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NEUTRON SCATTERING STUDY OF THE PHASE TRANSITIONS IN A DOPED POLYCRYSTALLINE Fe_3O_4 : $Zn_{0.005}Fe_{2.995}O_4$

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Temperature dependent neutron elastic scattering and resistivity measurements have been made on a polycrystalline sample of $Zn_{0.005}Fe_{2.995}O_4$, which displayed a well-separated, bifurcated, heat-capacity anomaly. The lower-temperature anomaly (near 110 K) was found to be associated with a lattice distortion, but no change in neutron intensity was observed at the higher-temperature anomaly (near 119 K). The electrical resistivity of this sample also exhibited an abrupt change only at the lower-temperature anomaly. The downward shift of the lower-temperature, λ-type anomaly as a result of the very low Zn impurity is, however, confirmed by the neutron scattering results and demonstrates the extreme sensitivity of the structural transition to impurities.

MAGNETITE (Fe_3O_4) is known to undergo a phase transition near 120 K, characterized by a lattice distortion and a sharp change in electrical conductivity.[1] The unusually high conductivity above 120 K of this inverse-spinel ferrite has been explained in terms of electron hopping between the Fe^{3+} and Fe^{2+} ions occupying equivalent octahedral (*B*) sites.[2] To explain the low conductivity below 120 K, Verwey[3] proposed an ordering scheme in which *B*-site Fe^{2+} and Fe^{3+} ions occupy separate, alternating layers stacked perpendicular to the *c*-axis. Hamilton's observation of the (002) magnetic reflection was interpreted as verifying this scheme.[4] However, recent work on a single crystal of pure magnetite[5–8] has shown that the ordering scheme is much more complex than that proposed by Verwey. The structural aspects of the transition are now well characterized, with a nearly rhombohedral lattice distortion ($\alpha = 89.83°$) and with the appearance of superlattice peaks.

In addition to the revelation by recent measurements of a more complex low-temperature structure than previously believed, the transition itself has been found to be complex. Westrum and Grønvold provided the first evidence for the step-wise nature of the Verwey transition in their observation of a bifurcation of the heat capacity anomaly in pure Fe_3O_4.[10] Further studies by Westrum, Bartel, and Evans on pure and doped Fe_3O_4[9–12] confirmed the furcation of the heat capacity anomaly, the multi-stage nature of the transition and the association of a lattice distortion with the lower-temperature anomaly. The furcation of the heat capacity anomaly and the positions of the peaks are strongly dependent on both the type and concentration of dopant. So far, no physical property measurement has provided any truly, revealing insights into the nature of the crystal interactions giving rise to the high-temperature heat capacity anomaly. Neutron diffraction measurements on a single-crystal of "pure" Fe_3O_4 evinced only one phase transition[13] but the heat capacity vs temperature curve of this sample also exhibited only one λ-type anomaly.[14] There is no question, however, that the furcation of the heat capacity anomaly observed initially in reference 10 is an intrinsic property of certain kinds of magnetites. First of all, the furcation has been observed in several different samples in the same laboratory.[11] Secondly, furcation of the heat capacity anomaly has also been observed in more recent, independent heat capacity measurements and for similar samples the results were in surprisingly good agreement with those of reference 10.[15] Unfortunately, the samples of reference 15

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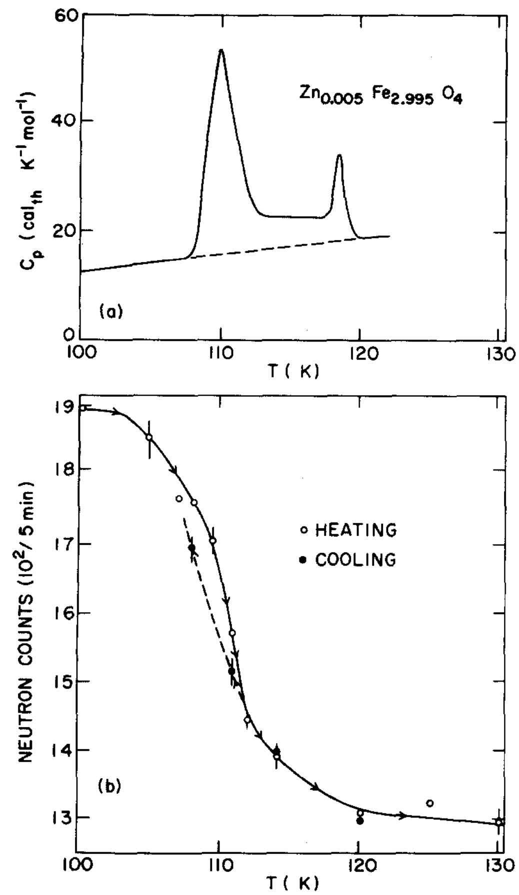

Fig. 1. (a) Bifurcated heat capacity anomaly of $Zn_{0.0005}Fe_{2.995}O_4$. (b) Variation of neutron intensity with temperature at $2\theta = 60.6°$.

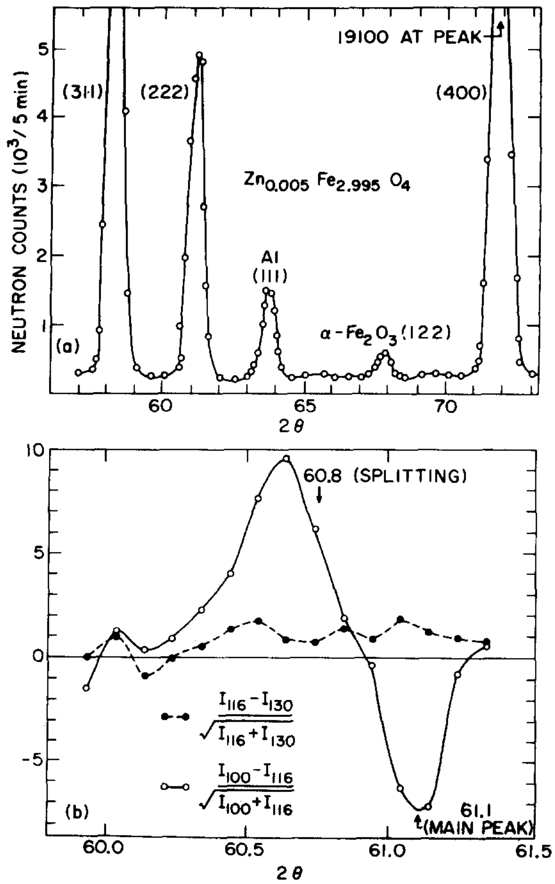

Fig. 2. (a) Powder diffraction pattern of $Zn_{0.005}Fe_{2.995}O_4$ at 130 K. (b) Relative differences in intensities (I) observed at 100, 116, and 130 K.

were unavailable in sufficient quantities for neutron diffraction studies.

Therefore, neutron scattering measurements have been made on a sample of doped Fe_3O_4, (i.e., $Zn_{0.005}Fe_{2.995}O_4$). Such measurements should lead to an understanding of the structural basis for the heat-capacity anomaly, which together with the resistivity measurements, will provide a unique opportunity to correlate the thermal, structural and electronic property changes at the Verwey transition. $Zn_{0.005}Fe_{2.995}O_4$ was chosen instead of Fe_3O_4 as the material to study since the λ-anomalies are separated by 8.5 K in $Zn_{0.005}Fe_{2.995}O_4$ and by only 5 K in pure Fe_3O_4.[10–12] Thus, this sample provides the best opportunity for determining whether distinct structural or electrical property variations are associated with the two anomalies. Although the total transitional enthalpy undergoes only a moderate change in going from Fe_3O_4 to $Zn_{0.005}Fe_{2.995}O_4$, the separate enthalpy increments for the two (still well developed, cf. Fig. 1) λ-type anomilies differ considerably from those of the "pure" compound and the lower-temperature anomaly is displaced downward.[10–12]

The powdered specimen of $Zn_{0.005}Fe_{2.995}O_4$ used was the *identical* sample on which heat capacity and Mössbauer measurements were previously performed.[9] The preparation and characterization of this sample has been reported.[9,11] The neutron diffraction data were obtained at the Brookhaven High-Flux Beam Reactor with an incident neutron wavelength of 2.46 Å. A triple-axis spectrometer was used with polygraphite crystals as the monochromator and the analyzer to improve the signal-to-noise ratio. A platinum, resistance thermometer was used to monitor the temperature to within ± 0.1 K. The sample gave a good powder diffraction pattern except for two peaks which were accounted for by an α-hematite impurity of less than 1%.

Preliminary neutron, elastic-scattering data, with 2θ ranging from 35 to 80° [Fig. 2 (a)], were taken at 110, 116, and 130 K in order to determine the best angle settings for monitoring the variation of neutron intensity with temperature. Based on these results, scans with high-statistical precision were taken around the (222) and (400) peaks, and the relative differences between intensities observed at these temperatures are plotted as a function of 2θ [Fig. 2 (b)]. To maximum relative change in intensity with temperature was found to occur near $2\theta = 60.6°$ and is due mainly to the (222)–(22$\bar{2}$) rhombohedral splitting with perhaps some contribution from a superlattice peak. Another large change in intensity occurred near $2\theta = 72.7°$, due to the growth with decreasing temperature of the (4 0 ½) superlattice peak.

A more detailed examination of the variation of neutron intensity with temperature was made at these two angular settings. At both settings, a sharp drop in intensity with increasing temperature occurred between 105 and 115 K [Fig. 1 (b)]. The magnitude of the decrease was roughly 30% at $2\theta = 60.6°$ and about 25% at $2\theta = 72.7°$. Hystereses were observed in both cases. No significant changes in intensity were observed between 116 and 130 K at either setting.

The results of this experiment prove that the heat capacity anomaly occurring at 110.6 K is associated with a lattice transformation as concluded previously but less definitively on the basis of Mössbauer measurements. No lattice distortion is associated with the higher-temperature anomaly.

Thus, despite the considerable influence of impurities on the heat capacity anomaly at the Verwey transition, the neutron diffraction measurements are rather similar for pure and doped Fe_3O_4 and do not mirror at all the complexity in the heat capacity even for pure Fe_3O_4. These data do show, however, that the phase transition as determined by neutron diffraction and due to a change in atomic coordinates gives rise to the lower-temperature heat capacity anomaly. The higher-temperature heat capacity anomaly must be due to more subtle effects. Recent resistivity vs temperature measurements on the sample employed in this study detected a conductivity change *only* in the neighborhood of the lower-temperature heat capacity anomaly.[16] In fact, the change in conductivity occurs on the low-temperature-side of the lower-temperature heat capacity anomaly with an offset of about −2 to −4 K between the peak of the heat capacity anomaly and maximum value of $\partial\sigma/\partial T$. No abrupt changes in conductivity are associated with the higher-temperature anomaly. Marked changes in the relative intensity of the *A* and *B*-site Mössbauer patterns have, however, been observed in the vicinity of the higher-temperature anomaly.[9] These findings, together with the results of the resistivity measurements, support the idea proposed by Siemons[17] and Evans,[9] namely, that the higher-temperature anomaly is a semi-metal to semi-conductor transition.

A question for further study is the actual mechanism by which doping produces bifurcation. Does the doping primarily affect the electronic ordering, or is the major effect on the lattice distortion, perhaps through induced strain in the lattice as suggested in mechanical stress experiments by Chikazumi *et al.*?[14] The change in the relative intensities of the *A*- and *B*-site patterns, the temperature offset between the conductivity and heat capacity anomalies and the preliminary indications of a change in the slope of the σ vs T curve in the vicinity of the higher-temperature anomaly provide some tempting clues for further studies of the furcation of the Verwey transition in Fe_3O_4.

Thus, the furcation of the heat capacity anomaly at the Verwey transition in Fe_3O_4 continues to be a conundrum, albeit a well-established one. Despite this, the present work establishes that the lower-temperature transition in magnetite is structural and that it is coupled with another in which structural changes were not detected. These results are in agreement with the connascence of atomic displacements and the lower-temperature heat capacity anomaly as indicated in the cited Mössbauer measurements.

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