B. Korneta, Wan Xiangang, L.E. DeLong, P. Schlottmann, G. Cao, J. Phys.: Condens. Matter 24 (2012) 345601.
[38] J.G. Zhao, L.X. Yang, Y. Yu, F.Y. Li, R.C. Yu, C.Q. Jin, Solid State Commun. 150 (2010) 36.
[39] M. Tachibana, Y. Kohama, T. Shimoyama, A. Harada, T. Taniyama, M. Itoh, H. Kawaji, T. Atake, Phys. Rev. B 73 (2006) 193107.
[40] T. Akazawa, Y. Inaguma, T. Katsumata, K. Hiraki, T. Takahashi, J. Cryst. Growth 271 (2004) 445.
[41] D. Pesin, L. Balents, Nat. Phys. 6 (2010) 376.
[42] Y. Machida, S. Nakatsuji, Y. Maeno, T. Tayama, T. Sakakibara, S. Anoda, Phys. Rev. Lett. 98 (2007) 057203.
[43] B.J. Kim, J. Hosub, S.J. Moon, J.-Y. Kim, B.-G. Park, C.S. Leem, J. Yu, T.W. Noh, C. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao, E. Rotenberg, Phys. Rev. Lett. 101 (2008) 076402.
[44] A. Shitade, H. Katsura, J. Kunes, X.-L. Qi, S.-C. Zhang, N. Nagaosa, Phys. Rev. Lett. 102 (2009) 256403.
[45] S.J. Moon, H. Jin, K.W. Kim, W.S. Choi, Y.S. Lee, J. Yu, G. Cao, A. Sumi, H. Funakubo, C. Benhard, T.W. Noh, Phys. Rev. Lett. 101 (2008) 226406.