PHYSICAL REVIEW B VOLUME 51, NUMBER 16 15 APRIL 1995-II

Verwey transition in magnetite: Finite-temperature mean-field solution of the Cullen-Callen model

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(Received 27 July 1994)

Verwey transition in magnetite is studied by solving the Cullen-Callen spinless one-band model at finite temperature, extending the work of Cullen and Callen from the $T=0$ to $T\neq 0$ regime. A complete phase diagram of the model in the $(U/t,T)$ plane is presented here, which exhibits three phases—a disordered phase and two ordered phases, one multiply ordered and one singly ordered. It is also explicitly shown that the transitions from the disordered phase to the ordered phases are of the first-order type, and they are entropy driven. I also find that for the transition temperature near the experimental value of 120 K, the transition is from the disordered state to the multiply ordered state, and not to the singly ordered state.

I. INTRODUCTION

The Verwey transition[1,2] in magnetite (Fe_3O_4) is a well-known metal-insulator phase transition, where the electrical conductivity of the Fe_3O_4 crystal decreases by a factor of ~ 100, as the temperature is decreased below the Verwey transition temperature, $T_V \sim 120$ K. Magnetite crystallizes in the spinel structure, and it is believed that the transition is due to ordering of Fe^{2+} and Fe^{3+} ions on the B sublattice, although the exact nature of the ordering in the low-temperature phase is still unclear.[3] Anderson[4] has shown that the Coulomb interaction between the ions on the B sublattice stabilizes and maintains the short-range order (SRO) across the Verwey transition, while the long-range order is lost in the Verwey transition.

Although the ionic picture of the Verwey transition captures the basic aspects of the transition, the simple Verwey model[1] based upon it has been ruled out by several experiments, e.g., Mössbauer spectroscopy,[5] neutron[6] and electron-diffraction,[7] and NMR spectroscopy.[8] A number of models, including the following, have been proposed that deal with the Verwey transition and the physics below T_V: the Cullen-Callen model[9] of itinerant electrons, electron correlation theory of Ihle and Lorenz,[10] and the molecular polaron and bipolaron pictures of Chakravarty[11] and Yamada.[12] Among these, the Cullen-Callen model has been very successful in explaining the origin of multiple peaks in experiments below T_V, for instance in Mössbauer spectroscopy, through the presence of multiple-order phase[9] for a certain parameter range in the model. Cullen and Callen, however, have performed their calculation at $T=0$ K, where the effect of raising the temperature is achieved by varying the parameters of the Hamiltonian. It is desirable to extend their work to $T\neq 0$ K to understand the thermodynamical aspects of the Verwey phase transition.

In the Cullen-Callen model, one describes the Verwey transition in terms of the motion and interactions of the electrons on the B sublattice. The Hamiltonian of this model consists of two terms: a hopping term with strength, t, and a nearest-neighbor interaction term with strength, U. Cullen and Callen[9] found that there is an order-disorder phase transition at $T=0$ K for the parameter value $U/t \sim 2.2$, which they identified with the Verwey transition. Recently, based on the electronic structure of magnetite in the local spin-density approximation (LSDA), Zhang and Satpathy[13] have proposed a three-band extension of the Cullen-Callen model, and Mishra, Zhang, and Satpathy[14] have found that their result agrees well with the Cullen-Callen one-band model, which lends support to studying the Cullen-Callen one-band model in detail.

In this paper, I study the Cullen-Callen one-band model at $T\neq 0$ K by a self-consistent method, map out the phase diagram, find the isotherms, and study the variation of Helmholtz free energy and entropy with temperature. The rest of the paper is organized as follows: Sec. II contains the Hamiltonian, followed by the definition of the order parameters in Sec. III; the results for the finite-temperature calculations are presented in Secs. IV and V, and Sec. VI contains the conclusion.

II. THE MODEL HAMILTONIAN AND THE MEAN-FIELD APPROXIMATION

The Hamiltonian for the Cullen-Callen model describes the d electrons in the singlet state, and can be written as

$$H=\sum_{\langle ij\rangle}(ta_i^\dagger a_j+U_{ij}a_i^\dagger a_i a_j^\dagger a_j)\ , \tag{1}$$

where $a_i^\dagger(a_i)$ are the creation (annihilation) operators of the electrons on the B lattice at the lattice site i. The sum, $\langle ij\rangle$, here runs over all the nearest-neighbor (NN) sites. The first term in the Hamiltonian is the tight-binding NN hopping term (also called the band-structure term), and the second term is the Coulomb interaction term. The second term can also be written as

$$U_{ij}n_in_j\ , \tag{2}$$

where n_i is the number operator at site i. We shall study this term in the Hartree approximation by making the following substitution:

$$n_i n_j \to \langle n_i \rangle n_j + n_i \langle n_j \rangle - \langle n_i \rangle \langle n_j \rangle \ , \tag{3}$$

where $\langle n_i \rangle$ refers to the quantum-mechanical and thermal average of the number operator at site i. The mean occupation numbers $\langle n_i \rangle$ are calculated from the eigenfunctions of the Hamiltonian (1) and the Dirac distribution of electrons in the eigenstates at temperature T; the eigenfunctions and eigenenergies of the Hamiltonian (1), in turn, depend on the $\langle n_i \rangle$. Thus, we determine $\langle n_i \rangle$ self-consistently by starting out with arbitrary values of $\langle n_i \rangle$ and repeating the procedure until convergence has been reached. The chemical potential (μ) at temperature T needed for the Dirac distribution is determined by imposing the condition that the total number of electrons in the system be equal to two times the number of k points in the Brillouin zone selected for the integration of (1) in k space, since based on the ionic picture there are two electrons per unit cell of the B sublattice of Fe_3O_4. In our study, we divide the Brillouin zone into 512 k points. We have experimented with higher values of a number of k points, and find that 512 k points are sufficient for the problem at hand.

At the time of investigation of this model by Cullen and Callen, there was no reliable estimate available for U_{ij}/t. However, recent calculations[13] of the electronic structure based on LSDA have yielded the following values: the average value of the hopping strength, $t \approx -0.13$ eV, and the nearest-neighbor Coulomb strength (with the assumption that $U_{ij} = U$ for all NN $\langle ij \rangle$ pairs), $U = 0.3 - 0.4$ eV. We will see in the following that the value of U must be greater than 0.32 eV for this model to show a first-order phase transition. In our study, we will fix the value of t at -0.13 eV, set $U_{ij} = U$ for all ij, and vary the value of U and temperature T in order to study the system.

III. ORDER PARAMETER(S)

There are four iron-ion sites in each unit cell of the B sublattice. The average number density of electrons at these sites is denoted as N_1, N_2, N_3, and N_4. In a perfect SRO state at $T = 0$, two of these will be zero and the other two will be equal to one each. However, due to the finite nonzero temperature, the SRO will be broken to some extent, and we allow all four number densities to vary but we impose the constraint that they add up to 2,

$$N_1 + N_2 + N_3 + N_4 = 2 \ . \tag{4}$$

Following Cullen and Callen,[9] we chose to study three order parameters built out of these charge densities:

$$m_1 = \tfrac{1}{2}(N_1 + N_2 - N_3 - N_4) \ , \tag{5a}$$

$$m_2 = \tfrac{1}{2}(N_1 - N_2 + N_3 - N_4) \ , \tag{5b}$$

$$m_3 = \tfrac{1}{2}(-N_1 + N_2 + N_3 - N_4) \ . \tag{5c}$$

These order parameters transform into one another under the operation of the space group of magnetite ($Fd3m$) and thus form an irreducible representation.[15] After calculating the N's, we order them with $N_1 \geq N_2 \geq N_3 \geq N_4$, and then find the values of the order parameters listed above. Similar to what Cullen and Callen[9] have claimed, I find that to study the nature of the Verwey transition near the experimental value of the transition temperature, all three order parameters m_1, m_2, and m_3 are important, and a transition temperature of 120 K requires that the transition be of the multiple-ordering type as shown below.

IV. PHASE TRANSITION

In Fig. 1, we plot the order parameter m_1 versus the parameter U/t and $\beta(=1/kT)$. It is seen that at any finite temperature, the system undergoes a phase transition from $m_1 = 0$ to 1 (singly ordering transition) as U/t value is raised from 0.5 to 10. On the other hand, for a fixed U/t there is a critical value of $U/t \cong 2.45$, below which there is no singly ordering transition from $m_1 = 0$ to 1 for any temperature. However, it will be seen in the following that a multiple-ordering phase transition for $U/t < 2.45$ takes place where all three order parameters are nonzero and comparable in magnitude (see Fig. 2).

From Fig. 1, one can derive the phase diagram of the system, which we present in Fig. 3. There are three phases—a disordered phase and two ordered phases consisting of a singly ordered phase and a multiply ordered

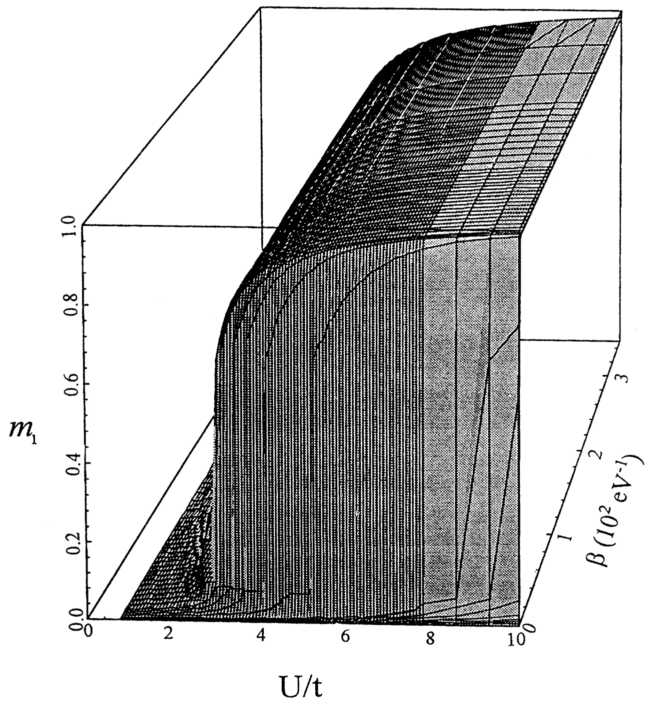

FIG. 1. Plot of the order parameter m_1 versus U/t and $\beta(=1/kT)$. $m_1 = 0$ refers to the metallic phase and $m_1 = 1$ refers to the insulating phase.

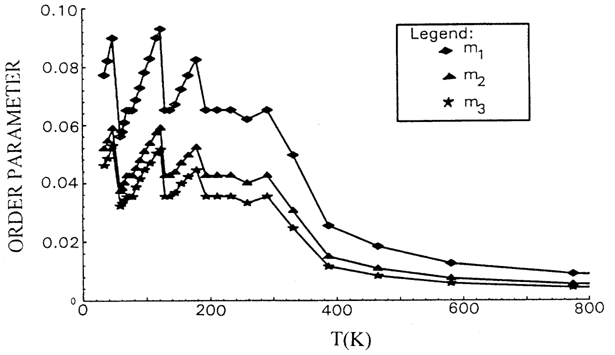

FIG. 2. Disordered to multiply ordered phase transition is illustrated for $U/t=2.23$. The multiple-ordering transition is distinguished from single-ordering transition by all three order parameters defined in the text, being nonzero and comparable in the ordered phase.

phase. The multiply ordered phase is distinguishable from the singly ordered phase by having comparable values of all three parameters m_1, m_2, and m_3, while in the singly ordered phase only m_1 is appreciable. The behaviors of order parameters m_1, m_2, and m_3 across the phase lines in the multiply ordered phase region and in the singly ordered regions are shown in Figs. 2 and 4, respectively. It is seen in Fig. 2 that the values of order parameters in the multiply ordered state are small and of comparable magnitudes. However, in the case of singly ordered transition, as seen from Fig. 4, m_1 goes through a transition of far higher magnitude than the other two, and in the ordered state, the value of $m_1 \gg (m_2$ or $m_3)$. The singly ordered phase is favored at stronger nearest-neighbor interaction and low temperature.

Although the transition to the singly ordered phase is accompanied by a considerable change in m_1, the maximum value of m_1 attained in the ordered phase does not reach 1.0 for physically reasonable values[13] of the parameter U/t. We illustrate this behavior of m_1 in Fig. 5, where we plot m_1 versus temperature for several values of U/t. It is seen that for $U/t \sim 2.5$, the value of m_1 reaches only ~ 0.5; the values of the other two order parameters are <0.01 in this region. As the interaction strength U/t reaches 3.0, the value of m_1 reaches ~ 0.8. It takes a very strong nearest-neighbor interaction, $U/t \sim 7.0$, for the value of m_1 to climb up to 0.9. The value of U/t obtained by the LSDA electronic structure calculation in the B sublattice is in the range 2.3–3.1. So, m_1 does not saturate the complete transition, and other order parameters may be involved. Figure 5 also shows that the lowest temperature found in this model for multiply to singly ordered phase transition is approximately 350 K, which takes place for $U/t \sim 2.45$. Although this value of U/t is in the physically reasonable range,[13] the transition temperature is quite high compared to the experimental T_v of 120 K. The likely cause of high transition temperature calculated is perhaps the mean-field approximation; for instance, it has been seen in other models such as the nearest-neighbor Ising model, where an exact solution is also available, mean-field calculations lead to higher transition temperatures: $T_c/T_c^{\mathrm{MFT}} \approx 0.5-0.8$ depending upon dimensionality and coordination number.[16] Thus, a simulation of the electrons' dynamics on the B sublattice of $\mathrm{Fe_3O_4}$ will be ex-

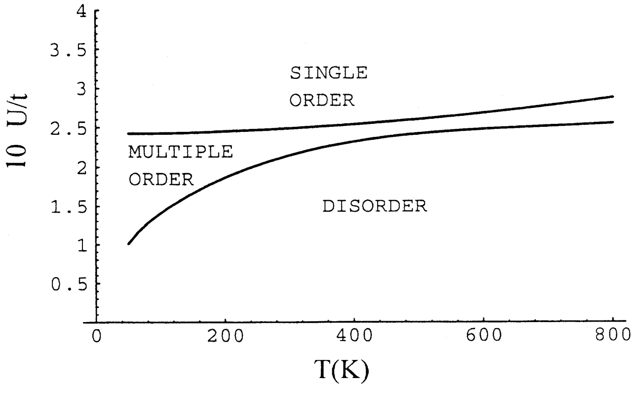

FIG. 3. Phase diagram in the $(U/t,T)$ plane. In the multiply ordered phase, the order parameters m_1, m_2, and m_3 are nonzero and comparable (see Fig. 2). In the singly ordered phase only m_1 is appreciable (see Fig. 4). In the disordered phase, all three order parameters are zero.

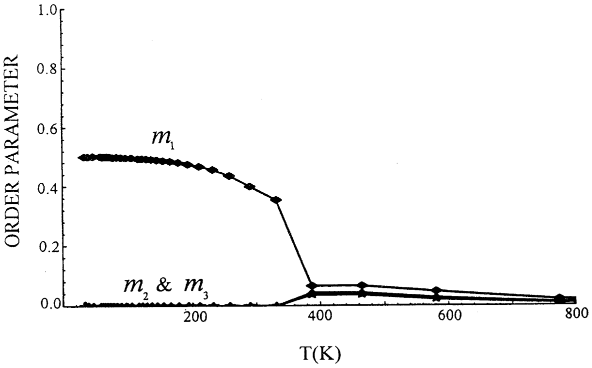

FIG. 4. Multiply ordered to singly ordered phase transition is illustrated for $U/t=2.46$. In the ordered phase, m_2 and m_3 are approximately zero, while m_1 approaches ~ 0.5.

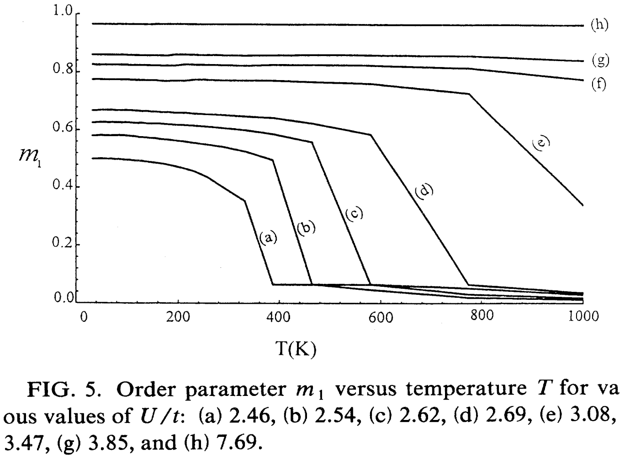

FIG. 5. Order parameter m_1 versus temperature T for various values of U/t: (a) 2.46, (b) 2.54, (c) 2.62, (d) 2.69, (e) 3.08, (f) 3.47, (g) 3.85, and (h) 7.69.

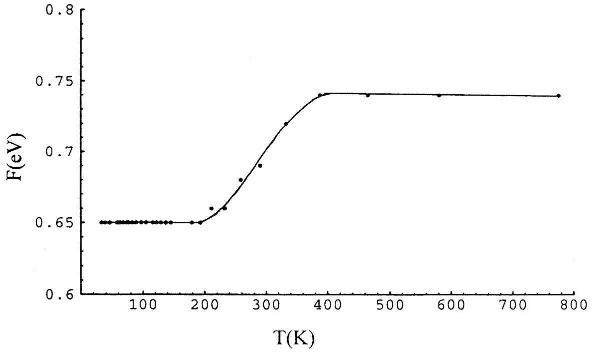

FIG. 6. Thermodynamic function Helmholtz free energy (F) versus temperature $T(K)$ for $U/t=2.46$.

pected to lead to a better value of the transition temperature. Inclusion of additional interactions, such as the electron-phonon coupling, will also reduce this temperature; however, one would need a very strong coupling to effect the temperature to fall by one-third. The experimental data with regard to the lattice effects on the transition supports some role of electron-phonon coupling in the Verwey transition.[2]

V. THERMODYNAMIC QUANTITIES

What are the orders of the phase transitions in this model? To address this question, I have studied Helmholtz free energy (F) and entropy (S) as a function of temperature for the parameter space $U/t>2.40$ (multiply ordered to singly ordered) as well as for the parameter space $1.0<U/t\leq 2.40$ (disordered to multiply ordered). Although the qualitative behavior of both free energy and entropy are similar in the two transitions, the disordered to multiply ordered transition shows a very small change in either free energy or entropy, and I present here (Figs. 6 and 7) the thermodynamic quantities in the phase region $U/t>2.4$. It is seen that the free energy shows a discontinuity across the transition, and therefore the specific heat ($\partial F/\partial T$) versus temperature will show a peak at the transition temperature, which is a hallmark of the thermodynamic first-order phase transition. The transition from the multiply ordered to singly ordered state is also accompanied by approximately tenfold increase in the entropy as seen from Fig. 7. Thus, it can be concluded that the phase transition in this model is driven by entropy change, as expected for an order-disorder transition. It is also seen from Fig. 7 that the entropy changes by approximately tenfold across the phase transition.

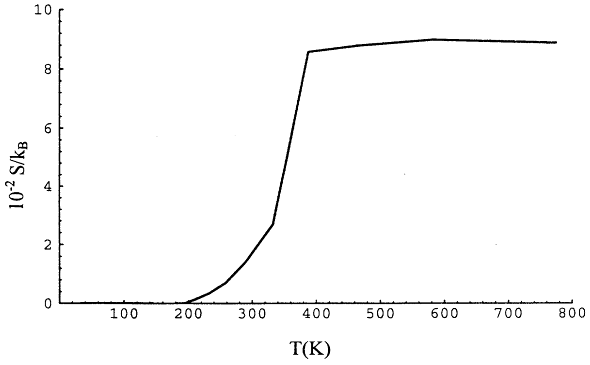

FIG. 7. Thermodynamic function entropy (S/k) versus temperature $T(K)$ for $U/t=2.46$.

The isotherms of the transition are presented in Fig. 8. The isotherms are similar to the liquid-gas transition with $1/(U/t)$ acting as "pressure" and m_1 as "volume." These isotherms show that the coexistence curve (the dashed lines in Fig. 8) from both the high-m_1 end (singly ordered phase) and the low-m_1 end (multiply ordered phase) approach each other, indicating that at some high temperature there is a critical point. The isotherms also point to the observation that the transition in the Cullen-Callen model is first order in nature, similar to the liquid-gas transition below the critical point.

VI. CONCLUSION

In this paper, I have studied the Cullen-Callen model for the Verwey transition in magnetite at finite temperature. The model exhibits three phases: a disordered phase and two ordered phases, one singly ordered and one multiply ordered. The singly ordered phase is stable only for $U/t>2.40$. So the scenario of phase transformations is as follows: for all $U/t>2.40$, as the temperature is lowered, the system goes from a disordered state (a conducting phase) to a multiply ordered phase (an insulating phase), and then to the singly ordered state (an insulating phase). The singly ordered and multiply ordered phases differ from each other in the arrangement of iron ions that they represent at low temperature. The multiply ordered state contains all four charge densities on the B sublattice, N_1, N_2, N_3, and N_4 to be nonzero, which

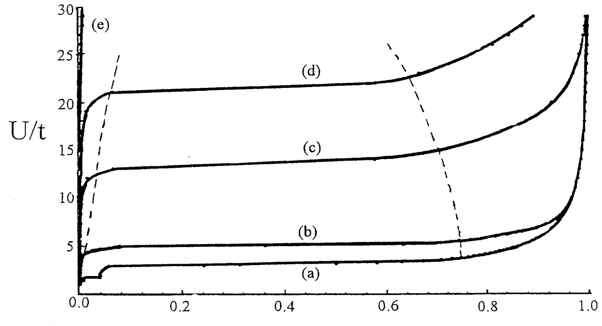

FIG. 8. Isotherms in the ($U/t,m_1$) plane at temperatures (a) ≤200 K, (b) 1900 K, (c) 7000 K, (d) 11 500 K, and (e) 19 000 K. The isotherms below 200 K are indistinguishable, and are labeled (a). The dashed curve represents the coexistence curve of multiple-ordered phase and singly ordered phase in analogy of the present model to the liquid-gas transition.

would explain the origin of extra peaks in experiments,[4–7] as Cullen and Callen[9] have claimed based on their zero-temperature calculation; for instance, the origin of five peaks in the Mössbauer measurements could be separated in one peak from the Fe^{2+} of the A sublattice and four other peaks could be attributed to arising from the multiple-ordered state of the B sublattice.

The order-disorder transition in this model is shown by the jump in free energy to be of the first-order type. The transition is also accompanied by approximately a tenfold rise in entropy, strongly suggesting that the transition is entropy driven. The first-order nature of the transition is further confirmed by the isotherms of the system, which has a strong analogy to the isotherms of the liquid-gas system below the critical point.

ACKNOWLEDGMENTS

The author would like to thank Dr. S. Satpathy for suggesting this problem and many valuable discussions, and S.K. Mishra for help with the computer program.

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[1] E. J. W. Verwey, Z. Kristallogr. **91**, 65 (1935); E. J. Verwey and P. W. Haayman, Physica **8**, 979 (1941); E. J. W. Verwey, P. W. Haayman, and F. C. Romejin, J. Chem. Phys. **15**, 181 (1947).

[2] For an overview of the Verwey transition in magnetite, see Philos. Mag. **42**, 327 (1980); the experimental situation is also reviewed in J. M. Honing, *The Metallic and Non Metallic States of Matter*, edited by P. P. Edwards and C. N. R. Rao (Taylor and Francis, London, 1985), p. 261.

[3] S. K. Mishra and S. Satpathy, Phys. Rev. B **47**, 5564 (1993), and references therein.

[4] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).

[5] R. S. Hargrove and W. Kündig, Solid State Commun. **8**, 303 (1970).

[6] E. J. Samuelson, E. J. Bleeker, L. Dobrzynski, and T. Riste, J. Appl. Phys. **39**, 1114 (1968).

[7] T. Yamada, K. Suzuki, and S. Chikazumi, Appl. Phys. Lett. **13**, 172 (1968).

[8] M. Rubinstein, Bull. Am. Phys. Soc. **16**, 425 (1971).

[9] J. R. Cullen and E.R. Callen, Phys. Rev. Lett. **26**, 236 (1971); Phys. Rev. B **7**, 397 (1973).

[10] D. Ihle and B. Lorenz, Philos. Mag. **42**, 337 (1980).

[11] B. K. Chakravarty, Solid State Commun. **15**, 1271 (1974).

[12] Y. Yamada, in *Magnetism and Magnetic Materials,* edited by C. D. Graham, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1975), p. 79; Ferroelectrics **16**, 49 (1977).

[13] Z. Zhang and S. Satpathy, Phys. Rev. B **44**, 13 319 (1991).

[14] S. K. Mishra, Z. Zhang, and S. Satpathy, J. Appl. Phys. **76**, 6700 (1994).

[15] J. R. Cullen and E. Callen, Solid State Commun. **9**, 1041 (1971).

[16] M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).