Changes in the nature of the Verwey transition in nonstoichiometric magnetite (Fe$_3$O$_4$)

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A relaxation calorimetry investigation of magnetite (Fe$_{3(1-\delta)}$O$_4$) single crystals, with controlled metal-to-oxygen stoichiometry, indicates a change in the nature of the Verwey transition. Beyond a critical composition ($\delta_{cr} \approx 0.0039$) the transformation changes from first to higher order and is marked by the loss of the latent heat of transition.

Despite intensive investigations over a period of fifty years, many aspects of the Verwey transition[1] in Fe$_3$O$_4$ are not understood. Part of the problem arises from conflicting data published in the literature, particularly with respect to the heat-capacity anomaly that accompanies this phase change.[2] We report here briefly on a previously undetected feature of the Verwey transition which appears to be an important component in the interpretation of this transformation.

The heat-capacity measurements summarized in Figs. 1 and 3 were performed on Fe$_{3(1-\delta)}$O$_4$ single crystals which were grown by a crucible-less skull melting technique[3] and annealed in appropriate buffered CO + CO$_2$ mixtures, with electrochemically monitored f_{O_2} to achieve the desired fractional deviation δ from the ideal 4:3 [O]/[Fe] ratio.[4] The samples were rapidly quenched and trimmed, preserving only the homogeneous interior regions for subsequent study. A relaxation-type calorimeter[5] was employed, with the capability for measuring heating and cooling curves. As reported elsewhere,[6] specimens with small departures from ideal stoichiometry in the range $-0.0002 \leq \delta \leq 0.0035$ exhibited a single, sharp peak in the heat capacity C_p, as shown on the right-hand side of Fig. 1 for a sample with $\delta = 0.0017$. Aside from a small pre- and postmonitory effect, as manifested by shoulders bracketing the transition temperature (115.8 K on heating and 114.9 K on cooling), the heat-capacity peak was so narrow that it could not be fully tracked; the peak location is indicated by a vertical line.
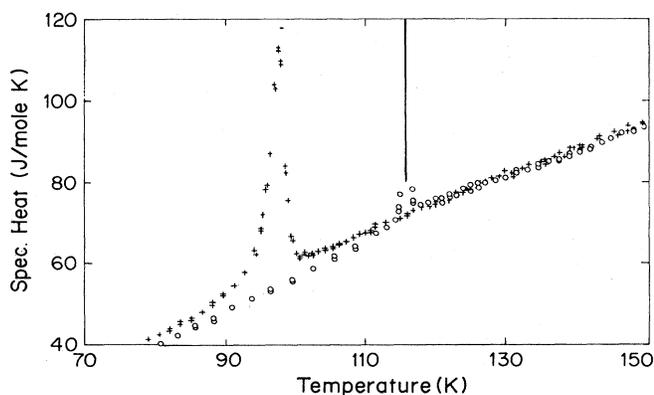
One of the corresponding heating curves is shown in Fig. 2(a); they are all characterized by a thermal arrest over a 0.2–0.4 K temperature interval about the C_p peak. This experiment documents that the transition is first order; Fig. 2(a) also permits an accurate determination[2] of the entropy of transition as $\Delta S_V = 5.3 \pm 0.1$ J/mole Fe$_3$O$_4$ K, exclusive of the pre- and postmonitory effects totaling approximately 0.25 J/mole Fe$_3$O$_4$ K. In this composition range the maximum value of $T_v = 124$ K and of $\Delta S_v = 5.88 \pm 0.05$ J/mole Fe$_3$O$_4 \approx R \ln 2$ correspond to samples with the ideal stoichiometry $\delta = 0$.[6]

The new feature in the current set of measurements is that beyond a critical δ value δ_{cr} the transition suddenly shifts to a second- (or higher-) order regime; from the measurements completed so far the critical value falls in the
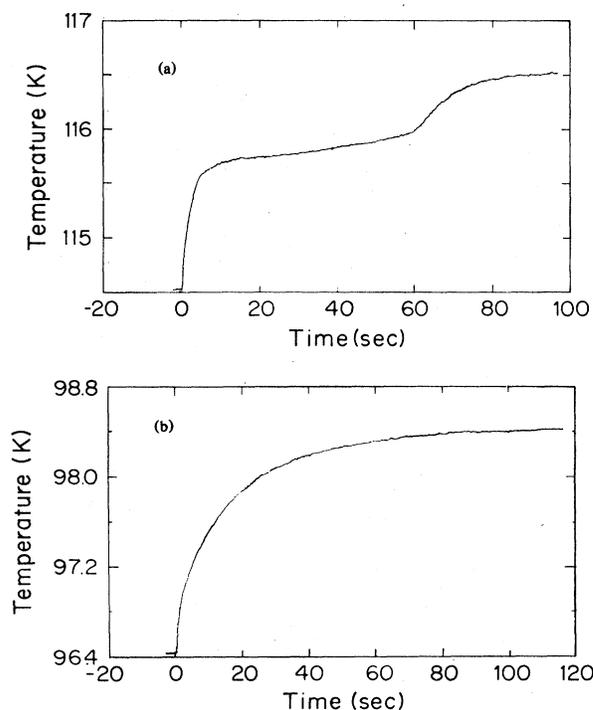

FIG. 2. Heating curves of two nonstoichiometric Fe$_{3(1-\delta)}$O$_4$ samples. (a) $\delta = 0.0017$, first-order transition; (b) $\delta = 0.0049$, higher-order transition. The curves represent original, unsmoothed traces.

FIG. 1. Specific heat of two nonstoichiometric Fe$_{3(1-\delta)}$O$_4$ samples. (O) $\delta = 0.0017$; (+) $\delta = 0.0049$.

range $0.0035 < \delta_{cr} < 0.0049$. A representative trace is shown on the left-hand side of Fig. 1 for a single crystal sample with $\delta = 0.0049$. The corresponding heating curve, reproduced in Fig. 2(b), shows no evidence of thermal arrest. This documents that for larger departures from ideal stoichiometry, $\delta > \delta_{cr}$, the nature of the transition is fundamentally altered.

Several additional features are noteworthy: (i) All C_p anomalies are superposed on a smoothly continuing heat-capacity background trace; no evidence is found for the existence of significant short-range order. (ii) The background traces of all samples coincide for the temperature range $126 < T < 346$ K; however, at lower temperatures the heat-capacity curves of samples undergoing the higher-order transformations lie above those of samples for which $\delta < \delta_{cr}$. This situation persists down to at least 5 K, as is indicated by a plot of C_p vs T in Fig. 3 for the range $4 < T < 20$ K. (iii) The cooling curves of all samples undergoing the higher-order transitions are strictly exponential. (iv) Thus, (ii) and (iii) render it unlikely that the C_p anomalies for samples with $\delta > \delta_{cr}$ are simply smeared-out versions of first-order transitions; the two sets of samples are really of different character. (v) In conformity with recent thermomagnetic analysis curves[7] and electrical measurements,[8] the Verwey transition temperatures decrease almost linearly from 124 K for $\delta = 0$ to 81 K for $\delta = 0.0121$, the latter composition lying close to the oxidation boundary of the stability range for magnetite. (vi) The stoichiometry $\delta = \delta_{cr}$ corresponds either to a tricritical point, or else to the proximity of a simple critical point. In either case, an unusual situation is encountered in that the first-order transition regime lies in a higher temperature range than does the region of higher-order transitions.

A tentative interpretation of the critical δ_{cr} value can be proposed in terms of current understanding of the magnetite structure below T_V. In the notation of Ref. 7, the number of vacancies (n_V) and interstitials (n_I) is related to δ by

$$\delta = (n_V - n_I)/n_\Sigma ,$$

where n_Σ is the normalizing parameter

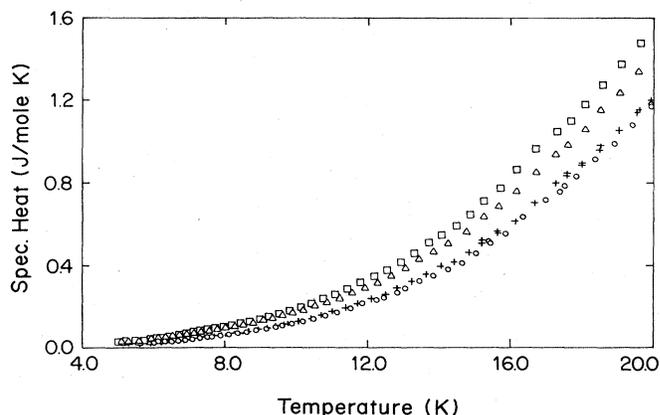$$n_\Sigma = n_{Fe^{2+}} + n_{Fe^{3+}} + n_V$$

FIG. 3. Low-temperature specific heat of $Fe_{3(1-\delta)}O_4$ samples. (○) $\delta = -0.00018$; (+) $\delta = 0.0002$; (△) $\delta = 0.0096$; (□) $\delta = 0.0121$.

for the total number cations and vacancies. The electroneutrality condition requires that

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

Since there are 32 formula units in the monoclinic unit cell generally adopted for the low-temperature phase,[9] $n_\Sigma = 96$. The formation of one vacancy by oxidation increases the difference $(n_{Fe^{3+}} - 2n_{Fe^{2+}})$ by 3, so that $\delta_{cr} = 3/(8 \times 96) = 0.0039$, which is within the range of the experimental limits on δ_{cr} cited above. A further elucidation of the above findings must await the identification and study of the appropriate order parameter.

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