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Specific heat of $Fe_3O_2BO_3$: Evidence for a Wigner glass phase

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We report specific-heat measurements for the homometallic Fe oxyborate $Fe_3O_2BO_3$. This material has a charge ordering crossover at $T_{co}\approx 220$ K as shown by the transport measurements. Below T_{co} we find a large linear temperature-dependent contribution to the specific heat that we identify as due to the excitations of a Wigner glass phase. At lower temperatures we observe two large anomalies associated with magnetic transitions. The lowest temperature specific heat is dominated by two-dimensional antiferromagnetic magnons.

Charge ordering is an important phenomenom occurring in Fe oxides with valence fluctuations. It is due to Mott[1]—the suggestion that charge ordering in magnetite at the Verwey transition could be described as a Wigner crystallization. The interest on this phenomenom goes beyond the Fe oxides. It also plays a role in manganites[2] and copper oxides.[3] An understanding of the nature of charge ordered states, their excitations, effects of disorder, dimensionality, and the interplay between long-range Coulomb interactions and the coupling of electrons to the lattice will be certainly a step forward in the study of condensed-matter systems.

In this paper we report specific-heat results in the valence fluctuating Fe oxyborate $Fe_3O_2BO_3$ which presents a charge ordering crossover at $T_{co}\approx 220$ K as evidenced by transport measurements. The temperature dependence of the specific heat in the charge ordered regime below T_{co} provides evidence for a Wigner glass phase in this material.

The magnetic and transport properties of $Fe_3O_2BO_3$ ludwigite below room temperature have recently been thoroughly investigated.[4] An antiferromagnetic transition has been observed at $T_N=112$ K which however does not involve all the Fe ions of the material but essentially the Fe^{3+} ions. Only below $T_w=70$ K does the remaining fraction of paramagnetic Fe ions, mostly Fe^{2+}, order in a weak ferromagnetic state. This ferromagnetic state, however, disappears below approximately $T_r=40$ K. Below this temperature all of the sample is in an antiferromagnetic state. In these investigations the first magnetic transition at 112 K did not show up in the ac susceptibility and dc magnetization measurements and could only be detected through Mössbauer spectroscopy. Reference 4 pointed out the similarities between the present Fe oxyborate and another Fe oxide, namely, hematite, which also presents a reentrant weak ferromagnetic state.

The transport properties of $Fe_3O_2BO_3$ could be described by activated behavior, with two characteristic energies, $\Delta_1/k_B=60$ K and $\Delta_2/k_B=1300$ K, above and below $T_{co}\approx 220$ K, respectively. Then the crossover temperature T_{co} is associated with a rise of the barrier for electron hopping by more than one order of magnitude. A rather similar behavior in the transport properties was observed in a closely related compound, the Fe warwickite Fe_2OBO_3,[5] where a change in activation energy occurs at $T_{co}=317$ K. In this case the transition at T_{co} has been identified as the localization of electrons due to electrostatic repulsion in *Wigner nanocrystals*. The nature of the charge ordered regime in the present system below T_{co} is one of the main points we try to clarify here using specific-heat measurements.

Before we present the specific-heat results let us briefly discuss the structure and charge organization in the ludwigites, as this will turn out to be important to interpret them. These materials, with chemical formula $2MO\cdot M'BO_3$, have a crystalline structure which consists of an assembling of subunits in the form of *walls*, with four nonequivalent octahedral sites, instead of two as in the warwickites, which are preferentially occupied by divalent or trivalent metallic ions, M and M', respectively (see Fig. 1). In the ludwigite unit cell (orthorhombic) there are four chemical formulas and consequently 12 iron ions occupying four different crystallographic sites. The charge balance requires two ions Fe^{2+} and one Fe^{3+} per chemical formula. In this way there are eight extra electrons available per unit cell to be distributed over a

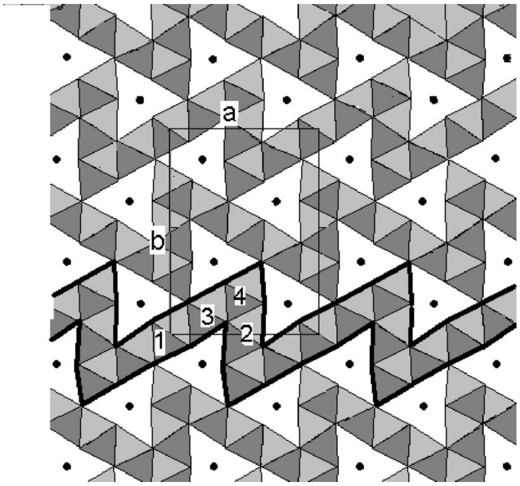

FIG. 1. Structure of the ludwigites showing the *ab* plane, perpendicular to the *c* axis. Notice the subunits in the form of walls that assemble to form the three-dimensional (3D) structure. The four different crystallographic sites occupied by metals and the *a* and *b* edges of the unit cell are indicated.

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TABLE I. Distances between ions in the Fe ludwigite according to Ref. 6. See Fig. 1 for the specification of the sites.

d_{31}	d_{32}	d_{34}	d_{41}	d_{AA} $(\overline{c})$
3.101	2.787	3.192	3.374	3.073

background of 12 Fe^{3+} ions. The sites 1 and 2 appear twice, whereas there are four sites 3 and 4 in a unit cell. The sites 1 and 4 are definitely divalent[6] so they trap six of the eight electrons available. The remaining two electrons are evenly distributed among the two triads of sites 3-2-3, one in each, present in the unit cell. As the distance d_{23} between sites 2 and 3 is very short (see Table I), a strong d-d overlap in the ab plane exits within each triad. The sites 2 and 3 have the same c coordinate so that each set of columns 3-2-3 form a stripe of a rectangular lattice. On the other hand, the distance between ions along the c-axis is 3.05 Å (the c edge of the unit cell),[6] which is just at the limit for direct d-d overlap. In the present case of an homometallic ludwigite with $M = M' = \mathrm{Fe}$, there is no positional disorder and the electrons may delocalize within the two-dimensional structures (the walls). This is in contrast with the heterometallic ludwigites ($M \neq M'$) which, due to intrinsic disorder and the low dimensionality of the structure, have a much higher resistivity (in fact infinite within the range of our multimeter).[7,8]

The $Fe_3O_2BO_3$ sample used in the experiments was prepared as described in Ref. 4. Specific-heat measurements were done from 28 to 238 K with an automated quasiadiabatic pulse technique. The absolute accuracy of the data, checked against a cooper sample, is better than 3%. The measured sample had a mass of approximately 0.4 g, and the addenda correction is less then 2%.

The specific-heat results are shown in Fig. 2. First, we note that the magnetic transitions at $T_N = 112$ K and $T_w = 70$ K are clearly visible in these measurements. This confirms the true thermodynamic character of the antiferromagnetic transition at $T_N = 112$ K which was not observed previously in the macroscopic magnetic measurements. Also we note a small shoulder in the specific-heat curve at approximately $T_r \approx 40$ K, the temperature at which the reentrant weak ferromagnetism disappears as indicated by the vanishing of the magnetization and of a hysteresis loop.[4] More remarkable, however, in this curve are the power-law behaviors exhibited by the specific heat at certain temperature ranges. First, as shown in Fig. 3, below approximately $T_r = 40$ K the plot of C/T versus T is linear indicating a T^2 behavior of the specific heat. Second, above $T_N = 112$ K up to nearly the highest measured temperature, the specific heat is clearly linear in temperature. Furthermore, *this linear contribution extrapolates to zero for* $T = 0$.

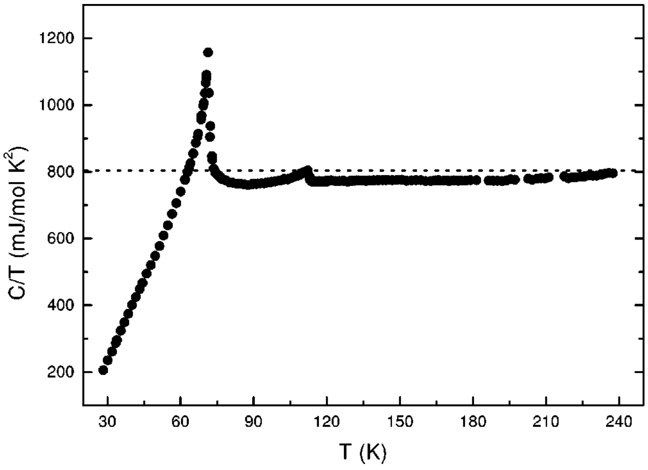

FIG. 2. Specific heat of the homometallic Fe ludwigite $Fe_3O_2BO_3$, C/T as a function of temperature. The dotted line is a reference line to evidence the constant behavior of C/T.

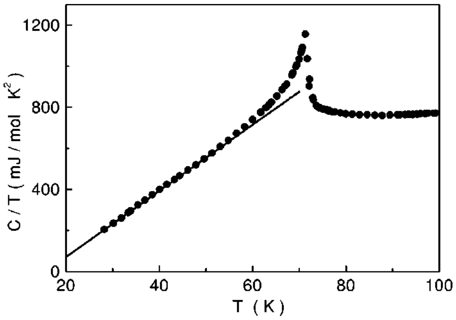

FIG. 3. Low-temperature specific heat, C/T versus T, of $Fe_3O_2BO_3$.The straight line indicates the T^2 behavior and its inclination is used to obtain the spin-wave stiffness.

We shall discuss first the low-temperature T^2 behavior in the antiferromagnetic phase, below $T_r = 40$ K. As we show below and anticipate now, this contribution is due to two-dimensional antiferromagnetic magnons with dispersion relation, $\hbar\omega_k = \sqrt{\Delta^2 + Dk^2}$, propagating within the walls. This T^2 temperature dependence arises for $k_B T \gg \Delta$, where Δ is the spin-wave gap. For $k_B T \ll \Delta$, the specific heat should be thermally activated, i.e., proportional to $\exp[-\Delta/k_B T]$, due to the gap in the magnon spectrum. Notice that indeed the T^2 term extrapolates to zero for a finite temperature as expected from the existence of this activated contribution at low temperatures. Such a gap, arising from anisotropic interactions is in fact necessary to stabilize a long-range antiferromagnetic state in two dimensions.

For $k_B T \gg \Delta$, we may take $\hbar\omega_k \approx \sqrt{D}k$. The total energy per mole associated with these spin-waves is given by[9]

$$\frac{E}{N} = \frac{1}{N} \sum_{\vec{k}} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1}.$$

Replacing the sum by an integral in the two-dimensional $\vec{k}$ space, we obtain

$$\frac{E}{N} = \frac{(k_B T)^3}{2\pi D (N/A)} \int_0^{\sqrt{D}k_{\max}/k_B T} \frac{dy y^2}{e^y - 1},$$

where (N/A) is the number of magnetic ions per unit area within the two-dimensional subunits or walls. Taking the upper limit as infinity, we get for the specific heat:

$$C_V = \frac{\partial(E/N)}{\partial T} \approx \frac{7.2 k_B^3}{2\pi D (N/A)} T^2 \equiv \alpha T^2.$$

The constant α can be obtained from the experimental results in Fig. 3 and turns out to be $\alpha=16.1$ mJ/mol K^3. Using

$$D=\frac{7.2k_B^3}{2\pi\alpha(N/A)}$$

with $(N/A)=3.0\times10^{-9}$ mole/cm^2, we obtain for the spin-wave stiffness, $D=60.8\times10^{-46}$ erg^2 cm^2. On the other hand, taking $\sqrt{D}=zJSa$ (Ref. 9) with $S=5/2$, $z=3$, $a=3.0\times10^{-8}$ cm, we get an estimate for the exchange coupling within the walls, which is, $J=0.29\times10^{-15}$ erg or $J/k_B=2.1$ K. Just to have an idea of the significance of this numerical result we can compare it with the value of $J/k_B=5.25$ K for the two-dimensional antiferromagnet CrCl$_3$ ($T_N=16.8$ K).[9] We have neglected in the calculation above details of the arrangement of the magnetic ions in the walls, as the different distances between these ions along the c and a, b axis. Also we considered a single value for the spin, namely $S=5/2$. Consequently this value for the coupling constant J corresponds to an average estimate.

We now turn to discuss the origin of the huge linear temperature-dependent contribution which dominates the specific heat above ≈112 K. Writing $C_V=\gamma T$, it turns out from the experiments that $\gamma=773$ mJ/mol K^2, an enormous contribution with an order of magnitude typical of strongly correlated metals like heavy fermions.[10] In our search for an explanation for the origin of such term in a nonmetallic system, it is natural to associate it with the magnetic Fe ions since this contribution vanishes at a temperature close to T_N, at which some of these ions order magnetically. The entropy associated with the linear term, calculated from the specific-heat curve from $T_1\approx112$ K to $T_2\approx190$ K, which is the temperature range of this term, corresponds to $S\approx60.3$ J/mol K. This is larger than the sum of the magnetic entropies associated with the Fe^{2+}, $S(\mathrm{Fe}^{2+})=2.N_a k_B\ln[2(2+1)]=26.7$ J/mol K, and that due to the Fe^{3+},$S(\mathrm{Fe}^{3+})=N_a k_B\ln[5/2(5/2+1)]=14.9$ J/mol K. Consequently, the linear term of the specific heat must involve additional degrees of freedom, such as structural excitations and/or electron tunneling.

Notice that one-dimensional phonons may give rise to a linear temperature-dependent specific heat, $C_{ph}(T\ll\theta_D)=\pi^2N_a k_B(T/\theta_D)$. The Debye temperature θ_D can be determined from the coefficient $gamma$ of the linear term of the specific-heat data and we get $\theta_D=106$ K. We are faced, however, with the difficulty that such a small Debye temperature required to yield the large specific-heat contribution is, on the other hand, incompatible with the condition $T\ll\theta_D$ necessary for the expression above to hold. Indeed since the linear term extends up to $T_2\approx190$ K, we need θ_D to be very large.

We are confronted with the same difficulty if we try to attribute the linear specific-heat term to small polarons.[11] The order of magnitude of the coefficient γ shows that we should be dealing with a strong coupling limit in which case the electron-phonon interaction can be dealt rigorously using the Lang-Firsov transformation.[11] The main effect of this interaction in this limit can be represented by a renormalization of the electron mass, i.e.,

$$m^*=\frac{m}{e^{-\alpha}},$$

where the parameter α is related to the strength of the electron-phonon coupling.[11] However, in this case the coherence temperature, below which the system shows Fermi-liquid behavior, is also reduced by the same factor such that the linear behavior of the specific heat should manifest only at very low temperatures. The case of heavy fermions, which present large quasiparticle masses, is very illustrative of this situation. In these systems large linear terms in the specific heat are observed but only below very small coherence temperatures.[10]

The essential ingredient to explain the large linear term in Fe$_3$O$_2$BO$_3$ is disorder. The columns corresponding to different metal sites are not occupied by ions with a single valency but contain both Fe^{2+} and Fe^{3+} in different proportions.[4] At high enough temperatures, $T\gg T_{co}=220$ K, the extra electrons can delocalize over the Fe^{3+} background but at low T they eventually freeze in random positions, due to electrostatic forces and/or electron-lattice coupling, giving rise to a Wigner glass. A plausible source for the linear term of the specific heat we observe is due to tunneling states which involve strongly coupled electronic, structural, and also magnetic degrees of freedom. The latter should be involved since, when the system orders magnetically, tunneling is inhibited and the linear contribution vanishes. In fact, the octahedra containing the Fe^{2+} ions are highly distorted[6] as compared to those containing the Fe^{3+} ions so that when an electron tunnels between different octahedra it is accompanied by a large lattice distortion. Besides, the tunneling probability depends on the orientation of the spins in the initial and final states.[12] The required distribution of the energy splittings[13] of the tunneling excitations, which should be constant in the energy scale of k_BT_2, arises ultimately from the random positions of the electrons in the different oxygen octahedra below T_{co}. The large energy scale of the tunneling states, compared with that of ordinary glasses,[13] is due to the fact that the interactions here have a Coulomb component and are not purely elastic. We expect the glassy state to form along stripes of triads 3-2-3, since sites 1 and 4 are essentially occupied by divalent ions. The tunneling states consequently are associated with excitations on the triads 3-2-3, where electron tunneling is allowed even at low temperatures due to the small d_{23} distance.

Note that for the Fe warwickite there is an exact equipartition of divalent and trivalent iron ions over the two cation sites.[5] In this case the transition at T_{co} is a true transition, accompanied by a lattice distortion and is associated with the formation of a Wigner crystal of the extra electrons on the Fe sites along the ribbons.[5] For the present system there is no exact charge equipartition over the four nonequivalent octahedral sites below T_{co}.[6,4] Also there is no lattice distortion at T_{co}, as evidenced by the similar x-ray results at room temperature and 90 K.[4] Then, while in the warwickite Fe$_2$OBO$_3$ Wigner nanocrystals are formed at T_{co},[5] in the ludwigite the transition at T_{co} is a glass transition. The excitations of this Wigner glass give rise to the linear temperature-dependent specific heat we observe. This glass phase is a compromise between the charge ordering found in the Fe warwickite and the complete charge segregation observed, for example, in the Mn warwickite.[14]

The density of tunneling states n_0 can be obtained from the expression $C_V = (\pi^2/12) n_0 k_B^2 T$ (Ref. 13) and is given by $n_0 = 4.94 \times 10^{45}\ \mathrm{J}^{-1}\,\mathrm{mol}^{-1}$ which is much larger than that of glasses.[13] We deal here with a nondilute system of tunneling excitations such that these modes represent tunneling between local minima in the configuration space of the whole system.

We have measured the specific heat of the ludwigite system $Fe_3O_2BO_3$. At low temperatures the magnetic system is ordered in a two-dimensional antiferromagnetic state. We have obtained the stiffness of the magnon excitations in this long-range ordered state. Below approximately 200 K a Wigner glass is formed whose excitations are tunneling states which give rise to a linear temperature-dependent specific heat.

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[1] N. F. Mott, Adv. Phys. **16**, 113 (1967); J. B. Sokoloff, Phys. Rev. B **3**, 3162 (1971).

[2] P. G. Radaelli, D. E. Cox, M. Marezio, and S. W. Cheong, Phys. Rev. B **55**, 3015 (1997).

[3] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).

[4] R. B. Guimarães, M. Mir, J. C. Fernandes, M. A. Continentino, H. A. Borges, G. Cernicchiaro, M. B. Fontes, D. R. S. Candela, and E. Baggio-Saitovitch, Phys. Rev. B **60**, 6617 (1999).

[5] J. P. Attfield, A. M. T. Bell, L. M. Rodriguez-Martinez, J. M. Greneche, R. J. Cernik, J. F. Clarke, and D. A. Perkins, Nature (London) **396**, 655 (1998).

[6] J. S. Swinnea and H. Steinfink, Am. Mineral. **68**, 827 (1983).

[7] J. C. Fernandes, R. B. Guimarães, M. A. Continentino, H. A. Borges, A. Sulpice, J.-L. Tholence, J. L. Siqueira, L. I. Zawislak, J. B. M. da Cunha, and C. A. dos Santos, Phys. Rev. B **58**, 287 (1998).

[8] M. A. Continentino, J. C. Fernandes, R. B. Guimarães, H. A. Borges, A. Sulpice, J.-L. Tholence, J. L. Siqueira, J. B. M. da Cunha, and C. A. dos Santos, Eur. Phys. J. B **9**, 613 (1999).

[9] See F. Keffer, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1996), Vol. XVIII, Pt. 2, p. 1

[10] M. A. Continentino, Phys. Rep. **239**, 179 (1994).

[11] E. V. L. de Mello and J. Ranninger, Phys. Rev. B **58**, 9098 (1998).

[12] C. Zener, Phys. Rev. **82**, 403 (1951).

[13] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972); P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[14] R. Norrestam, M. Kritikos, and A. Sjoerdin, J. Solid State Chem. **114**, 311 (1995).