Stoichiometry, Percolation, and Verwey Ordering in Magnetite

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Neutron scattering experiments on $Fe_{3(1-\delta)}O_4$ single crystals show that, for $\delta=0$, the well established additional Bragg peaks occur at $(h,0,l+\frac{1}{2})$, below $T_V=122.5$ K with abrupt disappearance of the diffuse planar scattering associated with 1D correlations along the cubic axis. For $\delta=0.006$, the superlattice peaks never become resolution limited, long-range order is not attained, and the diffuse scattering increases continuously with cooling. This composition exceeds the percolation limit beyond which the transition is inhibited by insufficient average charge per ordered unit cell.

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Magnetite ($Fe_{3(1-\delta)}O_4$) is the oldest known magnetic material and the original compound for Néel ferrimagnetism ($T_N=851$ K) and consequently one of the most intensively studied. In 1941, Verwey and Haayman [1] proposed that the additional phase transition observed at $T_V=122$ K was caused by ordering within the Fe^{2+} and Fe^{3+} cations of the octahedral (B) sublattice of the cubic inverse spinel structure. Electron and neutron diffraction studies showed that the appearance of superlattice peaks below T_V, at $(h,0,l+\frac{1}{2})$, results from atomic displacements, which suggested the coupling of charge ordering and lattice phonons [2]. Spotlike critical scattering was observed [3] at the $l+\frac{1}{2}$ positions for a narrow temperature range (~ 5 K) above T_V, and planar diffuse scattering was in evidence over a much wider temperature range [4] $T-T_V<100$ K, increasing rapidly on cooling to T_V, and abruptly disappearing concurrently with the occurrence of superlattice peaks.

In the last decade systematic surveys in $Fe_{3(1-\delta)}O_4$ confirmed that T_V is markedly depressed with increasing nonstoichiometry (δ) and specific heat measurements [5] showed that the latent heat of the transition is suddenly lost for cation deficiency in excess of a critical composition $\delta C=0.0039$, in an apparent [6] discontinuous change from first (T_V^{I}) to second (T_V^{II}) order. The results of the present neutron scattering investigation provide the first evidence that the long-range ordered structure is actually inhibited for $\delta>\delta_C$. Instead, a domain state with finite correlations sets in near T_V^{II} and is preserved even at the lowest investigated temperature (10 K). The correlation range (~ 28 unit cells) is consistent with the percolation argument that there is insufficient average charge to induce long-range order (LRO).

$Fe_{3(1-\delta)}O_4$ single crystals, grown by rf induction melting [7], from 99.999% pure Fe_2O_3 reagent, were annealed [8] under controlled oxygen fugacity conditions to produce δ values of 0.000 and 0.006. The former corresponds to a stoichiometric composition, with a first-order Verwey transition ($T_V^{\mathrm{I}}=122$ K), and the latter has cation deficiency beyond δ_C, with an apparently continuous transition at $T_V^{\mathrm{II}}=95$ K as determined from specific heat measurements [5,6]. The crystals were of irregular shape, had sample mosaics of less than 0.1°, and weighed 3.318 g ($\delta=0$) and 2.320 g ($\delta-0.006$). The samples were placed in an aluminum can filled with He gas and mounted in a closed-cycle refrigerator, controlled to within $+0.02$ K. No attempt was made to establish a unique low temperature axis by field-cooling techniques or inhibit basal twinning by application of anisotropic strain, since simple detection of the low temperature distortion was sufficient for the purpose of this investigation.

The neutron scattering experiments were performed on the H7 triple axis spectrometer at the Brookhaven High Flux Beam Reactor, with incident neutron energies of 30.5 meV, using pyrolytic graphite (PG) monochromator and analyzer and a PG filter to remove higher orders. The horizontal collimations were of 40 min before monochromator, 20 min before sample, 25 min after sample, and 80 min in front of the counter.

For $\delta=0$, the Verwey transition is characterized by the sudden appearance of a superlattice reflection $(8,0,\frac{1}{2})$ at $T_V^{\mathrm{I}}=122.5$ K [cf. Figs. 1(a) and 2(a)]. The double peak in Fig. 1(a) is evidence of twinning associated with low temperature monoclinic structure [9]. Each peak has a Gaussian line shape and is resolution limited. The transition occurs discontinuously between 122.5 and 123 K, consistently with the first-order character and no premonitory critical scattering is observed at this Q value. Also present is a ridge of diffuse scattering along the $[80\zeta]$ direction extending nearly uniformly in the plane perpendicular to the cubic [100] axis, derived from 1D correlations along $\langle 100\rangle$ directions in real space. The intensity of this ridge, monitored at (8,0,0.75) shows a gradual increase on cooling and disappears abruptly at T_V^{I} [cf. Fig. 2(b)].

The nonstoichiometric sample ($\delta=0.006$) behaves quite differently. There is a gradual buildup of intensity at $(8,0,\frac{1}{2})$ [cf. Fig. 2(a)] on cooling, with a change of

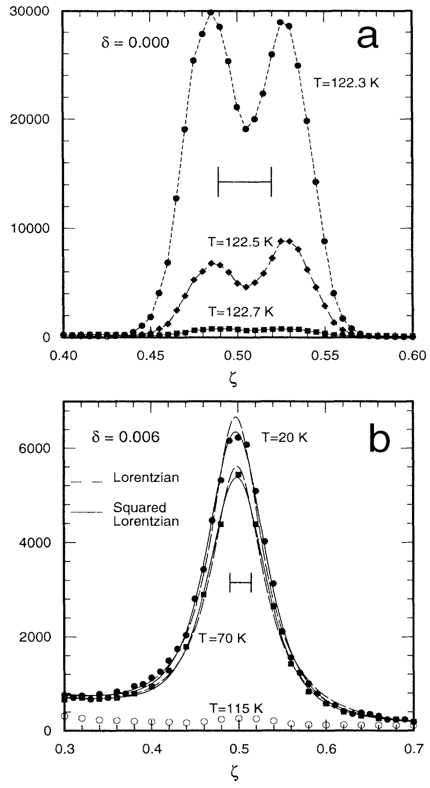

FIG. 1. [80ζ] scans, peak fits, and resolution (bracketed bar), for $\delta=0$ (a) and $\delta=0.006$ (b).

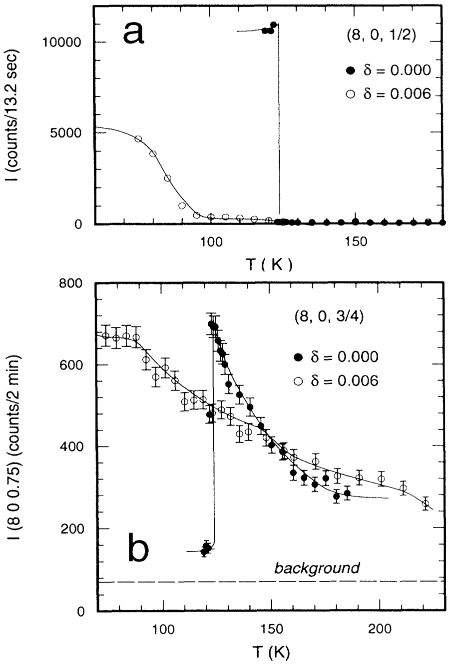

FIG. 2. Temperature dependence of the $(8,0,\frac{1}{2})$ peak (a), and (8,0,0.75) diffuse scattering (b), for $\delta=0$ and $\delta=0.006$ (lines are aids to the eye).

slope at ~95 K (T_V^{II}). Scans along [80ζ] show a single broad peak [cf. Fig. 1(b)], which deviates from the Gaussian line shape expected for LRO. In fact, the fit improves with a Lorentzian squared line shape characteristic of the domain states observed in random magnetic systems [10]. The linewidth is temperature independent and the half width at half maximum (HWHM) is 0.039 ± 0.001 cubic reciprocal lattice units (RLU), ~2.5 times the instrumental resolution. Thus, no LRO and hence, no phase transition occurs. The temperature dependence of the diffuse scattering at (8,0,0.75) increases with cooling to a constant low temperature value without any discontinuities near T_V^{II}.

The intensities in both samples can be expressed on a common relative scale with respect to the integrated intensity (I_0) of the Σ_2 *TA* phonon, measured for each crystal at $\mathbf{Q}=(4.25,0,3.75)$. The ratio of the two reference intensities was within 2% of the sample weight ratio. The inverse of the scaled diffuse scattering, measured at (8,0,0.75) and multiplied by temperature to account for the thermal occupation factor is shown in Fig. 3(b). For $\delta=0$, $T/(I/I_0)$ is linear in temperature, with an intercept at ~108 K, in agreement with earlier measurements on a completely different sample. The $T/(I/I_0)$ dependence for $\delta=0.006$ is linear in the same temperature range and extrapolates to ~83 K but deviates from linearity below 120 K and remains finite at the lowest measured temperature (10 K).

The sudden disappearance of LRO beyond the nonstoichiometric composition δ_C is evidence of its role as a percolation limit. The Bethe lattice provides the simplest model for which percolation probabilities can be calculated exactly [11], with the same result in either the bond or site conventions, namely, $p_c=1/\sigma$, where p_c is the critical value, below which the probability of infinite self-avoiding walks or LRO is identically zero, and σ is the dimensionality of the lattice. The smallest possible unit cell, with which all Bragg reflections observed in the low temperature phase can be indexed, is the base-centered monoclinic $(\sqrt{a},\sqrt{a},2a)$ superlattice of the cubic $a=8.386$ Å lattice parameter. Hence, a minimal model representation for 3D Verwey charge order is a Bethe infinite tree [11] of monoclinic unit cells at vertices of degree 4 and the critical probability $p_c=\frac{1}{3}$ results from the loss of one electron, or branch, per vertex.

The relation between the chemical nonstoichiometry parameter (δ) and the percolation probability (p) follows from the pertinent point defect equilibrium reactions [12] in $\mathrm{Fe}_{3(1-\delta)}\mathrm{O}_4$. Vacancies ($V$) and interstitials ($I$) may be created by configurational disorder from an Fe cation in a normal lattice position,

$$\mathrm{Fe}\rightarrow V+I\,, \tag{1}$$

to form a Frenkel pair; by addition of an oxygen atom

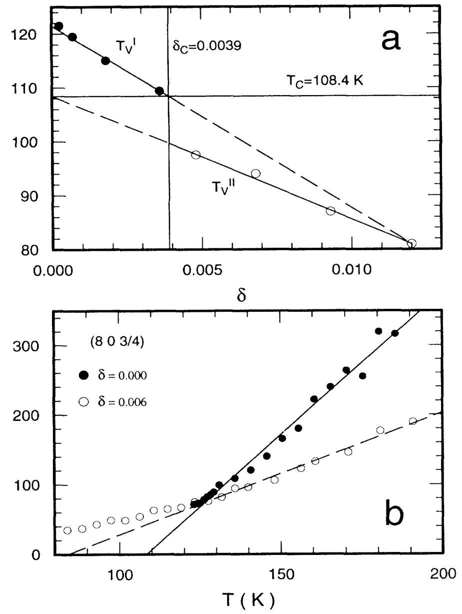

FIG. 3. (a) Calorimetric transitions (Ref. [6]) and percolation limit coordinates. (b) Inverse of the scaled diffuse scattering intensity. Lines are unconstrained regressions of data above 125 K.

with concurrent creation of $\frac{3}{4}$ of a vacancy,

$$\mathrm{Fe}^{2+} + \tfrac{1}{4}\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + \tfrac{1}{2}\mathrm{O}^{2-} + \tfrac{3}{8}V\,; \tag{2}$$

or equivalently by assimilation of $\frac{3}{4}$ of an interstitial,

$$\mathrm{Fe}^{2+} + \tfrac{1}{4}\mathrm{O}_2 + \tfrac{3}{8}I \rightarrow \mathrm{Fe}^{3+} + \tfrac{1}{2}\mathrm{O}^{2-}\,, \tag{3}$$

with concurrent oxidation of one Fe^{2+} to Fe^{3+}. The nonstoichiometric cation fraction (δ) is determined by mass balance, with the difference of the number of vacancies and interstitials divided by the appropriate normalizing summation of cation and vacant sites (n_Σ),

$$\delta = \frac{1}{n_\Sigma}(n_V - n_I)\,, \tag{4}$$

thus excluding equilibrium defects associated only with thermal Frenkel disorder, and inspection of Eqs. (2) and (3) shows that electroneutrality is preserved if

$$n_V - n_I = \tfrac{1}{8}\left(n_{\mathrm{Fe}^{3+}} - 2n_{\mathrm{Fe}^{2+}}\right). \tag{5}$$

The oxidation of one Fe^{2+} to Fe^{3+}, corresponding to the loss of one electron, increases the difference above by 3. Since there are 32 formula units ($n_\Sigma = 96$) in the low temperature base-centered monoclinic unit cell [9], $\delta_C = 0.0039$, by substitution into Eqs. (4) and (5), in agreement with the experimental observation [5] for the loss of latent heat of transition ($T_V^{\mathrm{I}} = 108.4$ K).

The limit $p=0$ corresponds to $3\delta_C = 0.012$, with the average loss of three electrons or one cation per vertex, provides a very good approximation of the cation deficiency beyond which no further anomalies in physical properties are observed [cf. Fig. 3(a)]. Formally, the connectivity [11] of the tree has been reduced to 1, or the contents of 4 cubic unit cells.

Between these two limits ($\delta_C, 3\delta_C$), the range of order is never infinite. The increase in correlation length (ξ) with decreasing temperature is arrested by the lack of sufficient charge, for a cluster size $S(p)$ determined by nonstoichiometry ($\delta > \delta_C$), namely,

$$p = \frac{1}{2}\left[1 - \frac{1}{3}\frac{\delta}{\delta_C}\right]. \tag{6}$$

Below a characteristic temperature T_V^{II}, ξ becomes temperature independent and the system saturates, as observed for $\delta = 0.006$ (i.e., $p = 0.25$) below 95 K. The divergence of $S(p)$ below p_C has been evaluated in a few model systems. For the three-dimensional Bethe tree [11] adopted here, $S(0.25) \approx 7$ (i.e., 28 cubic unit cells) provides a good approximation of the HWHM observed in the nonstoichiometric sample.

Recently, it has been shown [13] that the lower limit for $T_V^{\mathrm{I}} = 108.4$ K is consistent with that predicted for a simple Ising problem, treated in the mean-field approximation, for charge ordering of the four $\mathrm{Fe}^{2+}{}_B$ octahedral nearest neighbors (z) of an $\mathrm{Fe}^{3+}{}_A$ tetrahedral cation, in the spinel structure, with an effective exchange parameter $J_{AB}/k_B = 27.1$ K. Within the limits of this description, the effects of short-range order are approximated by the well-known quasichemical [14] expression

$$\frac{kT_C}{zJ} = \frac{-2/z}{\ln(1-2/z)}\,, \tag{7}$$

which reduces the critical temperature to ≈ 78 K, in good agreement with the empirical $T_V^{\mathrm{II}} = 81$ K, at $3\delta_C$. However, this value can only be regarded as a limit, since the LRO implicit below this temperature cannot materialize [15]. Comparison of the mean-field and quasichemical solutions immediately shows that for any given effective interaction J_{AB}, short-range order scales the mean-field critical temperatures by $\frac{1}{2}\ln 2$, without assumptions on the nature of the microstates.

The noted similarities with critical behavior in dilute magnetic systems result from the existence of two divergent correlation lengths, namely, the cluster size $S \sim (\delta - \delta_C)^{-\zeta}$, with $\delta_C = 0.0039$, and the correlation length $\xi \sim (T - T_C)^{-\nu}$, with $T_C = 108.4$ K, instead of the $T_C = 0$ characteristic of dilute ferromagnets. Anomalies occur at T_V^{II}, when $S = \xi$, and the empirically observed linear dependence of T_V^{II} on δ [cf. Fig. 3 (a)] is justified, if $\zeta = \nu$, for a crossover critical exponent $\phi = 1$. The decrease in slope by $\frac{1}{2}\ln 2$ corresponds to the mean-field approximation $\nu = \frac{1}{2}$ of an Ising model. In both cases, these scaling laws reflect the onset of three-dimensional ordering from a collection of one-dimensional chains [16], manifest in associated diffuse scattering with the same critical parameters.

The anomalous physical behavior observed for $\delta > \delta_C$, such as enhanced low temperature heat capacity [6], initial magnetic permeability, and self-reversals of remanent moment [13], are readily justified by the sensitive dependence of these properties on cluster size [11].

In summary, we have shown that the Verwey transition in $Fe_{3(1-\delta)}O_4$ is destroyed beyond δ_C, due to lack of sufficient charge per unit cell for LRO of the Fe^{2+}/Fe^{3+} sublattice.

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