Structural Transition and Pair Formation in $Fe_3O_2BO_3$

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We observe for the first time a structural phase transition in the oxyborate $Fe_3O_2BO_3$ which occurs along three leg ladders present in this material. X-ray diffraction shows that this transition at 283 K is associated with a new phase where atomic displacements occur in alternate directions perpendicular to the axis and within the plane of the ladders. Magnetic data show that these displacements lead to the formation of singlet pairs which dissociate close to the structural transition. Anomalies in the transport properties also occur close to 283 K showing that the structural transition is related to a charge ordering phenomenon in a low dimensional structure.

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Recently, there is an enormous interest in strongly correlated systems in low dimensional structures [1]. Among these is the oxyborate $Fe_2^{2+}Fe^{3+}O_2BO_3$ which has in its structure low dimensional units in the form of three leg ladders (3LL) with sites occupied by Fe ions in intermediate valence states. These ladders are responsible for its singular physical properties. In this system, antiferromagnetism and paramagnetism coexist between 70 and 112 K as observed by Mössbauer spectroscopy [2]. The ac-magnetic susceptibility curve does not present any visible anomaly at 112 K but a sharp peak appears at 70 K [2]. The specific heat curve presents a peak at each temperature and, above 112 K, it is rigorously linear with temperature up to $\approx$190 K [3]. EPR measurements show, between 10 and 300 K, only a wide single line due to Fe^{2+} ions [4]. The current vs tension isotherms present strong nonlinearity above room temperature [5].

The present Letter reports new measurements of x-ray diffraction, magnetic susceptibility, and resistivity on single crystals of $Fe_3O_2BO_3$. Using a single crystal four circle diffractometer *Enraf-Nonius*, equipped with a Kappa charge-coupled device detector, we were able to observe for the first time, at 283 K, a structural transition for which the low temperature phase shows alternate displacements of the metallic ions within the columns corresponding to the crystallographic site 2 (see Figs. 1 and 2). This implies a doubling of the lattice period along the c axis and the pairing of these ions with those in adjacent columns (sites 4). The magnetization measurements show that the pairs form in singlet states which are progressively decoupled as temperature increases close to the structural transition. The transport measurements show an anomaly on the derivative of the resistivity close to the structural transition at $T_C \approx 283$ K as expected for a charge ordering phenomenon in a low dimensional system. These results indicate the formation of singlet dimers in the 3LL associated with the columns of sites 4-2-4, as discussed below. Although the structure of $Fe_3O_2BO_3$ has been reported earlier to be orthorhombic with space group *Pbam* [6,7], there is no mention to any structural transition.

The synthesis of crystalline needles is described in Ref. [2]. A black cylindrically shaped crystal of dimensions $0.04 \times 0.04 \times 0.60$ mm was used for data collection from x-ray diffraction. The radiation employed was a graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data were collected up to 60^0 in 2θ, with a redundancy of 4. The final unit cell parameters

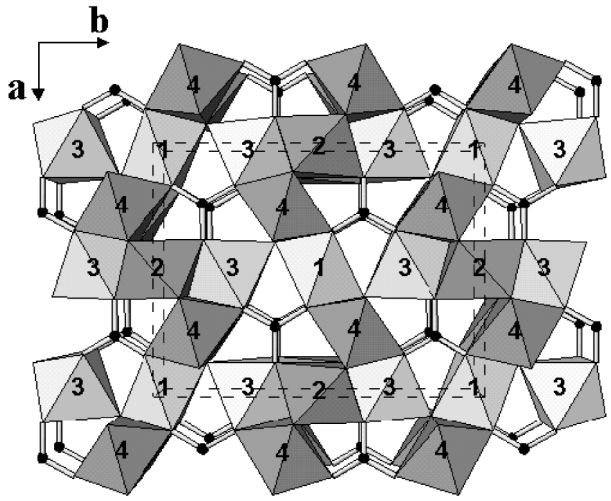

FIG. 1. The structure of $Fe_3O_2BO_3$ projected along the c axis. Along the ladder the sites are occupied by Fe^{3+} ions with one extra electron per triad. The dashed lines indicate sides a and b of the unit cell.

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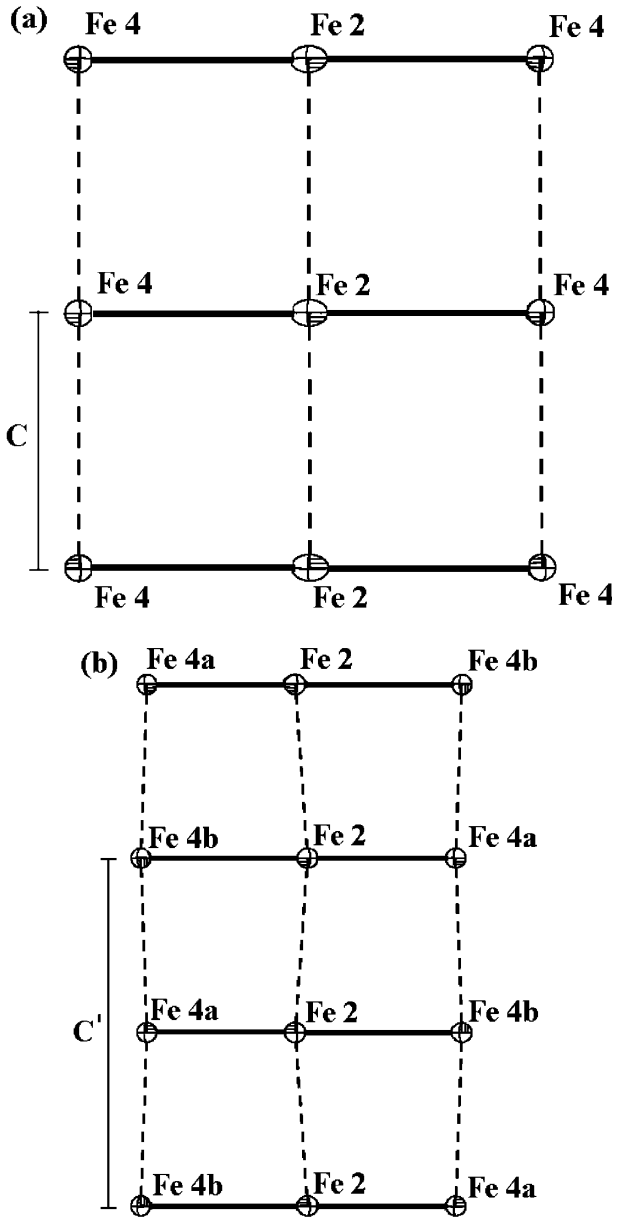

FIG. 2. The columns of triads in $Fe_3O_2BO_3$ above (a) and below (b) the structural phase transition. The measurements yield $C' = 2C$.

were based on all reflections. Data collections were made using the COLLECT program [8]; integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [9]. Absorption corrections were carried out using the multiscan method [10]. The structures were solved using Patterson methods with SHELXS-97 [11]. The Patterson maps showed all Fe atoms. All other atoms were found in successive difference Fourier maps. The models were refined by full-matrix least-squares procedures on F_2 using SHELXL-97 [12]. The program WINGX was used to analyze and prepare the data for publication [13].

The unit cell was determined at several temperatures. This procedure showed the existence of a reversible phase transition at 283 K in which the structure goes from one to another orthorhombic unit cell with the c parameter doubled. We decided to perform a structure determination at 294 K and another one at 144 K, to compare the crystal phases in analogous experimental conditions. Tables I and II summarize our results. As expected from the reversibility of the phase transition, the changes in the atomic positions induced by the transition are very small, this being consistent with the appearance of some faint new peaks in the low temperature diffraction pattern. In this superlattice, the weak reflections correspond to Miller indexes with l odd. The structure shows a trinuclear cluster (triad) formed from Fe4-Fe2-Fe4, in which the Fe4 atoms are related by the b glide plane, piling up along the c axis (see Fig. 2a). At 294 K, the distance Fe4-Fe2 is 2.786(1) Å. In the low temperature structure the Fe4 iron ions are no longer symmetrically related (see Fig. 2b) and the bond distances are different: Fe4a − Fe2 = 2.616(1) Å and Fe4b − Fe2 = 2.942(1) Å at 144 K. The columns along the c axis formed by the triads have a slight zigzag appearance in the low temperature structure due to the small displacement of the central Fe2 ions (see Fig. 2b). This displacement generates both the different Fe4a-Fe2 bond lengths and the duplication of the c axis. In both structures, the Fe-O bond lengths around the Fe1 and the Fe3 atoms are consistent with those of divalent iron ions. In the low temperature structure, the environment of the other iron positions, Fe2, Fe4a, and Fe4b, is indicative of an intermediate Fe^{2+} and Fe^{3+} valence. Figure 3 shows the temperature dependence of some reflections.

The magnetic measurements were performed on a bundle of parallel needles weighing 25 mg. A conventional magnetometer *Quantum Design PPMS* was employed for measurements between 4 and 340 K in several external magnetic fields. Field-cooled (FC) and zero-field cooled (ZFC) procedures were adopted and no hysteresis observed. In Fig. 4 we show the inverse FC magnetization under a field of 3 T. The large anomaly

TABLE I. Structure determination and refinement results.

Structure at 294 K	Structure at 144 K
Space group: $Pbam$(N^0 55)	Space Group: $Pbnm$(N^0 62)
a = 9.462(2) (Å)	a = 9.4490(2) (Å)
b = 12.308(2) (Å)	b = 12.2823(3) (Å)
c = 3.075(1) (Å)	c = 6.1502(1) (Å)
V = 358.11(15) (Å)^3	V = 713.76(3) (Å)^3
Z = 4	Z = 8
615 independent reflections	1133 independent reflections
θ_{max} = 30.0	θ_{max} = 30.0
$R(F)$ = 0.0335	$R(F)$ = 0.0363
$wR(F_2)$ = 0.0948	$wR(F_2)$ = 0.1328
S = 1.233	S = 1.233

TABLE II. Fractional atomic coordinates and equivalent isotropic displacement parameters U (in Å^2) in $Fe_3O_2BO_3$.

Atom	x/a	y/b	z/c	U
		294 K		
Fe1	0.500 00	0.500 00	0.000 00	0.0103(3)
Fe2	0.000 00	0.500 00	0.500 00	0.0135(3)
Fe3	0.999 71(6)	0.725 75(5)	0.000 00	0.0101(3)
Fe4	0.744 48(6)	0.387 53(5)	0.500 00	0.0102(3)
O1	0.6566(3)	0.5425(2)	0.500 00	0.0118(6)
O2	0.1126(3)	0.5789(3)	0.000 00	0.0116(6)
O3	0.8771(3)	0.6385(2)	0.500 00	0.0111(7)
O4	0.6125(4)	0.3590(2)	0.000 00	0.0111(6)
O5	0.8408(3)	0.2358(3)	0.500 00	0.0114(6)
B	0.7315(6)	0.6380(4)	0.500 00	0.0104(9)
		144 K		
Fe1	0.500 00	0.500 00	0.000 00	0.0079(3)
Fe2	0.011 48(7)	0.497 49(4)	0.250 00	0.0082(3)
Fe3	0.000 18(4)	0.725 96(5)	0.002 51(5)	0.0078(2)
Fe4*a*	0.749 05(5)	0.390 59(5)	0.250 00	0.0078(2)
Fe4*b*	0.259 73(6)	0.615 09(5)	0.250 00	0.0079(2)
O1*a*	0.6546(3)	0.5436(2)	0.250 00	0.0087(6)
O1*b*	0.3424(3)	0.4582(3)	0.250 00	0.0087(6)
O2	0.1117(3)	0.5784(2)	0.0098(2)	0.0089(5)
O3*a*	0.8744(3)	0.6393(2)	0.250 00	0.0085(6)
O3*b*	0.1196(3)	0.3621(2)	0.250 00	0.0085(6)
O4	0.6126(3)	0.3591(2)	0.0030(2)	0.0091(6)
O5*a*	0.8436(3)	0.2374(3)	0.250 00	0.0086(6)
O5*b*	0.1619(3)	0.7650(3)	0.250 00	0.0086(6)
B1	0.7281(6)	0.6401(4)	0.250 00	0.0089(10)
B2	0.2664(5)	0.3627(4)	0.250 00	0.0083(10)

occurs at a temperature $T_N = 70$ K as observed previously [2] and is associated with the antiferromagnetic ordering of the material. There is a hardly noticeable anomaly at 112 K, the temperature at which the Mössbauer splitting of the Fe^{3+} occurs [2]. For a range of temperature, from approximately 120 to 180 K, the inverse magnetization clearly displays a Curie-Weiss behavior from which we can extract an antiferromagnetic Curie-Weiss temperature, $\theta = 485$ K and a Curie constant $C = 10.9$ (emu K/mol Oe). From this value of C and assuming that this contribution comes from all the Fe^{2+} ions including those in the triads, we obtain an effective number of Bohr magnetons $p = 6.6$. This value should be compared with $p = g\sqrt{J(J+1)} = 6.7$ obtained taking into account the full orbital contribution of the electrons in the Fe^{2+} ion. The existence of large hysteresis cycles at low temperatures is consistent with the unquenching of the orbital contribution [2].

Above ≈200 K, there is an additional contribution to the magnetization, M_d, obtained subtracting the Curie-Weiss term from the experimental data, which increases with temperature as shown in the lower inset of Fig. 4. This is due to the singlet pairs of the dimerized phase which start to dissociate as the structural transition at which the pairs form is approached. This is clearly indicated by the fact

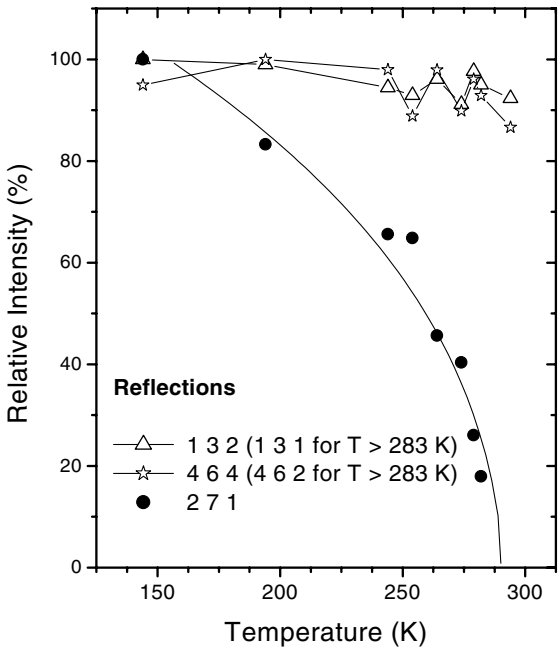

FIG. 3. Temperature dependence of the intensity of three selected x-ray reflections normalized to their measured maximum values. Two of them exist in the whole temperature range of the experiments. That with index l odd appears only below the structural phase transition and its temperature dependence is characteristic of all l-odd reflections. The lines are guide to the eyes.

that the derivative $\partial M_d/\partial T$ has a broad maximum close to $T_C \approx 283$ K (see Fig. 4). From the fit of the initial rise of the magnetization with temperature $M_d(T)$, using a spin 5/2 dimer Heisenberg model we extract a gap for excitation $\Delta = 2150$ K. However, $M_d(T)$ clearly deviates from the results of this model at higher temperatures.

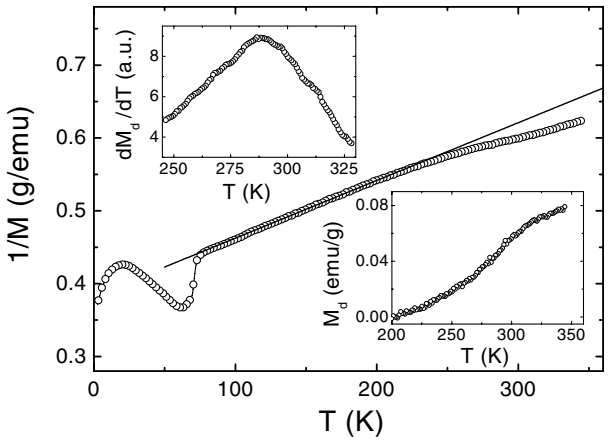

FIG. 4. The inverse magnetization of $Fe_3O_2BO_3$ as a function of temperature. The peak at 70 K occurs at the antiferromagnetic transition. The straight line is the Curie-Weiss law from which we extract the parameters C and θ. Notice the appearance of an excess magnetization above ≈200 K. This and its derivative are shown in the insets.

As shown previously [2], the $Fe_3O_2BO_3$ system above 70 K can be considered as essentially two weakly interacting magnetic subsystems. One is constituted by Fe^{2+} ions in columns 1 and 3 and the other by Fe^{3+} ions in the triads with one extra electron per triad. The analysis above points to a configuration below T_C where the dimers are formed by Fe^{3+} ions in singlet states and the extra electron or the Fe^{2+} ion is located opposite to the dimers along the triad. Clearly, this is a simplified picture. Notice that this configuration minimizes the Coulomb repulsion among the extra electrons. The argument for assuming that the singlet pairs are basically formed by Fe^{3+} ions is the absence of their signal in the EPR spectra below 300 K as mentioned previously [4].

Resistivity has been measured using a standard four-point technique in different magnetic fields from 360 to 200 K in ZFC and FC procedures. A field of 9 T has no effect in the resistivity. The behavior of the resistivity and that of the coefficients of the IxV curves [5] show that the transport properties are clearly influenced by the structural or pair formation transition and that the charge transport occurs along the 4-2-4 ladders (see Fig. 5). Because of the low dimensionality of these structures, fluctuations play an important role in a large temperature range around T_C. However, there is a clear anomaly in the derivative of the resistivity close to the structural transition as seen in the upper inset of Fig. 5. Also, because of the one-dimensional character of the ladders, localization effects are important and the system is not metallic above T_C. Note also that the activation energy extracted from the transport data below 283 K (2550 K) is very close to that required to break the singlet pairs as obtained from the excess magnetization, $M_d(T)$, in the same temperature range (2150 K). Notice that the dimers are not static and must fluctuate. This is clear from the fact that the Mössbauer splitting of the Fe^{3+} occurs only at 112 K [2], which should be identified as the freezing temperature of the dimers.

In conclusion, we have shown the existence of a structural phase transition in the oxyborate $Fe_3O_2BO_3$ at 283 K where ions of Fe^{3+}, in alternating positions along the columns 4, form dimers with those in columns 2. Our x-ray data on single crystals allows for a complete characterization of this transition. The magnetic measurements show that the dimers are formed in singlet states. The appearance of the dimerized state is accompanied by anomalies in the transport properties which extend over a large temperature region around T_C due to the low dimension of the conducting ladders.

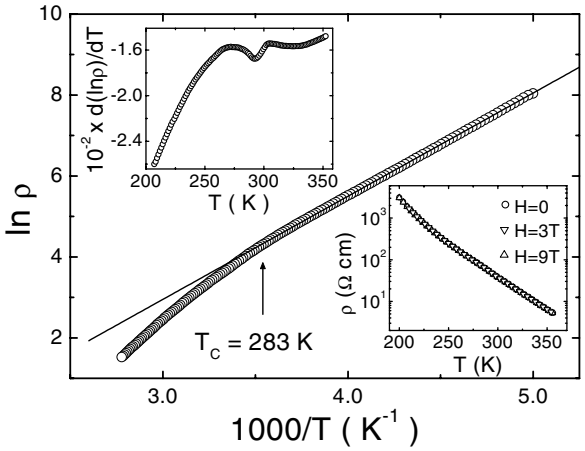

FIG. 5. The logarithm of the resistivity of $Fe_3O_2BO_3$ as a function of inverse temperature showing the exponential activated regime below T_C. The insets show the anomaly of the resistivity close to T_C and the resistivities in 0, 3 T, and 9 T, respectively.

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