Magnetization and exchange in nonstoichiometric magnetite

Ricardo Aragón
Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716
(Received 5 August 1991; revised manuscript received 9 January 1992)

Measurements of saturation magnetization and remanence in $Fe_{3(1-\delta)}O_4$ single crystals with ($0.000 < \delta < 0.006$) between 4.2 and 300 K are reported. The exchange constants J_{AB}, evaluated with spin-wave theory in the harmonic approximation, agree with those derived from low-temperature heat-capacity investigations. A discontinuous change in behavior for $\delta > 0.0039$ is consistent with the change from a first- to second-order Verwey transition, associated wtih splitting of the octahedral electronic levels. A self-reversal of the remanent moment is observed at T_V, in the second-order regime. Simple nearest-neighbor models, in the mean-field approximation, suffice to account for all electronic and magnetic critical temperatures, in the Ising two-state and Heisenberg formulations, respectively.

I. INTRODUCTION

Investigations of the inverse spinel Fe_3O_4 have contributed substantially to our understanding of magnetic oxides. The identification of its ferrimagnetic[1] ordering and verification[2] of spin-wave-theory results are representative examples of its significance. However, these early successes have proven difficult to reconcile with evidence for other electronic and magnetic phenomena, including the Verwey[3] phase transition (~ 122 K) and magnetic aftereffect[4] (~ 250 K) anomalies.

The sensitive dependence of the physical properties of transition-metal compounds on any deviation from ideal metal-oxygen stoichiometry readily provides a justification for some of the discrepancies in numerous prior studies of this material. In the last decade, the availability of high-quality cation-diffusion[5] and phase-equilibrium[6] data provided the basis for the corroboration of the pertinent point-defect equilibrium model[7] and the development of adequate preparation techniques for the synthesis of single crystals[8] of homogeneous controlled stoichiometry.[9]

A systematic characterization of the influence of nonstoichiometry on the physical properties of magnetite has demonstrated that, with due attention to their compositional dependence, simple mean-field parameters[10] provide a description of the Verwey-transition criticality and electrical transport. The purpose of this investigation is to show that magnetic properties are consistent with this approximation, without loss of generality, specifically, that the dependence of a single interaction parameter (J_{AB}) on nostoichiometry accounts for all electronic and magnetic critical temperatures.

II. EXPERIMENTAL DETAILS

Three $Fe_{3(1-\delta)}O_4$ single crystals, grown[8] by rf induction melting from 99.999%-pure Fe_2O_3 reagent, were annealed[9] under controlled oxygen fugacity conditions, by techniques described elsewhere,[11] to produce δ values of 0.000 and 0.003, respectively, corresponding to stoichiometric and cation-deficient samples with first-order Verwey transitions, and $\delta = 0.006$, to induce cation deficiency beyond the critical value 0.0039, for which second-order[12] Verwey transitions are observed. The crystals were ground in a diamond abrasive air mill to spheres of 3–5 mm diameter, with sphericity of 10^{-2}, oriented by Laue backreflection x-ray techniques on the cubic [100] axis, within 1°, and rigidly mounted with epoxy on quartz tubing. Upon completion of these experiments, the crystals were removed to obtain a blank correction for the mount.

Magnetization was measured in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS2) from liquid helium to room temperature, at fixed fields above 3 kOe, after cooling in a 10-kOe field, applied parallel to the [100] mounting axis. No attempt was made to inhibit basal twinning below the Verwey transition. In separate experiments a tube with internal diameter closely matching the sample diameter was used to induce self-orientation of the crystal by rotation during field cooling below the transition. Scan lengths of 3 cm were used, and the calibration was verified with a Pd standard; the effect of field inhomogeneity was evaluated with a Ni standard. Absolute accuracy was better than 1%, and the precision for six independent scans at each temperature was better than 0.1%.

The remanent moment, obtained by field cooling to 4.5 K at 10 kOe and nulling with no overshoot, was monitored, at zero applied field, on the heating cycle. The residual remanence of the superconducting solenoid is less than 1 Oe.

III. RESULTS

The effect of nonstoichiometry on the temperature dependence of magnetization is apparent in Fig. 1 for a representative set of measurements at 10 kOe in each sample. The difference with the values extrapolated to infinite field was found commensurate with experimental uncertainty.

Extrapolation to 0 K, to evaluate the absolute saturation magnetization, yields a dependence on non-

 ©1992 The American Physical Society

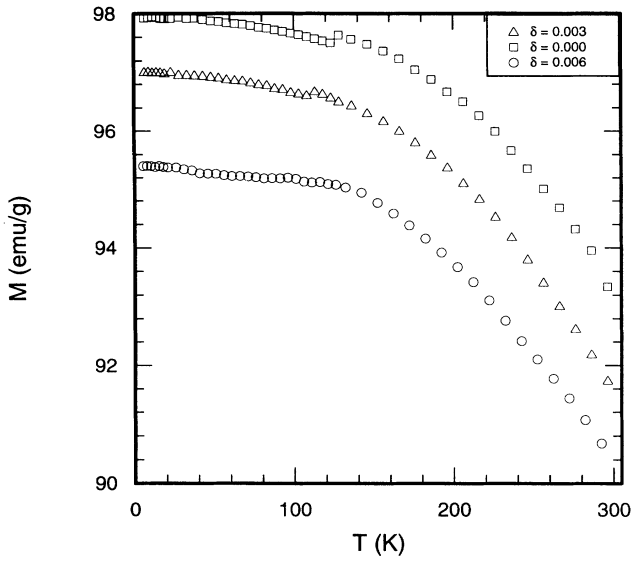

FIG. 1. Magnetization at 10 kOe for samples with $\delta=0.000$ (squares), 0.003 (triangles), and 0.006 (circles).

stoichiometry, fully justified by associated changes in the $[Fe^{2+}]/[Fe^{3+}]$ ratio of the octahedral sublattice, in substantial agreement with previous investigations.[13]

Corroborating prior reports,[14] a small ($\sim 0.1\%$) discontinuous change in magnetization, which persists even after correction for anisotropy, is observed at the Verwey temperature (T_V), in samples with $\delta < 0.0039$ and first-order transitions. The magnitude of the discontinuity decreases with δ, proportionally to diminishing transition entropies,[15] and vanishes for $\delta > 0.0039$, consistently with the second-order character of the transition (cf. Fig. 2).

These effects are mirrored by the behavior of the 4.5-K remanence, which decreases sharply at T_V, discontinuously for first-order and continuously for second-order transitions (cf. Fig. 3). Above T_V the moment remains positive for first-order transitions, whereas a self-reversal to negative values is observed in the second-order regime, again reversed, this time discontinuously at 225 K (cf. Fig. 4). In all cases a minimum is observed at the isotropic point, namely, 130 K for first-order and 125 K for second-order samples. Albeit small, these phenomena are three orders of magnitude above experimental uncertainty.

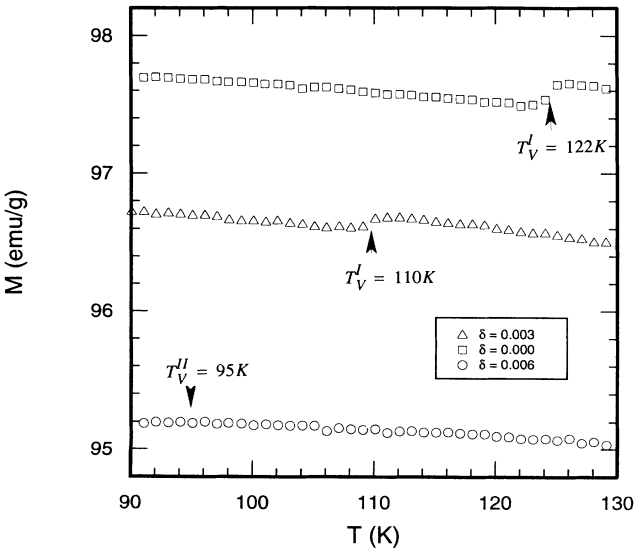

FIG. 2. Magnetization at 10 kOe for samples with $\delta=0.000$ (squares), 0.003 (triangles), and 0.006 (circles), in the temperature range of their respective Verwey transitions.

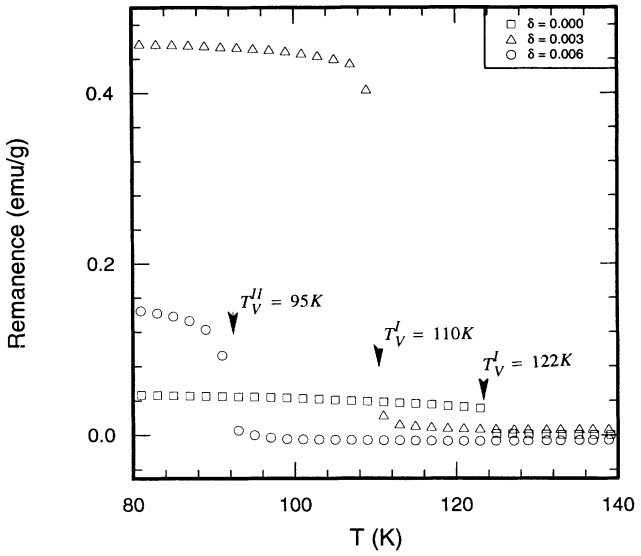

FIG. 3. Change in the remanent moment obtained by field cooling to 4.5 K at 10 kOe and heating in zero applied field, for samples with $\delta=0.000$ (squares), 0.003 (triangles), and 0.0006 (circles).

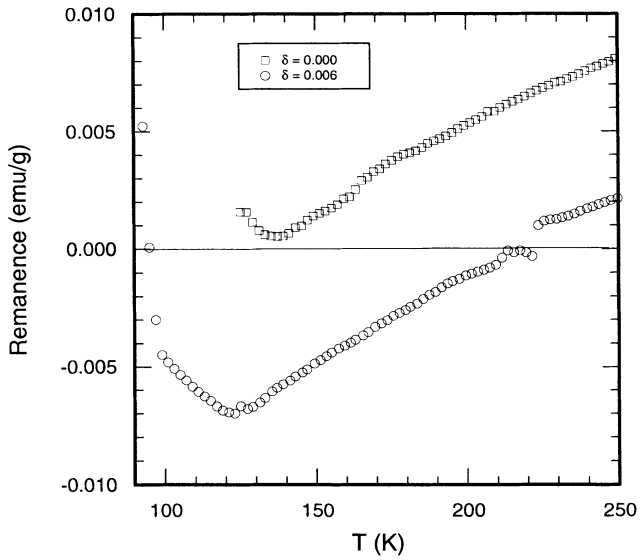

FIG. 4. Detail of the change in the remanent moment obtained by field cooling to 4.5 K at 10 kOe and heating in zero field for samples with $\delta=0.000$ (squares) and 0.006 (circles), showing self-reversal between 95 and 225 K for the second-order Verwey-transition regime.

A. Evaluation of J_{AB} exchange constants

The computation of an effective exchange constant from the temperature dependence of heat capacity and magnetization follows from fundamental results of spin-wave theory[16] in the harmonic approximation.

With neglect of exchange interactions between ions in the same sublattice (i.e., AA and BB, tetrahedral and octahedral, respectively) of the inverse spinel structure, the dispersion relation[17] for the acoustic magnon[18] to order k^2 is

$$\hbar\omega = \frac{11}{16}\frac{J_{AB}S_A(S_{B1}+S_{B2})}{S_{B1}+S_{B2}-S_A}k^2a^2 , \tag{1}$$

where ω is the frequency; k the spin-wave momentum; a the cubic unit-cell parameter, $S_A=S_{B1}=2.5$, the spin of Fe^{3+} in tetrahedral and octahedral sites, $S_{B2}=2$ the spin of Fe^{2+} in the octahedral sublattice; J_{AB} the exchange constant between tetrahedral and octahedral sites; and the fraction accounts for the number of 12 octahedral and 4 tetrahedral nearest neighbors for an A site in the face-centered structure.

Neglecting the effect of applied magnetic fields and anisotropy, the dispersion relation may be used to compute the appropriate partition function[19] or integrated directly[20] to obtain the spin-wave contribution to heat capacity ($C_{\rm mag}$) and to the magnetization along the applied-field axis z (M_z), which yields the pertinent forms of the celebrated Bloch[21] result:

$$C_{\rm mag}\cong 0.113R\left[\frac{4(S_{B1}+S_{B2}-S_A)k_BT}{11J_{AB}S_A(S_{B1}+S_{B2})}\right]^{3/2} , \tag{2}$$

where k_B is Boltzmann's constant, R the ideal gas constant, and

$$M_z=M_{z0}\left[1-\frac{0.058\,64}{4(S_{B1}+S_{B2}-S_A)}\times\left[\frac{16(S_{B1}+S_{B2}-S_A)k_BT}{11J_{AB}S_A(S_{B1}+S_{B2})}\right]^{3/2}\right] , \tag{3}$$

where M_{z0} is the magnetization at 0 K. The error committed by the assumed quadratic k dependence has been shown[22] to be commensurate ($\sim$5%) with experimental uncertainty.

A linear regression of the low-temperature magnetization with respect to $T^{3/2}$ (cf. Fig. 5) for a stoichiometric sample, self-oriented by field cooling to induce a net moment coaxial with the applied field, yields the corresponding value of J_{AB} ($J_{AB}/k_B=23$ K) by direct substitution in Eq. (3). This result is compared graphically (cf. Fig. 6) with equivalent evaluations, obtained from Eq. (2), with data on low-temperature heat capacity[15,23] of single crystals prepared with the same techniques employed in this investigation. The strong dependence on nonstoichiometry precludes the inclusion of results from prior work[24] for which the value of δ in the samples is difficult to ascertain.

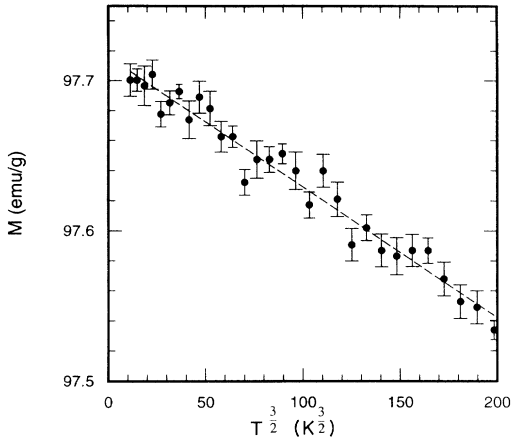

FIG. 5. Magnetization at 10 kOe for a self-oriented field-cooled stoichiometric crystal ($\delta=0.000$) below 30 K vs $T^{3/2}$. Bars represent only the standard deviation of six scans fitted by iterative regression at each temperature.

IV. DISCUSSION

A. Exchange, acoustic, and optical magnons

The experimental difficulties associated with measurements of small deviations from a large overall value of magnetization at very low temperature have promoted a preference for heat-capacity investigations to characterize spin-wave contributions to a physical property which tends to zero at 0 K. With due attention to composition, the complementary nature of both experiments yields a consistent set of J_{AB} parameters (cf. Fig. 6), with a clear discontinuous change at $\delta_C=0.0039$.

The restriction of Eqs. (2) and (3) to the acoustic mag-

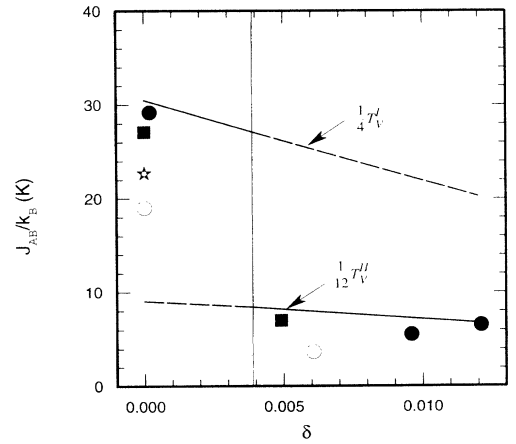

FIG. 6. J_{AB} exchange constants vs nonstoichiometry obtained from magnetization data (star, this work), relaxation calorimety (solid circles, Ref. 15), adiabatic calorimetry (solid squares, Ref. 23) [computed from Eq. (5)], and critical magnetic temperatures of 851 and 225 K (open circles) and Ising-model limits given by $\frac{1}{4}$ and $\frac{1}{12}$ of the Verwey-transition temperatures, in first- and second-order regimes, respectively (solid and dashed lines) above and below $\delta_C=0.0039$.

non contribution is expected to fail for $T \sim J_{AB}/k_B$, as a result of appreciable excitation of the optical modes of the predicted six-branch spectrum, which requires magnetization measurements below the lower limit (4.5 K) of the instrumentation used in this work, for the second-order regime ($J_{AB}/k_B \approx 6$ K). Interestingly, the elusive[25] anomalies in magnetization,[26] heat-capacity,[27] and magntoelectric effects,[28] reported below $T \sim 10$ K, for nominally more closely stoichiometric samples,[29] would be justified by minor contamination with a phase of $\delta > \delta_C$, which would be otherwise undetectable.

Remarkably, the straight-line dependence of the magnetization on $T^{3/2}$, for samples with $\delta < \delta_C$, is preserved almost to the onset of their respective first-order Verwey transitions at temperatures well in excess of J_{AB}/k_B. It may be surmised, therefore, that the optical magnons are not appreciably excited in this case and that the small discontinuous change in magnetization may reflect a partial condensation of these modes. Direct evidence does exist for optical-phonon condensation at T_V from neutron-scattering experiments.[30]

The most fundamental evidence for spin waves is found in direct measurements of the magnon-dispersion relations by magnetic inelastic neutron scattering. The available data,[31] obtained at room temperature using a natural single crystal,[32] is in good agreement[33] with Eq. (1) for $J_{AB}/k_B = 23$ K.

B. Charge ordering: Verwey transitions

In a previous paper,[10] the use of a very simple two-state model,[34] treated in the mean-field approximation, was shown to be sufficient to account for the first- and second-order regimes of the Verwey transition and their compositional dependence, if the respective degeneracies of the ground and excited states are changed to allow for a decrease in internal energy for $\delta < \delta_C$ associated with the splitting of the associated electronic levels. In common with numerous other empirical forms of the mean-field approximation, the appropriate internal-energy parameters are obtained in terms of experimental transition temperatures through conditions on the Helmholtz potential and its derivatives, which provide for thermodynamic consistency.

It has been repeatedly pointed out[35,36] that these heuristic forms of the mean-field approximation should not obscure the fact that they find their formal justification in a very limited number of elementary models of true physical significance, in which a bilinear interaction is linearized by the introduction of an effective field. Ultimately, order-disorder phenomena result from nearest-neighbor interactions represented by the pertinent exchange parameter (J). For the two-state Ising problem, the well-known[37] result for the transition temperature (T_V) is

$$k_B T_V = zJ \ , \tag{4}$$

where z represents the number of nearest neighbors.

For $\delta > \delta_C$ the value of J_{AB}, derived from heat capacity[23] ($J_{AB}/k_B = 7.1$ K) and $z = 12$, yields a critical temperature of 84 K, in excellent agreement with the lower limit[38] for possible Verwey transitions at 81 K. Hence the experimental range for second-order transitions,[10] namely, $81 < T < 101$ K, corresponds to $6.7 < J_{AB}/k_B < 8.4$ K (cf. Fig. 6).

For $\delta < \delta_C$ it must be recognized that the electronic states are no longer equally degenerate. An elementary application of Kramer's theorem restricts splitting to the Fe^{2+} cations (i.e., an even number of electrons d^6, as opposed to $Fe^{3+}[d^5]$). The number of nearest-neighbor Fe^{2+} cations (z), in the 12 B sites surrounding an A site, can easily be found, avoiding overcounting; associating one $Fe^{2+}{}_B$ with each of the $Fe^{3+}{}_A$, in the four A sites of the nearest-neighbor set; hence $z = 4$. A value of $J_{AB}/k_B = 20$ K yields the same estimate of a lower limit for T_V, namely, the 81-K invariant, whereas the heat-capacity measurement[23] ($J_{AB}/k_B = 27.1$ K) yields 108.4 K, coinciding with the lower limit for first-order transitions at $\delta = \delta_C$. The first-order regime (i.e., $\delta_C > \delta > 0$) $108.4 < T_V < 122$ K corresponds to $27.1 < J_{AB}/k_B < 30.5$ K (cf. Fig. 6).

C. Magnetic ordering: Curie point

A generalization of the two-state Ising model allows for multiple values of spin, which, in the mean-field approximation, is entirely equivalent to the Heisenberg problem, since only the spin component along the applied magnetic field is relevant.[39] This yields the familiar molecular-field result for the Curie temperature:[2]

$$kT_C \cong 4\sqrt{2} J_{AB} \sqrt{S_A S_B (S_A + 1)(S_B + 1)}$$
$$\cong 45.2 J_{AB} \ . \tag{5}$$

As is immediately verified, a value of $J_{AB} = 19$ K is consistent with the experimental Curie temperature of 851 K. However, it should be emphasized that it is impossible to measure the effect of nonstoichiometry on J_{AB} by direct determination of T_C. The evidence from phase equilibrium[9] clearly demonstrates that significant levels of nonstoichiometry can only be preserved metastably by a rapid quench from high annealing temperatures. At 850 K the equilibrium values of δ are below 10^{-6}, judging from the well-established stability-field boundaries and the thermal dependence of the intrinsic oxygen fugacity. Prolonged heating, significantly above room temperature, of any nonstoichiometric magnetite phase will invariably result in segregation of Fe_2O_3 at the expense of cation deficiency, or $Fe_{1-x}O$, from any measure of cation excess. These processes result from isochemical exsolution and cannot consequently be prevented by encapsulation or atmosphere control. The amount of segregated second phase is controlled by the lever rule and can easily fall below the detection limit of standard analytical techniques. Therefore, it is not surprising that the exchange parameters obtained from fits of the molecular-field expressions to high-temperature data[40] should yield values consistent with those reported here for closely stoichiometric compositions. In addition, it should be apparent that the stoichiometry of the sample will be a strong function of temperature in these experiments. In-

terestingly, there is evidence that the natural crystal used in the inelastic neutron-scattering investigation was heated during the experiment, which, added to its Ti contaminant,[31,32] similarly accounts for the value ($J_{AB}/k_B = 23$ K) obtained.

The reciprocal argument, for the low values of J_{AB} ($5 < J_{AB}/k_B < 7$ K) obtained for $\delta > \delta_C$, warrants separate consideration. Application of Eq. (5) predicts critical temperatures of 225–320 K, which would seem unsupported by experimental evidence, as noted by Kouvel,[2] however, in the limit of negligible applied fields assumed in Eqs. (2) and (3), pronounced changes in initial permeability,[9] magnetic relaxation,[41] and resonance, associated with magnetic aftereffects[42] and characterized by muon scattering,[43] are readily apparent in cation-deficient phases at ~250 K. This perturbation of magnetic ordering is reflected in the discontinuous change in remanence at 225 K (cf. Fig. 4).

D. Self-reversal of remanence at T_V^{II} for $\delta > \delta_C$

A quantitative interpretation of remanence is complicated by the multidomain character of the sample; however, this does not preclude the description of magnetic behavior below saturation,[44] over an appropriate statistical average, for a number of fully saturated domains. Time-reversal considerations are equally valid for the macroscopic observable of this ensemble, as for the single-domain case.

A review[45] of all known cases of broken symmetry indicates that, coupled with the verified presence of hysteresis,[46] in second-order Verwey transitions only, the self-reversal of the remanent moment observed at T_V^{II} provides circumstantial evidence for the breaking of time-reversal symmetry for $\delta > \delta_C$, which would prove an essential element for a microscopic model of Verwey ordering phenomena.

V. CONCLUSIONS

The physical description which emerges from the characterization of the influence of nonstoichiometry on the properties of magnetite exceeds the scope of merely resolving discrepancies among the results of numerous experimental investigations. The fundamental laws necessary to describe all associated phenomena are well established and, within experimental error, lead to consistent results.

The exchange parameters, J_{AB} obtained from fits of experimental data to the spin-wave $T^{3/2}$ dependence, predict critical temperatures for the associated Ising problem, which correlate within experimental error with the first- and second-order regimes observed for the Verwey transition. The same mean-field approximation, applied to the Heisenberg problem, yields the corresponding magnetic critical temperatures. Direct observation of these transitions is limited only by the boundaries of the magnetite stability field, as a function of temperature and nonstoichiometry. For $\delta < \delta_C$ the magnetic observables yield J_{AB} values consistent with the lower limit of the mean-field prediction, whereas calorimetric measurements converge at its upper boundary (cf. Fig. 6).

The only additional necessary elements are found in the dependence of the driving interactions on composition and on the fact that, at some critical level ($\delta_C = 0.0039$), the electronic states are rearranged to minimize the Helmholtz potential by a decrease in internal energy. It has long been recognized that these interactions, albeit parametrized by nearest-neighbor exchange terms, are largely of Coulombic origin[47] and should include longer-range components. Treated in the mean-field approximation, the contribution of the associated order-disorder phenomena to all macroscopic properties can be readily quantified. However crude, the thermodynamic potential obtained is a general result.

The main purpose of pursuing the mean-field approximation to its ultimate consequences is to expose those aspects of physical behavior which remain unaccounted by this description. Thus, whereas a unique quantitative agreement between critical temperatures, be it Verwey transitions or Curie points, has been obtained for the second-order regime ($\delta > \delta_C$), a similar comparison for the first-order regime ($\delta < \delta_C$) yields two different results for the lower limit of T_V^I, namely, 81 K, the lowest[10] possible Verwey transition, if J_{AB} is evaluated from purely magnetic measurements, such as the Curie temperature, low-temperature magnetization or magnon-dispersion curves, and 108.4 K, the lowest detectable T_V^I at δ_C, when low-temperature heat-capacity evaluations of J_{AB} are used in Eq. (4). Therefore, a microscopic theory of Verwey ordering in the first-order regime should address a mechanism for the modulation of the exchange interaction beyond the verified composition (δ) dependence. In "single-ion" descriptions, this is accomplished by spin-orbit coupling terms; the corresponding collective interaction is of the phonon-magnon type.

A purely empirical approach, such as expansion of the Bragg-Williams approximation implicit in the Ising problem, into quasichemical solutions, for instance, cannot produce new results, because the additional fitted parameters do not have an independent physical definition and, consequently, cannot be verified by scattering or spectroscopic experiments. It is preferable to recognize that "a system of interacting particles has been approximated by a system of noninteracting particles"[39] and seek evidence for specific terms of a more realistic model Hamiltonian to evaluate the most probable, rather than the average, state of the system by renormalization techniques.

Albeit circumstantial, experimental evidence for these interaction terms may be found in the apparent condensation of optical magnons in first-order Verwey transitions. It has been shown[48] that lattice vibration modes, coupled to oscillating crystal fields, may modulate the effective exchange interaction by admixing low-lying orbital excited states into the ground state of the magnetic ion. Without neutron-scattering characterization of the low-temperature magnon-dispersion relations, evidence for these effects is inconclusive. However, the formalism for optical magnon-phonon interactions in ferromagnetic insulators yields specific results, which are well suited for experimental corroboration. Perhaps the most immediate is the observed[49] thermal dependence of the gyromag-

netic ratio between 130 K and room temperature ($2.03 < g < 2.17$), which is consistent with progressively incomplete quenching of the orbital contribution. Ferromagnetic resonance should corroborate the existence[50] of two maxima in the relaxation frequency. Additional evidence could be derived from optical Raman scattering or from experimental verification of the predicted[51] neutron-scattering cross section. Fortunately, nonstoichiometric phases with $\delta > \delta_C$ and states of equal degeneracy provide a natural control for the interpretation of these and similar experiments.

ACKNOWLEDGMENTS

The generous cooperation of Dr. Richard Harlow and Lou Lardear in providing access to the real-time Laue backreflection instrument at the Du Pont Experimental Station is gratefully acknowledged.

[1]L. Néel, Ann. Phys. (N.Y.) **3**, 137 (1948).
[2]J. S. Kouvel, Phys. Rev. **102**, 1489 (1956).
[3]E. J. Verwey and P. W. Haajman, Physica (Utrecht) **8**, 979 (1941).
[4]H. Kronmüller, R. Schütenauer, and F. Walz, Phys. Status Solidi A **24**, 487 (1974).
[5]R. Dieckmann and H. Schmalzried, Ber. Bunsenges. Phys. Chem. **81**, 344 (1977).
[6]R. Dieckmann and H. Schmalzried, Ber. Bunsenges. Phys. Chem. **81**, 414 (1977).
[7]H. Flood and D. G. Hill, Z. Elektrochem. **61**, 18 (1957).
[8]H. R. Harrison and R. Aragón, Mater. Res. Bull. **13**, 1097 (1978).
[9]R. Aragón, D. J. Buttrey, J. P. Shepherd, and J. M. Honig, Phys. Rev. B **31**, 430 (1985).
[10]R. Aragón and J. M. Honig, Phys. Rev. B **37**, 209 (1988).
[11]See Ref. 8 for crystal growth and Ref. 9 for annealing conditions and techniques.
[12]J. P. Shepherd, R. Aragón, J. W. Koenitzer, and J. M. Honig, Phys. Rev. B **32**, 1818 (1985).
[13]Z. Kakol and J. M. Honig, Phys. Rev. B **40**, 9090 (1989).
[14]S. Umemura and S. Ida, J. Phys. Soc. Jpn. **40**, 679 (1976).
[15]J. P. Shepherd, J. W. Koenitzer, R. Aragón, J. Spalek, and J. M. Honig, Phys. Rev. B **43**, 8461 (1991).
[16]J. Van Kranendonk and J. H. Van Vleck, Rev. Mod. Phys. **30**, 1 (1958).
[17]J. S. Kouvel (unpublished).
[18]M. L. Glasser and F. J. Milford, Phys. Rev. **130**, 1783 (1963).
[19]H. Unruh, Jr. and F. J. Milford, Phys. Rev. **123**, 1619 (1961).
[20]See, for instance, Ref. 16.
[21]F. Bloch, Z. Phys. **74**, 295 (1932); C. Möller, *ibid.* **82**, 559 (1933).
[22]R. P. Kenan, M. L. Glasser, and F. J. Milford, Phys. Rev. **132**, 47 (1963).
[23]J. W. Koenitzer, P. H. Keesom, and J. M. Honig, Phys. Rev. B **39**, 6231 (1989).
[24]For a representative review, cf., for instance, E. Gmelin, N. Lenge, H. Kronmüller, Phys. Status Solidi A **79**, 465 (1983).
[25]For the absence of this anomaly, cf., for instance, E. Gmelin, N. Lenge, and H. Kronmüller, Phys. Status Solidi A **79**, 465 (1983); S. Yumoto, M. Mizoguchi, and S. Iida, J. Phys. Soc. Jpn. **53**, 26 (1984); J. P. Shepherd *et al.*, Phys. Rev. B **31**, 1107 (1985).
[26]See, Ref. 14 and S. Chikazumi, in *Magnetism and Magnetic Materials—1975 (Philadelphia)*, Proceedings of the 21st Annual Conference on Magnetism and Magnetic Materials, edited by J. J. Becker, G. H. Lander, and J. J. Ryne, AIP Conf. Proc. No. 29 (AIP, New York, 1976).
[27]S. Todo and S. Chikazumi, J. Phys. Soc. Jpn. **43**, 1091 (1977).
[28]Y. Miyamoto and S. Chikazumi, J. Magn. Magn. Mater. **31-34**, 863 (1983); K. Kato and S. Iida, Phys. Soc. Jpn. **50**, 2844 (1981).
[29]As deemed from Verwey transitions $T_V > 108$ K.
[30]M. Izmui and G. Shirane, Solid State Commun. **17**, 433 (1975).
[31]H. Watanabe and B. N. Brockhouse, Phys. Lett. **1**, 189 (1962).
[32]The metal-oxygen stoichiometry is uncertain; the main (1%) Ti^{4+} impurity [cf. B. N. Brockhouse, Phys. Rev. **106**, 859 (1957)] necessarily increased Fe^{2+} concentration; cf. R. Aragón and R. H. McCallister, Phys. Chem. Miner. **8**, 112 (1982).
[33]See Ref. 19 for a discussion of the effects of the k^2 approximation.
[34]S. Strässler and C. Kittel, Phys. Rev. **139**, A758 (1965).
[35]J. M. Ziman, *Models of Disorder* (Cambridge University Press, Cambridge, England, 1979), p. 143.
[36]H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. (Wiley, New York, 1985), p. 445.
[37]Cf., for instance, Ziman, Ref. 35, p. 145 and Callen, Ref. 36, p. 443.
[38]Corresponding to the intersection with the first-order Maxwell set (cf. Ref. 10).
[39]Callen, Ref. 36. p. 445.
[40]C. M. Srivastava, G. Srinivasan, and N. G. Nanadikar, Phys. Rev. B **19**, 499 (1979).
[41]H. Kronmüller, R. Schützenauer, and F. Walz, Phys. Status Solidi A **24**, 487 (1974).
[42]F. Walz *et al.*, Phys. Status Solidi B **110**, 471 (1982).
[43]C. Boekema *et al.*, Phys. Rev. B **31**, 1233 (1985); **33**, 210 (1986); J. Magn. Magn. Mater. **54-57**, 353 (1986).
[44]R. B. Birss, *Symmetry and Magnetism* (North-Holland, Amsterdam, 1964), p. 153.
[45]P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin/Cummings, Menlo Park, CA, 1984), p. 68.
[46]R. Aragón, R. J. Rasmussen, J. P. Shepherd, J. W. Koenitzer, and J. M. Honig, J. Magn. Magn. Mater. **54-57**, 1335 (1986) and Ref. 15.
[47]P. W. Anderson, Phys. Rev. **102**, 1008 (1956).
[48]For a review, cf., for instance, K. P. Sinha and N. Kumar, *Interactions in Matgnetically Ordered Solids* (Oxford University Press, New York, 1980), p. 101.
[49]L. R. Bickford, Jr., Phys. Rev. **78**, 449 (1950).
[50]N. Kumar and K. P. Sinha, Physica **36**, 655 (1976).
[51]A. W. Joshi and K. P. Sinha, Proc. Phys. Soc. London **91**, 97 (1967).