PHYSICAL REVIEW B VOLUME 49, NUMBER 13 1 APRIL 1994-I

Structural and magnetic studies of Sr_2IrO_4

M. K. Crawford, M. A. Subramanian, and R. L. Harlow
DuPont, Wilmington, Delaware 19880-0356

J. A. Fernandez-Baca
Solid State Division, MS 6393, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831

Z. R. Wang and D. C. Johnston
Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

(Received 11 October 1993)

The discovery of high-temperature superconductivity in doped copper oxides, which in their insulating forms are nearly ideal two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnets, has stimulated great interest in finding additional examples of such magnetic systems. We find that Sr_2IrO_4, which has the K_2NiF_4 structure and should have a $5d^5$ low-spin ($S=\frac{1}{2}$) electronic configuration, develops a ferromagnetic moment near 250 K. The small size of the remanent moment ($10^{-2}\mu_B$), and our structural studies, however, imply that this is weak ferromagnetism which appears at the Néel temperature due to a Dzyaloshinsky-Moriya interaction, in a manner analogous to that seen in La_2CuO_4.

Interest in spin-$\frac{1}{2}$ two-dimensional Heisenberg antiferromagnets has greatly increased in recent years due to the discovery of high-temperature superconductivity in copper oxides which, in their insulating (undoped) phases, fall into this magnetic category. Although a number of oxides are known with the La_2CuO_4 (K_2NiF_4) structure, no spin-$\frac{1}{2}$ two-dimensional antiferromagnetic oxides other than the cuprates have been thoroughly studied.[1] In order to deepen our understanding of the magnetic properties of the cuprates, and to expand the range of materials which might exhibit high-temperature superconductivity, we are investigating other metal oxides which would be expected to have one unpaired d electron per metal ion. Here we describe our results for Sr_2IrO_4.

Sr_2IrO_4, which has the K_2NiF_4 structure,[2] has octahedrally coordinated Ir^{4+} ions. The electronic configuration of the Ir^{4+} ions is $\{Xe\}4f^{14}5d^5$. Due to the large crystal field and very large spin-orbit coupling,[3] the Ir^{4+} ion should be in the low-spin configuration t_{2g}^5, with the ground state being ${}^2T_2$. This state is split by spin-orbit coupling and the tetragonal crystal field (see below) into three Kramers doublets. Thus, the ground state for Ir^{4+} in Sr_2IrO_4 is expected to be a spin-$\frac{1}{2}$ Kramers doublet, where the unpaired spin occupies a half-filled d_{xy} band, similar to the situation found for Cu^{2+} in La_2CuO_4.[4]

Samples were prepared by standard solid-state synthetic techniques.[2] Synchrotron x-ray powder diffraction measurements were performed at beamline X-3A2 at the National Synchrotron Light Source at Brookhaven National Laboratory.[5] Neutron powder diffraction measurements were performed at the HB-4 High Resolution Powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory.[6] Magnetic susceptibility measurements were made with a Quantum Design SQUID magnetometer and an Oxford Instruments Faraday balance. We note that preliminary electrical resistivity measurements indicate that Sr_2IrO_4 is an insulator, although further measurements on single crystals are highly desired.

Initial synchrotron x-ray-diffraction data for Sr_2IrO_4 at temperatures between 300 K and 20 K demonstrated that this material is tetragonal, in agreement with a previous study.[2] However, closer inspection of the x-ray data revealed several weak superlattice reflections, not previously observed (nor expected for the assumed $I4/mmm$ symmetry),[2] which could be indexed using a larger cell with dimensions of $\sqrt{2}a\times 2c$, where a and c are the cell parameters for the (small) $I4/mmm$ cell. Thus, the x-ray data indicated that a crystallographic distortion was present in this material, but the weakness of the x-ray superlattice reflections, together with our belief that the most likely distortions leading to such reflections would involve primarily oxygen atom displacements, suggested that neutron-diffraction measurements should be made.

In Fig. 1 (top), we show the results of the neutron-diffraction measurements together with the Rietveld refinement and difference plots for Sr_2IrO_4 at 13 K. A structure which gives a reasonably good fit to the diffraction data is one in which the IrO_6 octahedra are rotated about the crystallographic c axis by about 11°, reducing the space group symmetry from $I4/mmm$ to $I4_1/acd$ and generating an enlarged unit cell with dimensions $\sqrt{2}a\times 2c$, in agreement with the x-ray data. The rotation scheme is shown in Fig. 2. A similar structural distortion has been observed in K_2NiF_4-type Ca_2MnO_4 (Ref. 7). The transformation from $I4/mmm$ to $I4_1/acd$ symmetry is allowed via a second-order (continuous) structural phase transition involving a Brillouin zone boundary phonon of P_2 symmetry.[8] In Fig. 1 (bottom), we show the diffraction data in the regions where the su-

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perlattice reflections which characterize this structural distortion, the (21l), l odd, and the (41l), l odd, appear. It can be seen that the $I4_1/acd$ space group correctly gives these superlattice reflections, although the less than perfect agreement of the observed and calculated intensities indicates that some deficiencies remain in the structural solution. In this regard, diffuse x-ray scattering streaks located between particular reciprocal-lattice points were observed in Weissenberg films obtained using single crystals and, although not obvious, small positive deviations of the observed data points from the calculated background suggest that diffuse scattering is also present in the neutron data. These observations imply that some structural disorder is present, probably involving the rotations of the IrO_6 octahedra. The results of the structural refinements are given in Table I for the three temperatures at which data were taken. It should also be noted that the IrO_6 octahedra are elongated in the c direction, similar to the distortion exhibited by the CuO_6 octahedra in La_2CuO_4. This may be a Jahn-Teller distortion, or merely an effect of the anisotropic crystal structure (3).

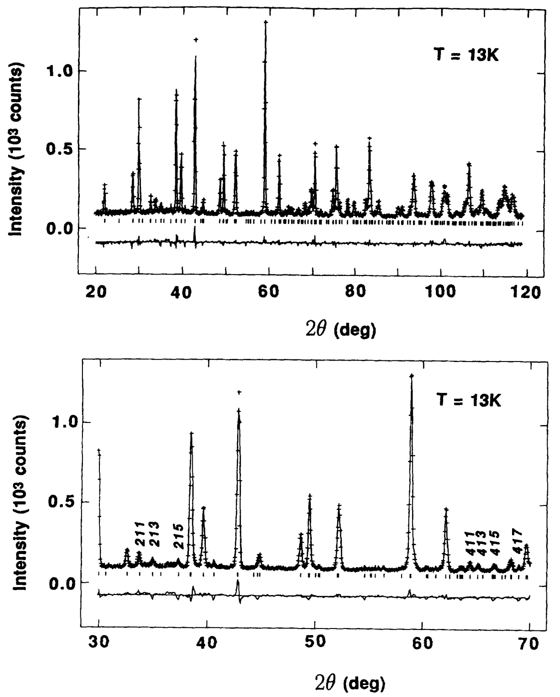

FIG. 1. (Top) Neutron powder diffraction pattern and Rietveld refinement for Sr_2IrO_4 at 13 K. The crosses are the data, the solid line is the fit, the vertical markers indicate expected peak positions, and the residuals appear at the bottom of the figure. The neutron wavelength was 1.4163 Å. (Bottom) Neutron-diffraction data for Sr_2IrO_4 at 13 K showing superlattice reflections due to the IrO_6 rotational distortion.

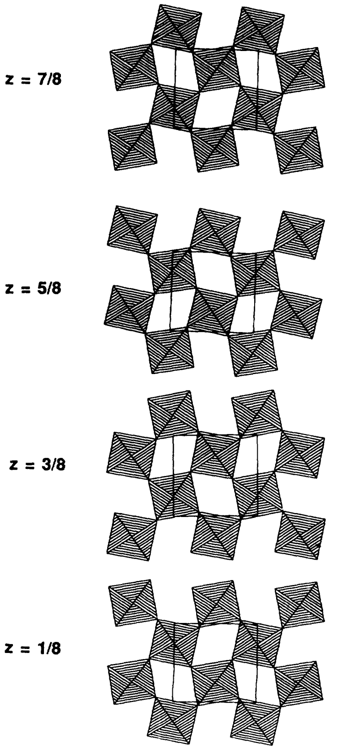

FIG. 2. Structure diagram of Sr_2IrO_4 with $I4_1/acd$ space group symmetry, showing the IrO_6 octahedra rotation pattern in each layer of the unit cell. The z coordinates for each layer are indicated. The square figure superimposed on each layer is the unit-cell outline. The c axis is perpendicular to the page.

TABLE I. Crystallographic information for Sr_2IrO_4. The structure was refined in the tetragonal space group $I4_1/acd$ at all three temperatures. The four unique atoms have the following positions: Ir, $(0, \frac{1}{4}, \frac{3}{8})$; Sr, $(0, \frac{1}{4}, z)$; O1, $(0, \frac{1}{4}, z)$; O2, $(x, \frac{1}{4}+x, \frac{1}{8})$. Refinement of the oxygen occupancy indicated that both oxygen sites were fully occupied.

	295 K	200 K	13 K
	Lattice constants		
a, Å	5.497 9(2)	5.491 6(2)	5.484 6(2)
c, Å	25.798(1)	25.797(1)	25.804(1)
V, Å^3	779.8(1)	778.0(1)	776.2(1)
	Refinement information		
Data points	2 293	2 229	1 980
Reflections	228	215	184
Variables	20	20	20
R_p	0.044	0.040	0.044
R_{wp}	0.054	0.051	0.059
R_n	0.035	0.031	0.032
	Positional and thermal parameters		
Ir: U_{iso}	0.003 6(4)	0.003 1(4)	0.000 6(5)
Sr: z	0.550 56(6)	0.550 60(5)	0.550 53(6)
U_{iso}	0.007 9(4)	0.005 0(4)	0.000 9(5)
O1: z	0.454 75(7)	0.454 72(6)	0.454 73(7)
U_{iso}	0.007 9(4)	0.005 3(4)	0.002 1(5)
O2: x	0.201 2(3)	0.200 1(2)	0.199 1(3)
U_{iso}	0.010 8(5)	0.009 0(5)	0.006 3(6)
	Selected bond distances (Å) and angles (deg)		
Ir-O1 (×2)	2.058(2)	2.056(2)	2.057(2)
Ir-O2 (×4)	1.981(1)	1.980(1)	1.979(1)
Sr-O1 (×1)	2.472(2)	2.474(2)	2.472(2)
Sr-O1 (×4)	2.752(1)	2.749(1)	2.746(1)
Sr-O2 (×2)	2.477(2)	2.470(2)	2.465(2)
Sr-O2 (×2)	3.015(2)	3.018(2)	3.024(2)
Ir-O2-Ir	157.9(1)	157.4(1)	157.0(1)

We now turn to the magnetic measurements which we have made on this material. In Fig. 3 (top), we show the temperature dependence of the magnetic susceptibility. There is a distinct magnetic transition at approximately 250 K. In order to clarify the nature of this magnetic transition, in Fig. 3 (bottom) we show magnetic hysteresis measurements (magnetization versus magnetic field) for this sample at a temperature of 5 K. There is a significant magnetic hysteresis, demonstrating that the magnetic structure has a ferromagnetic component. The magnitude of the ferromagnetic moment estimated from these data is far too small (10^{-2} Bohr magnetons per Ir ion) to attribute to full ferromagnetically aligned spin-$\frac{1}{2}$ Ir^{4+} ions, which should have a magnetic moment of 1.1 Bohr magnetons, perhaps renormalized downward by quantum fluctuations as in La_2CuO_4. Instead it seems more reasonable to attribute the ferromagnetic behavior to canted antiferromagnetism.[9] The magnetic transition we observe is thus probably due to the appearance of long-range three-dimensional antiferromagnetic order of the Ir^{4+} moments. Furthermore, since Ir^{4+} should be a spin-$\frac{1}{2}$ ion it has no first-order single-ion magnetic anisotropy, and therefore the magnetic properties of Sr_2IrO_4 are expected to be Heisenberg-like. If this is so, apart from the copper oxides, Sr_2IrO_4 would be, to our knowledge, the second spin-$\frac{1}{2}$ two-dimensional Heisenberg antiferromagnetic oxide reported, although the layered vanadates (for example, Sr_2VO_4) may also belong to this category. Muon spin rotation and neutron-diffraction[10] measurements should be made to verify the magnetic ordering temperature and determine the magnetic structure.

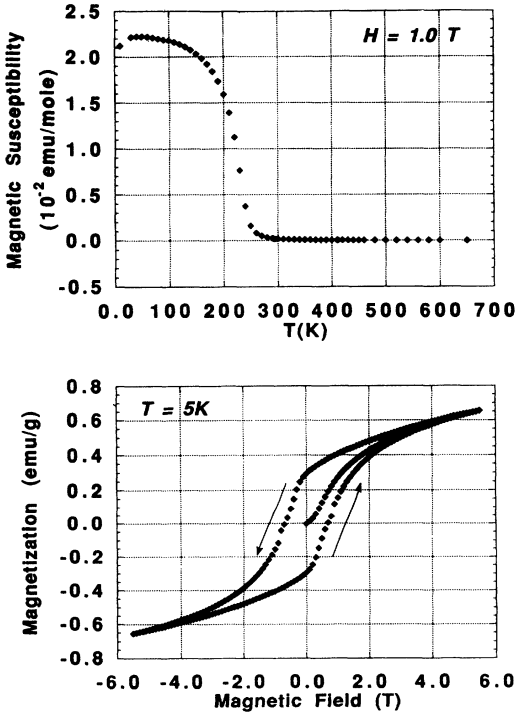

FIG. 3. (Top) Magnetic susceptibility data measured with a Faraday balance from 5 to 650 K. (Bottom) Magnetic hysteresis curve measured with a SQUID magnetometer at 5 K. The arrows indicate the direction in which the field is changing.

Without single-ion anisotropy to cause moment canting, a different origin must be found for the appearance of weak ferromagnetism in this system. The most likely cause is a Dzyaloshinsky-Moriya[11,12] (DM) interaction which arises as a result of the structural distortion described above. The rotational distortion destroys the inversion center which exists midway between the Ir^{4+} ions along the (100) and (010) directions for $I4/mmm$ symmetry and thereby permits an antisymmetric superexchange term to appear in the spin Hamiltonian due to the DM interaction.[11-13] A DM interaction also generates canted Cu^{2+} moments as a direct result of the tilting distortion of the CuO_6 octahedra in La_2CuO_4.[14]

The strength of the Dzyaloshinsky-Moriya interaction is proportional to the amount of anisotropy in the Landé g factor, $|\vec{D}| \sim (\Delta g/g)J$, where $\Delta g = g - 2$.[12] Since anisotropy of g is a consequence of spin-orbit coupling, and the spin-orbit coupling in Ir^{4+} is large (~ 2000 cm^{-1}), it is expected that the Dzyaloshinsky-Moriya interaction is comparable to or larger in this $5d$ system than in $3d$ Cu^{2+} (spin-orbit coupling ~ 800 cm^{-1}). Furthermore, the relative magnitudes of the rotational distortions of the IrO_6 octahedra in Sr_2IrO_4 ($\sim 11°$) and the CuO_6 octahedra in La_2CuO_4 ($\sim 3°$) also lead one to expect a larger DM interaction in the former material.[14] These facts are consistent with our observation of a canted moment in Sr_2IrO_4 1 order of magnitude larger than that observed in La_2CuO_4 ($\sim 10^{-3}$ Bohr magnetons).

Figure 3 (top) also shows the high-temperature magnetic susceptibility of Sr_2IrO_4. The susceptibility decreases with temperature above the Néel temperature, but not in a fashion consistent with Curie-Weiss behavior. Similar data above the Néel temperature in La_2CuO_4, which also do not follow a Curie-Weiss temperature dependence, were interpreted by a theory[14] which clarified the role of the canted weak ferromagnetism in determining the magnetic properties of that material at temperatures above and below the Néel temperature. However, in contrast to the situation in La_2CuO_4, where the canted moments are antiferromagneticaly aligned in successive layers, our data (Fig. 3) indicate that in Sr_2IrO_4 the canted moments in successive layers are ferromagnetically aligned. This is similar to results we have reported [15] for $La_{2-x}Nd_xCuO_4$, where low-temperature structural phase transformations induce a magnetic transition from an antiferromagnetic to a ferromagnetic interlayer arrangement of the Cu^{2+} spins.

It should be noted that a peak associated with two-dimensional short-range antiferromagnetic order does not appear in the raw susceptibility data above the Néel temperature in Sr_2IrO_4. Observation of such a peak would demonstrate the two-dimensional nature of this magnetic system, which is expected on the basis of its layered structure, and would allow simple determination of the strength of the in-plane superexchange interaction between Ir^{4+} ions. If the peak lies at a temperature above the maximum temperature measured, we can estimate a lower limit for the in-plane magnetic superexchange of $J_{ab} > 650$ K, a value not quite as large as that of La_2CuO_4

($J_{ab} \sim 1500$ K). Nevertheless, the magnetic properties of Sr_2IrO_4 have much in common with those of La_2CuO_4 and should offer fertile ground for further comparative study. Finally, we note that the Néel temperature in Sr_2IrO_4 is relatively insensitive to the annealing conditions used,[16] indicating either that the oxygen stoichiometry is fixed, or that the introduction of holes into the Ir-O sheets has a far less detrimental effect upon magnetic ordering than in La_2CuO_4.

In conclusion, we report magnetic and structural data for Sr_2IrO_4, a material which should be a two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnet. This material, which has a structural distortion which leads to weak ferromagnetism, has much in common with copper-oxide high-temperature superconductors and should serve as an important example of this class of low-dimensional antiferromagnetic oxides. In particular, study of Sr_2IrO_4 will further our understanding of the delicate connection between structural distortions and magnetism in such materials. It will also be of interest to see if Sr_2IrO_4 can be made metallic by choice of an appropriate doping scheme.

The authors acknowledge the technical assistance of W. Marshall, L. Lardear, D. Groski, and T. Calvarese. We also thank D. E. Cox and H. Chou (Brookhaven National Laboratory), J. W. Lynn (NIST), and J. B. Goodenough (University of Texas) for useful discussions. The work at the National Synchrotron Light Source, Brookhaven National Laboratory was supported by the U.S. Department of Energy, Division of Materials Sciences, and Division of Chemical Sciences. The work at Oak Ridge National Laboratory was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84-OR21400 with Martin Marietta Energy Systems, Inc. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. The work at Ames was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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[10] We have made a preliminary (unsuccessful) search for magnetic reflections by neutron diffraction. Measurements are continuing, but the combination of a small (expected) ordered moment and the appreciable neutron absorption cross section of Ir may prevent detection of magnetic reflections in this material until single crystals are available.

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[12] T. Moriya, Phys. Rev. **120**, 91 (1960); T. Moriya, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I, Chap. 3.

[13] Strictly speaking, for an Ir^{4+} ion at a site of $\bar{4}$ symmetry, the Ir^{4+} moments must lie parallel to the fourfold (in this case, *c*) axis and canting via a DM interaction is not allowed. If the symmetry is lowered appropriately, however, the moments can lie in the *ab* plane and canting via a DM interaction is allowed. [See, for example, G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliot, and J. M. Hastings, Phys. Rev. **112**, 1917 (1958); R. R. Birss, *Symmetry and Magnetism* (Wiley, New York, 1964); W. Opechowski and R. Guccione, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA, Chap. 3.]

[14] T. Thio *et al.*, Phys. Rev. B **38**, 905 (1988).

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[16] Samples were synthesized in O_2 at 1150 °C, and several portions were then annealed in flowing N_2 at 600 °C or in 150 atm O_2 at 550 °C. These post-synthetic anneals had little effect upon the Néel temperature, indicating either that the Néel temperature is relatively insensitive to the precise oxygen content, or that the oxygen content does not change under the annealing conditions described above. In contrast, the antiferromagnetic ordering in La_2CuO_4 is extremely sensitive to the oxygen content, decreasing from approximately 320 to 0 K when the oxygen content is increased from 4.00 to 4.02.