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## Theory of Verwey and Charge-Density-Wave-State Ordering in Magnetite

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The Cullen-Callen Hartree-approximation band model of magnetite is solved self-consistently, and it is found that if one starts with the three-order-parameter state of Cullen and Callen, the solution iterates self-consistently to the Verwey ordered state. A charge-density-wave-state ordering is proposed to explain recent neutron- and electron-diffraction, magnetic-resonance, and Mössbauer-effect experiments on magnetite, which suggest a larger unit cell than occurs in the Verwey ordering. It is argued that the Verwey ordering could very easily be unstable to the formation of such a state. A discussion is also given of small polarons in a degenerate electron system and applied to magnetite.

### I. INTRODUCTION

Recently, Cullen and Callen have proposed that the low-temperature insulating phase of magnetite (i. e., below 120 °K) could be described by a Hartree-approximation band model in which the Hartree self-consistent field does not have the full symmetry of the lattice.<sup>1</sup> Within such a model, it is possible to have a Verwey-type ordering<sup>2</sup>—that is, an octahedral-site charge density per site which alternates between two values on adjacent planes of octahedral sites along one of the crystallographic axes called the *c* axis.<sup>3,4</sup> (See Fig. 1 in Ref. 4.) The octahedral-site ions, however, need not be pure Fe<sup>+3</sup> or Fe<sup>+2</sup> as originally suggested by Verwey.<sup>2</sup> Recent neutron-diffraction,<sup>5</sup> electron-microscopy,<sup>6</sup> Mössbauer-effect,<sup>7,8</sup> and magnetic-resonance<sup>8</sup> experiments have shown that the ordering is apparently more complicated than the simple Verwey ordering. In this paper, the Cullen and Callen model is reinvestigated. A self-consistent calculation shows that the three-parameter ordering suggested in Ref. 1 does not lead to a self-consistent solution of the Hartree-approximation equations. Rather, it is found that if we start with

the three-parameter ordering, successive interactions in the self-consistency scheme take us towards the Verwey ordering. It is proposed that experimentally observed deviations from the Verwey state can be explained as being due to an instability of the Verwey state to the formation of an excitonic insulating state. It is further shown that if the Verwey order parameter is chosen small enough for the insulating gap to just disappear, a gap is not produced by also introducing the two additional order parameters suggested by Cullen and Callen. This fact together with the self-consistency calculation, which is done for larger values of the Verwey order parameter, cast doubt on the existence of the three-parameter ordering, although it is admittedly possible that for some particular values of the three order parameters suggested by Cullen and Callen, a self-consistent solution might be possible. Although no gap is introduced at the point  $\vec{k} = (0, 0, \pi/a)$ , it is still possible for a gap to appear at other points in the zone. Thus, the results are not conclusive.

### II. SELF-CONSISTENCY OF THE CULLEN-CALLEN MODEL

Following Cullen and Callen, we assume a clos-

est-neighbor tight-binding approximation. In the absence of Verwey or any other type of ordering, the secular matrix is given by

$$H_{\alpha\beta}(\vec{k}) = 1 + e^{2i\vec{k}\cdot\vec{T}_{\alpha\beta}}, \quad (1)$$

if  $\alpha \neq \beta$  and  $H_{\alpha\alpha}(\vec{k}) = 0$  (in units of the overlap integral), where  $\vec{T}_{\alpha\beta}$  is the vector connecting the  $\alpha$ th and  $\beta$ th sites in the unit cell ( $\alpha$  and  $\beta$  take values from 1 to 4).<sup>1</sup> This matrix is easily diagonalized for wave vector  $\vec{k}$  in the  $\langle 100 \rangle$  directions to yield the energies<sup>9</sup>

$$\epsilon_1(\vec{k}) = -2, \quad (2a)$$

$$\epsilon_2(\vec{k}) = -2, \quad (2b)$$

$$\epsilon_3(\vec{k}) = 2 - 4 \cos \frac{1}{2}ka, \quad (2c)$$

$$\epsilon_4(\vec{k}) = 2 + 4 \cos \frac{1}{2}ka, \quad (2d)$$

where  $\vec{k}$  goes from 0 to  $\pi/a$ , the Brillouin-zone boundary of the fcc primitive lattice of  $\text{Fe}_3\text{O}_4$ . These energies are plotted in Fig. 1. With the Verwey ordering we write

$$H_{\alpha\alpha}(\vec{k}) = \pm Um = \pm \epsilon_0,$$

where the plus sign is taken for  $\alpha = 1, 3$  and the minus sign for  $\alpha = 2, 4$ , and where

$$U = U_1 - \bar{U}.$$

Here

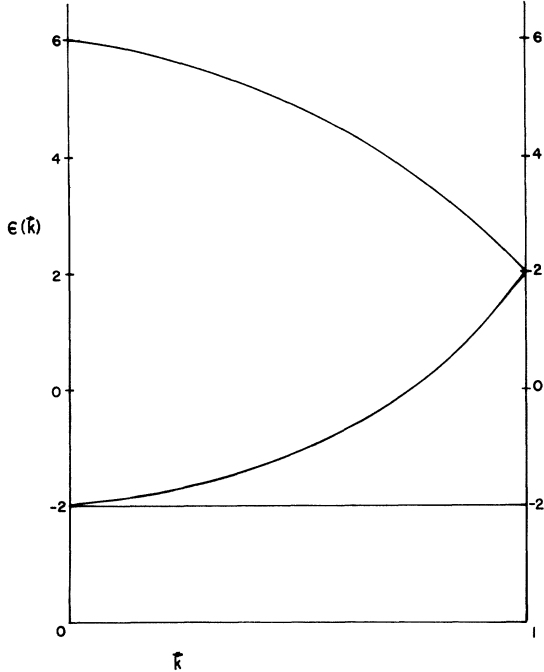


FIG. 1. Band structure for  $\vec{k}$  in  $[100]$  direction with no Verwey ordering (energy in units of the near-neighbor overlap integral and  $\vec{k}$  in units of  $\pi/a$ ).

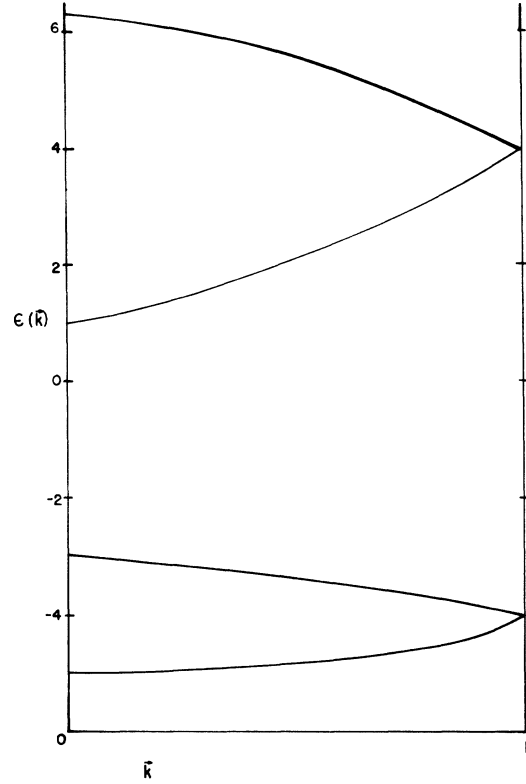


FIG. 2. Band structure for  $\vec{k}$  in  $[100]$  direction with Verwey ordering with order parameter  $\epsilon_0 = 3$  (energy in units of the overlap integral and  $\vec{k}$  in units of  $\pi/a$ ).

$$U_1 = \sum_j V(\vec{R}_i + \vec{a}_\alpha - \vec{R}_j - \vec{a}_\beta),$$

where  $\alpha \neq \beta$  and  $\bar{U} = \sum_j V(\vec{R}_i - \vec{R}_j)$ , where  $\vec{R}_j$  label unit cells and  $\vec{a}_\alpha$  gives the positions of atoms in the unit cell.  $V$  is the Coulomb interaction of electrons divided by an internal dielectric constant. The Verwey-state energies for  $\vec{k}$  in the  $[100]$ ,  $[100]$ ,  $[010]$ , and  $[0\bar{1}0]$  directions are

$$\epsilon_1(\vec{k}) = -2 \cos \frac{1}{2}ka + [4(1 - \cos \frac{1}{2}ka)^2 + \epsilon_0^2]^{1/2}, \quad (3a)$$

$$\epsilon_2(\vec{k}) = 2 \cos \frac{1}{2}ka - [4(1 + \cos \frac{1}{2}ka)^2 + \epsilon_0^2]^{1/2}, \quad (3b)$$

$$\epsilon_3(\vec{k}) = -2 \cos \frac{1}{2}ka - [4(1 - \cos \frac{1}{2}ka)^2 + \epsilon_0^2]^{1/2}, \quad (3c)$$

$$\epsilon_4(\vec{k}) = 2 \cos \frac{1}{2}ka + [4(1 + \cos \frac{1}{2}ka)^2 + \epsilon_0^2]^{1/2}, \quad (3d)$$

plotted in Fig. 2. Along the  $[001]$  direction, the energies are

$$\epsilon_1(\vec{k}) = \epsilon_0 - 2, \quad (4a)$$

$$\epsilon_2(\vec{k}) = -\epsilon_0 - 2, \quad (4b)$$

$$\epsilon_3(\vec{k}) = 2 + [\epsilon_0^2 + 16 \cos^2 \frac{1}{2}ka]^{1/2}, \quad (4c)$$

$$\epsilon_4(\vec{k}) = 2 - [\epsilon_0^2 + 16 \cos^2 \frac{1}{2}ka]^{1/2}, \quad (4d)$$

illustrated in Fig. 3. We see in Fig. 2 that the lower two bands are split from the upper two bands

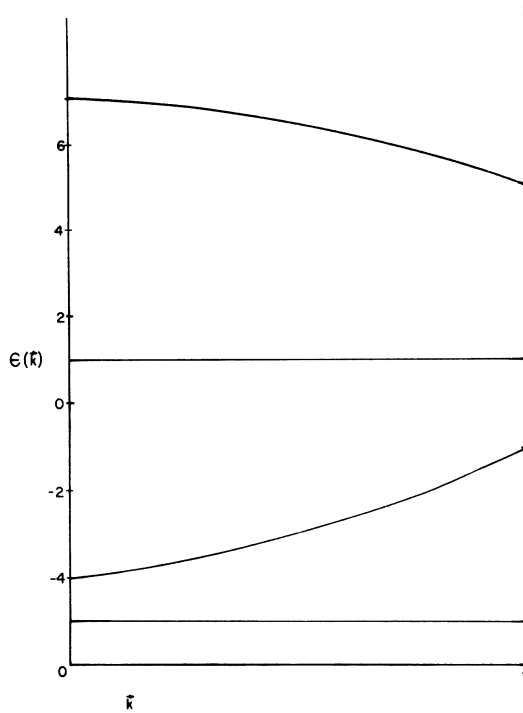


FIG. 3. Band structure for  $\vec{k}$  in [001] direction with Verwey ordering with order parameter  $\epsilon_0 = 3$  (energy in units of the overlap integral and in units of  $\pi/a$ ).

in this direction of  $\vec{k}$ .<sup>6</sup> In fact, we find from Eq. (3) that this splitting occurs for any nonzero value of  $\epsilon_0$ . In the [001] direction, a gap occurs for  $\epsilon_0 > 2$ . Using the computer to diagonalize the secular matrix at many points throughout the Brillouin zone and comparing the energies, it was found that the highest energy of the second-lowest band occurs at  $\vec{k} = (\pi/a)(0, 0, 1)$  and the lowest energy of the second-highest band occurs all along the [001] direction. Thus, if there is any Verwey ordering with  $\epsilon_0 > 2$ , the bands are split throughout the Brillouin zone; that is, Verwey ordering alone can give an insulating ground state. This does not, however, explain the experimentally observed deviations from Verwey ordering.

In order to see if the three-order-parameter ordering suggested by Cullen and Callen is a stable self-consistent solution, the model was solved self-consistently as follows: For general ordering, the diagonal elements of the matrix are given by

$$H_{\alpha\alpha} = \epsilon_{\alpha} = -(U_1 - \bar{U})n_{\alpha} + U_1 \sum_{\beta} n_{\beta}, \quad (5)$$

where  $n_{\alpha}$  is the fraction of an electron on the  $\alpha$ th site. The last term can be absorbed into the chemical potential. We can find  $U$  from the following relationship:

$$U = U_1 - \bar{U} = -\frac{\epsilon_1 - \epsilon_2 + \epsilon_3 - \epsilon_4}{n_1 - n_2 + n_3 - n_4}. \quad (6)$$

We begin the self-consistent-field calculation by giving values to  $\epsilon_1$ ,  $\epsilon_2$ ,  $\epsilon_3$ , and  $\epsilon_4$ , diagonalizing the matrix to find  $n_1$ ,  $n_2$ ,  $n_3$ , and  $n_4$ , calculating  $U$  from Eq. (6), and then using  $U$  and the  $n$ 's to find the  $\epsilon$ 's again from Eq. (5). We then use these new  $\epsilon$ 's to solve the resulting secular problem again, and then repeat the procedure. This is not the usual self-consistent calculation because we let  $U$  vary, but we do this because we are interested in seeing if self-consistency is possible for any value of  $U$ . The same procedure has also been used with  $U$  held fixed and the results are precisely the same. The result of this procedure (shown in Table I) is that if we start with  $\epsilon$ 's corresponding to the three-order-parameter ordering assumed by Cullen and Callen,<sup>1</sup> we find that this procedure always leads to a Verwey ordering (but with fractional occupancy of the atoms). The  $n$ 's were calculated by diagonalizing the secular matrix at over 3000 points in the Brillouin zone, taking the square of the absolute value of those elements of the eigenvectors which correspond to each atom in the unit cell, summing it over these 3000 points in the Brillouin zone, and dividing by the number of points. This number of points used was found to be sufficient by repeating the calculation using twice as many points. The result was found to be changed by only about 0.2%. The calculation illustrated in Table I was done starting with  $Um_1 = 2$ ,  $Um_2 = Um_3 = 1$ , as used by Cullen and Callen.<sup>1</sup> In fact, for  $Um_1$  less than 2, the system is not an insulator (see Appendix A).

### III. EXCITONIC-INSULATOR INSTABILITY OF THE VERWEY-ORDERED STATE

The question that arises now is how to explain the experimental data which show that Verwey ordering is not sufficient. As in Ref. 1, we have not discussed states in which translational sym-

TABLE I.  $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$  in successive interactions (bandwidth units).

$\epsilon_1$	Chemical potential = 0		
	$\epsilon_2$	$\epsilon_3$	$\epsilon_4$
4.700	-1.300	-1.3000	0.7000
3.5825	-1.3250	-1.2748	1.8177
2.5128	-1.8100	-1.7768	1.9003
2.8015	-1.3068	-1.2930	2.5987
2.7399	-1.2962	-1.2909	2.6729
2.7174	-1.2945	-1.2926	2.6953
2.7100	-1.2939	-1.2932	2.7027
2.7076	-1.2936	-1.2934	2.7052
2.7068	-1.2936	-1.2935	2.7060
2.7065	-1.2936	-1.2935	2.7062

metry is broken so far. If we examine the Verwey ordering, illustrated in Figs. 2 and 3 as well as Eqs. (3) or (4), we see that the gap in the  $z$  direction (i. e., along the  $c$  axis) goes to zero when  $\epsilon_0$  becomes equal to 2, whereas in the  $x$  direction it does not. Thus, we can make the gap in the  $z$  direction nearly zero without making the gap in the  $x$  direction that small. Furthermore, since the maximum energy in the higher of the two lowest bands occurs at  $\vec{k} = (0, 0, \pi/a)$ , there exists the possibility that if  $\epsilon_0$  were close to 2, the Verwey state might be unstable to the formation of an excitonic-insulating or charge-density-wave state,<sup>10</sup> with wave vector along the  $z$  axis equal to Brillouin-zone radius in this direction. This would double the unit cell along the  $z$  axis, which would explain the neutron-diffraction data of Samuelson.<sup>5</sup> Since the lower of the two highest bands is flat in the  $z$  direction, however, we have no *a priori* reason to believe that the charge-density wave should have this particular wave vector; it appears that it can have any wave vector. To determine whether this wave vector is the correct one, we must study the possibility of such an instability in more detail.

We start with the following many-body Hamiltonian written in second quantization, which uses the Verwey bands as a basis:

$$\mathcal{H} = \sum_{\vec{k}} \epsilon_{\alpha}(\vec{k}) C_{\vec{k}\alpha}^{\dagger} C_{\vec{k}\alpha} + \frac{1}{2} \sum_{\substack{\vec{k}, \vec{k}', \vec{q}' \\ \alpha, \beta, \gamma, \delta}} V_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', \vec{q}') \\ \times C_{\vec{k}+\vec{q}', \alpha}^{\dagger} C_{\vec{k}', \alpha}^{\dagger} C_{\vec{k}, \beta} C_{\vec{k}+\vec{q}', \gamma} C_{\vec{k}\beta} - \text{Hartree-potential terms}, \quad (7a)$$

where  $\epsilon_{\alpha}(\vec{k})$  are the one-electron energies in the Verwey-ordered state and

$$V_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', \vec{q}') = \int d^3r d^3r' \psi_{\vec{k}+\vec{q}', \alpha}^*(\vec{r}) \psi_{\vec{k}\beta}(\vec{r}) \frac{e^2}{\kappa |\vec{r} - \vec{r}'|} \\ \times \psi_{\vec{k}', \delta}^*(\vec{r}') \psi_{\vec{k}, \gamma}(\vec{r}'), \quad (7b)$$

where  $\psi_{\vec{k}\alpha}(\vec{r})$  is the one-electron wave function of wave vector  $\vec{k}$  of band  $\alpha$  and  $\kappa$  is the dielectric constant in the crystal. (Note that spin does not enter the problem because in magnetite below the Néel temperature only spin-up octahedral-site states are occupied by conduction electrons.<sup>11</sup>) Besides the terms shown explicitly in Eq. (7a), we must subtract off the Hartree potential for the Verwey state. We will now make the Hartree approximation, and these terms will cancel those terms in the Hartree potential already included in  $\epsilon_{\alpha}(\vec{k})$ . Exchange-interaction terms, which occur in the Hartree-Fock approximation, are secondary effects in this problem.<sup>10</sup> The only important terms in the Hartree-approximation potential in a discussion of a modification of the Verwey state are the following, which mix the highest valence band and

the lowest conduction band (call them 1 and 2):

$$\sum_{\vec{k}, \vec{k}'} \sum_{\substack{\alpha\beta\gamma\delta=1,2 \text{ only} \\ \alpha \neq \beta, \gamma \neq \delta}} V_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', \vec{Q}) \langle C_{\vec{k}', \delta}^{\dagger} C_{\vec{k}+\vec{Q}, \gamma}^{\dagger} \rangle C_{\vec{k}+\vec{Q}, \alpha}^{\dagger} C_{\vec{k}\beta}, \quad (8)$$

where  $\vec{Q}$  is the wave vector of the assumed excitonic or charge-density-wave state. If we make the rough approximation of replacing  $V$  by an average over  $\vec{k}$  and  $\vec{k}'$  such that

$$U(\vec{Q}) = \frac{1}{N^2} \sum_{\vec{k}, \vec{k}'} V_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', \vec{Q}), \quad (9)$$

the solution is identical to that for the itinerant-electron-antiferromagnet ground state, and we obtain the following self-consistency conditions for the gap parameter  $g$  of the excitonic state

$$1 = \frac{1}{2N} U(\vec{Q}) \sum_{\vec{k}} \frac{n_{\vec{k}1'} - n_{\vec{k}2'}}{\{\frac{1}{2}[\epsilon_1(\vec{k} + \vec{Q}) - \epsilon_2(\vec{k})]^2 + g^2\}^{1/2}}, \quad (10a)$$

where the new energies are given by

$$E_{(\pm)}(\vec{k}) = \frac{1}{2} [\epsilon_1(\vec{k} + \vec{Q}) + \epsilon_2(\vec{k})] \\ \pm \{\frac{1}{2}[\epsilon_1(\vec{k} + \vec{Q}) - \epsilon_2(\vec{k})]^2 + g^2\}^{1/2}, \quad (10b)$$

where 1' and 2' denote the bands in the charge-density-wave state.<sup>10,12,13</sup> The  $\vec{Q}$  which gives the largest  $U(\vec{Q})$  will give the largest  $g$ , and hence, the lowest-energy charge-density-wave state. To find this  $\vec{Q}$ , we note that we may write Eq. (7b) as

$$V_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', \vec{q}') = \sum_{\vec{\tau}} F_{\alpha\beta}(\vec{q}' + \vec{\tau}, \vec{k}) F_{\gamma\delta}^*(\vec{q}' + \vec{\tau}, \vec{k}') \\ \times \frac{4\pi e^2}{\kappa |\vec{q}' + \vec{\tau}|^2}, \quad (11a)$$

where

$$F_{\alpha\beta}(\vec{q}' + \vec{\tau}, \vec{k}) = \int d^3r \psi_{\vec{k}+\vec{q}', \alpha}^*(\vec{r}) e^{i(\vec{q}'+\vec{\tau})\cdot\vec{r}} \psi_{\vec{k}\beta}(\vec{r}) \quad (11b)$$

and  $\vec{\tau}$  is a reciprocal-lattice vector. We will make the approximation of neglecting values of  $\vec{\tau}$  in the summation for which  $\vec{q}' + \vec{\tau}$  is greater than a reciprocal-lattice vector since for such values of  $\vec{q}' + \vec{\tau}$ , both  $F$ <sup>14</sup> and  $1/|\vec{q}' + \vec{\tau}|^2$  become small enough for these contributions to be neglected. With this approximation, we can easily show that

$$\sum_{\vec{\tau}} 1/|\vec{q}' + \vec{\tau}|^2 \approx 2 \cdot 2a^2/\pi^2 \quad (12a)$$

for  $\vec{q}' = (0, 0, \pi/2a)$ , and that for  $\vec{q}' = (0, 0, \pi/a)$ ,

$$\sum_{\vec{\tau}} 1/|\vec{q}' + \vec{\tau}|^2 \approx 14 \cdot 4a^2/\pi^2. \quad (12b)$$

Similarly we find that this quantity is smaller for most values of  $\vec{q}$  along the  $z$  axis than for  $q' = \pi/a$ . Near  $\vec{q}' = 0$ , the  $\tau = 0$  term diverges as  $1/q'^2$ , but since  $F_{12}(\vec{q}', \vec{k})$  goes to zero as  $q'^2$ ,<sup>11</sup>  $V$  actually

goes to zero for small  $q'$ . We have also evaluated the quantity

$$F_{12}(\vec{Q}) = \sum_{\vec{k}} F_{12}(\vec{Q}, \vec{k})$$

for three values of  $Q$  along the  $[001]$  direction, as shown in Table II. The values in Table II are actually  $F$  divided by the atomic form factor,<sup>11</sup> but the atomic form factor remains close to 1 for  $Q \leq \hbar/a$ .<sup>14</sup> The right-hand side of Eq. (10a) has also been evaluated at zero temperature for  $g=0$ . That is, we have found

$$\sum_{\vec{k}} \frac{1}{\epsilon_1(\vec{k} + \vec{Q}) - \epsilon_2(\vec{k})}$$

for three values of  $Q$  in the  $[001]$  direction from 0 to  $\pi/a$ . The results are also listed in Table II. We see that both  $F$  and this quantity increase slightly as we go from  $Q=0$  to  $\pi/a$ . This combined with our evaluation given in Eqs. (12) indicates that the Verwey state may be unstable to a charge-density-wave or excitonic-insulating state of wave vector  $(0, 0, \pi/a)$  if the Verwey-state gap is sufficiently small, thus explaining the neutron-diffraction data.<sup>5</sup>

The additional spectral lines found by electron-microscopy,<sup>6</sup> Mössbauer-effect,<sup>7,8</sup> and magnetic-resonance experiments can be explained using a suggestion made by Kohn.<sup>15</sup> He proposed that the excitonic-insulating phase might itself be unstable against the formation of an additional excitonic-insulating phase of smaller wave vector. In fact, he proposed that there might be a whole nested sequence of excitonic-insulating phases. This would lead to an almost unlimited number of lines in the electron- and neutron-diffraction, Mössbauer, and magnetic-resonance spectra. It would be interesting to see these experiments repeated at various temperatures up to the transition temperature and under applied pressure to see if Kohn's suggested phase diagram for such states is observed.

In order to have such an excitonic-insulating-state instability of the Verwey state, the gap for  $\vec{k}$  along the  $c$  axis must be small and possibly negative,<sup>10,15</sup> certainly smaller than for  $\vec{k}$  along any other direction. This is consistent with Calhoun's data,<sup>16</sup> which show larger conductivity along the  $c$

TABLE III. Reciprocal-effective-mass tensor  $(1/m)_{\alpha\alpha}$  for Verwey state with  $\epsilon_0=3$ .

Point in zone	$\left(\frac{1}{m}\right)_{zz}$ (arbitrary units)	$\left(\frac{1}{m}\right)_{xx}$ (arbitrary units)
$(0, 0, 1)\pi/a$ = top of valence band	0.0015	5.3802
$(0, 0, 0)$ = bottom of conduction band	-12.1738	-14.1144

axis than in any other direction. This will be found in the present model if we assume that below  $T_v$  the conductivity is due to tunneling from valence to conduction bands rather than due to band conduction by thermally activated carriers. We neglect the charge-density-wave distortion of the Verwey state here. If the conductivity in the Verwey-ordered state were due to thermally activated carriers, the reciprocal-effective-mass tensor would have to be larger along the  $c$  axis than in any other direction to explain Calhoun's data. We find exactly the opposite. Table III shows the reciprocal-effective-mass-tensor components  $(1/m)_{xx}$  and  $(1/m)_{zz}$  (where  $z$  is the  $c$  axis) at the highest point in the valence band and lowest point in the conduction band. Thus, the major part of the conductivity must be due to tunneling. As we approach  $T_v$ , the conductivity becomes less anisotropic, because there are more thermally activated carriers as we approach  $T_v$ .

#### IV. DEGENERATE-SMALL-POLARON THEORY APPLIED TO MAGNETITE

It has been suggested by many people<sup>17</sup> that electrical conductivity in magnetite may be described by small-polaron hopping. For one thing, as the temperature increases above  $T_v$ , the conductivity continues to increase. It would also do this in a degenerate semiconductor.<sup>18</sup> Since the gap has already disappeared, however, magnetite should behave more like a metal, in which the conductivity decreases with temperature, than like a semiconductor. If the conductivity above  $T_v$  were described by thermally activated small-polaron hopping, however, this behavior could easily be understood. The question then arises as to what right we have to describe the electronic states below  $T_v$  by band theory. It would have to be quite a coincidence for the band conductivity to become smaller than the hopping conductivity at precisely  $T_v$ , so that we can use band theory below  $T_v$  but not above. As shown in the Appendix B, however, the two lower bands are completely flat in the absence of the Verwey ordering. Since the slope (and hence velocity) of the next-highest band is zero at the point where it touches the lowest bands [as seen in Eq. (2)], there can be no significant band conductivity above  $T_v$ .

TABLE II.  $F(\vec{Q})$  and  $(1/N) \sum_{\vec{k}} [1/(\epsilon_1(\vec{k} + \vec{Q}) - \epsilon_2(\vec{k}))]$  for Verwey state with  $\epsilon_0=2.1$ ,  $\vec{Q}$  in  $[100]$  direction.

$Q$	$\frac{1}{N} \sum_{\vec{k}} \frac{1}{\epsilon_1(\vec{k} + \vec{Q}) - \epsilon_2(\vec{k})}$	$F(\vec{Q})$ ÷ atomic form factor
0	96.4121	0.0000
$0.5\pi/a$	96.6066	0.0312
$1.0\pi/a$	96.9071	0.0343

One question regarding the possibility of small-polaron hopping in magnetite that has never been answered with any degree of rigor is how to describe polarons in a many-electron system, since the usual polaron problem is only a one-electron problem. It can easily be seen that in a many-electron system, the formation of a lattice distortion around one electron may be interfered with by the presence of a second electron that is nearby. Clearly a treatment of a many-electron polaron system is in order. In magnetite the number of electrons is not small compared to the number of lattice sites, as it is in doped-semiconducting and -insulating crystals to which conventional polaron theory is usually applied. Rather, the number of conduction electrons is half the number of octahedral sites on which they reside. Our discussion in this section will make use of Holstein's one-dimensional treatment of small polarons.<sup>19</sup> The one-dimensional treatment should be sufficient to give the important physical results. Other one-dimensional models will also be discussed. We will first examine a straightforward generalization of Holstein's model to the case of a many-carrier system.

The equation of motion corresponding to Eq. (5) in Holstein's<sup>19</sup> second paper is

$$\frac{i\partial a_{\{n\}}}{\partial t} = \sum_{m=1}^N \left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_m^2} + \frac{1}{2} M \omega_0^2 x_m^2 + \frac{1}{2} M \omega_1^2 x_m x_{m+1} + A P_m x_m \right) a_{\{n\}} - J \sum_m P_m (a_{\{n\}', m+1} + a_{\{n\}', m-1}), \quad (13)$$

where  $a_{\{n\}}$  is the vibrational wave function when there are electrons located at the set of lattice sites denoted by  $\{n\}$ . The subscript  $\{n\}' m \pm 1$  means that the  $m$ th occupied site in the set  $\{n\}$  is replaced by  $m \pm 1$ , and  $P_m$  is 0 if site  $m$  is unoccupied and 1 if it is occupied by an electron. In order to focus attention on electron-lattice effects, we will ignore the Coulomb interaction of electrons for the moment. We now transform to the normal coordinates  $q_k$  used by Holstein, i. e.,

$$x_n = (2/N)^{1/2} \sum_k q_k \sin(kn + \frac{1}{4}\pi). \quad (14)$$

We then obtain the equation

$$\frac{i\partial a_{\{n\}}(\{q_k\})}{\partial t} = \sum_{k'} \left[ \left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_{k'}^2} + \frac{1}{2} M \omega_{k'}^2 q_{k'}^2 \right) - \left( \frac{2}{N} \right)^{1/2} A q_{k'} \sum_m P_m \sin(k'm + \frac{1}{4}\pi) \right] a_{\{n\}}(\{q_k\}) - J \sum_m P_m [a_{\{n\}', m+1}(\{q_k\}) + a_{\{n\}', m-1}(\{q_k\})]. \quad (15)$$

Completing the square in Eq. (15), we get the following equation for a displaced harmonic oscillator:

$$\frac{i\partial_{\{n\}}(\{q_k\})}{\partial t} = \sum_{k'} \left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_{k'}^2} + \frac{1}{2} M \omega_{k'}^2 (q_{k'} - q_{k'}^{(n)})^2 - \frac{1}{2} M \omega_{k'}^2 (q_{k'}^{(n)})^2 \right) a_{\{n\}}(\{q_k\}) - J \sum_m P_m (a_{\{n\}', m+1} + a_{\{n\}', m-1}), \quad (16)$$

where the equilibrium positions  $q_k^{(n)}$  are given by

$$q_k^{(n)} = \frac{2A}{M \omega_k^2} \left( \frac{2}{N} \right)^{1/2} \sum_m P_m \sin(km + \frac{1}{2}\pi). \quad (17)$$

Thus, there is now a binding-energy term given by

$$-\frac{1}{2} \sum_k M \omega_k^2 (q_k^{(n)})^2 = -\sum_k \frac{2A^2}{M \omega_k^2} \frac{2}{N} \sum_{m m'} P_m P_{m'} \times \sin(km + \frac{1}{2}\pi) \sin(km' + \frac{1}{4}\pi). \quad (18)$$

This term gives an effective interaction between all pairs of electrons, caused by distortion of the lattice. It is this type of interaction which can give rise to the phenomenon of superconductivity in metals. If we neglect phonon dispersion by setting  $\omega_1$  in Eq. (1) equal to zero (i. e., replace  $\omega_k$  above by  $\omega_0$ ), we find that the interaction in Eq. (18) becomes

$$-\frac{2A^2}{M \omega_0^2} \sum_m P_m^2 = -\frac{2A^2 N_e}{M \omega_0^2},$$

where  $N_e$  is the number of electrons in the crystal. Thus, there is no electron-electron interaction because the basic lattice distortion is intramolecular and hence does not affect neighboring molecules. Since phonon dispersion introduces intermolecular effects, there is an interaction when there is phonon dispersion.

Let us now consider another model, which, although it does not give a correct description of magnetite, indicates what effects to expect in a degenerate-polaron system. The model consists of a linear chain of atoms of separation  $a$ . Every other atom will be taken to be a "metallic ion" which is capable of holding electrons, and the rest of the atoms will be "ligand atoms" which cannot hold electrons. There will be an overlap integral  $J$  between "metallic ions" as in Holstein's model. This can be understood as a parameter which describes electron hopping between metallic atoms, primarily by an indirect process occurring through the "ligand atoms" similar to superexchange.<sup>20</sup> The energy reduction in an electron on site  $p$  due to displacement of neighboring ligand atoms away from it will be assumed for simplicity to be linear in their displacement and of the following form:

$$A(x_p - x_{p-1}),$$

where  $x_p$  is the displacement of the ligand in the  $p$ th unit cell and  $A$  is a positive constant. We will

also take the mass of the metallic ions to be much greater than that of the ligand atoms, and hence, we will assume that the optical phonon consists only of motion of the ligand atoms for simplicity. The resulting equation of motion for the phonon amplitudes will have exactly the same form as Eq. (13), but with the term

$$-A \sum_m P_m x_m \quad (19)$$

replaced by

$$-A \sum_m P_m (x_m - x_{m-1}). \quad (20)$$

$$-\frac{1}{2} M \sum_k \omega_k^2 (q_k^{(m)})^2 = -\frac{2}{N} \frac{1}{2} \frac{A^2}{M} \sum_k \frac{1}{\omega_k^2} \sum_{pp'} P_p P_{p'} \{ \sin(kp + \frac{1}{4}\pi) \sin(kp' + \frac{1}{4}\pi) + \sin[k(p-1) + \frac{1}{4}\pi] \times \sin[k(p'-1) + \frac{1}{4}\pi] - \sin(kp + \frac{1}{4}\pi) \sin[k(p'-1) + \frac{1}{4}\pi] - \sin[k(p-1) + \frac{1}{4}\pi] \sin(kp' + \frac{1}{4}\pi) \}. \quad (22)$$

This is again clearly an electron-electron interaction. If we neglect phonon dispersion (i. e., write  $\omega_k = \omega_0$ ), we obtain

$$-\frac{1}{2} M \sum_k \omega_k^2 (q_k^{(m)})^2 = -\frac{A^2}{M \omega_0^2} N_e + \frac{A^2}{M \omega_0^2} \sum_{p=1}^N P_p P_{p+1}, \quad (23)$$

where  $N_e$  is the number of electrons in the system. This is clearly a near-neighbor repulsive electron-electron interaction of the same magnitude as the polaron binding energy, and thus much greater than the hopping integral  $J$ . Its physical origin is the fact that when the metallic sites on both sides of a ligand are occupied, displacement of the ligand does not affect the energy of these electrons in this model [this is a consequence of the linearity of Eq. (19) in lattice displacement]. The ground state of such a system is a state with an electron on every other metallic site if there are half as many electrons as metallic sites, as occurs in magnetite. If there are fewer electrons, we have a strongly interacting system of polarons with bandwidth

$$2J e^{-(1/N) \sum_k \gamma_k}, \quad (24a)$$

where

$$\gamma_k = (4A^2/M^2 \omega_k^4) (N_k + \frac{1}{2}) \sin^4 \frac{1}{2} k, \quad (24b)$$

obtained by the methods used by Holstein.<sup>19</sup> Holstein's model has  $\sin^2 \frac{1}{2} k$  instead of  $\sin^4 \frac{1}{2} k$  in the expression for  $\gamma_k$ .<sup>19</sup> Thus, we see that although both the bandwidth and interaction of the polarons depend on the model used, in both models considered the picture is basically that noninteracting electrons in a polarizable crystal behave at low temperature as a typical many-electron system with an effective interaction caused by lattice distortion and with the bandwidth reduced as in the single-polaron

Transforming to normal coordinates as done in Holstein's model, we again obtain an equation of the same form of Eq. (16), but with the equilibrium position  $q_k^{(m)}$  given by

$$q_k^{(m)} = \frac{A}{M \omega_k^2} \left( \frac{2}{N} \right)^{1/2} \sum_{p=1}^N P_p \{ \sin(kp + \frac{1}{4}\pi) - \sin[k(p-1) + \frac{1}{4}\pi] \}. \quad (21)$$

The binding-energy term corresponding to Eq. (18) now becomes

problem. As the temperature increases, we go over to the hopping regime in which the system behaves as a system of electrons which hop from site to site but with the restriction that no two electrons can hop onto the same site, because of the exclusion principle. The diffusion constant  $D$  is found from the hopping rate as in Holstein's paper and from it the mobility  $\mu$  is easily shown to be

$$\mu = (1-n) D / kT, \quad (25a)$$

where

$$n = (e^{-\beta\rho} + 1)^{-1}, \quad (25b)$$

where  $\rho$  is the chemical potential and  $\beta = 1/kT$ .<sup>21</sup>

Another interesting one-dimensional model is a chain of atoms containing electrons where the electron on a particular lattice site interacts with other ions in the system by a Coulomb interaction. Then, the electron-ion interaction can be written

$$-A \sum_{pn} \frac{p-n}{|p-n|^3} P_p x_n (1 - \delta_{pn}). \quad (26)$$

If we carry through the previously described procedures and neglect phonon dispersion, the effective electron-electron interaction becomes

$$-\frac{A}{M \omega_0^2} \sum_{pp'} \frac{(p-n)(p'-n)}{|p-n|^3 |p'-n|^3} n_p n_{p'} (1 - \delta_{p,n}) (1 - \delta_{p',n}). \quad (27)$$

This interaction is attractive if  $p$  and  $p'$  are sufficiently close, because then there will be more values of  $n$  for which  $(p-n)$  and  $(p'-n)$  are negative than for which one is negative and one positive. To this term we must add the Coulomb interaction between the electrons themselves.

Let us now try to apply these ideas to magnetite. We consider a row of octahedral-site metallic ions

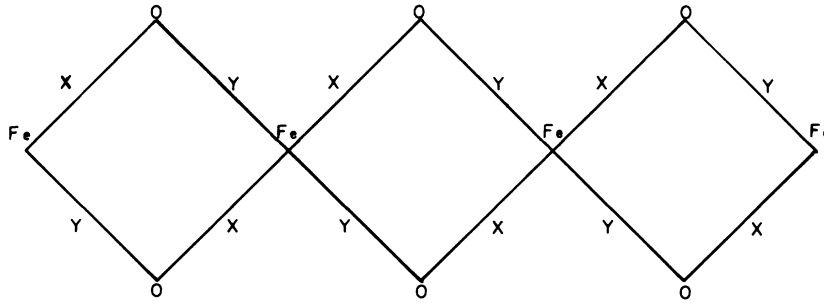


FIG. 4. Row of iron atoms in magnetite (labeled Fe). Neighboring oxygen atoms are labeled O.

in magnetite and some neighboring oxygen atoms, as illustrated in Fig. 4.<sup>4</sup> There are also oxygen atoms directly below and above each of the metallic ions shown, but they will not contribute to the effective interaction of electrons due to lattice distortion to lowest order. Since we have seen that the major part of the effective electron interaction can be accounted for in an Einstein model, we will assume one here. Then, making the commonly made assumption that each oxygen atom can vibrate only along or perpendicular to its bond with a metallic ion, each oxygen can be treated as a harmonic oscillator described by the following Hamiltonian:

$$\mathcal{H} = (1/2M)(p_x^2 + p_y^2) + \frac{1}{2}M\omega_0^2(x^2 + y^2), \quad (28)$$

where  $x$  and  $y$  directions are the directions of the bonds connecting it to its two nearest-neighbor metallic ions (shown in Fig. 4). Placing an electron on a metallic site displaces its four near-neighbor oxygen atoms. If we assume the resulting energy change of the electron due to an oxygen displacement can be treated by adding a term  $Ax$  or  $Ay$  to Eq. (28), depending on whether it is an  $x$  or  $y$  bond from the electron to the oxygen atom, we find that the oxygen is displaced by an amount

$$x_0 = A/M\omega_0^2$$

in either the  $x$  or  $y$  direction, and the energy of the system is reduced by

$$\frac{1}{2}M\omega_0^2 x_0^2.$$

For each electron, the total reduction due to its four oxygen neighbors is four times this. It is easily seen that this energy is the same for each electron in the system, independent of their relative positions. Thus, they do not have an effective interaction in the linear approximation. This implies that there may possibly not be a large effective interaction between electrons in magnetite and that they might be described as polarons interacting just with the screened electron-electron Coulomb interaction. Of course, if terms higher order in the oxygen displacement were included, there could be an effective interaction due to oxygen displacement.

We know that in magnetite the interactions of

the electrons are actually affected by lattice displacements and polarization. For example, since  $T_v$  is very low compared to energies usually associated with Coulomb interactions, the interaction of electrons in the crystal must be greatly reduced by an internal dielectric constant due to long-range polarization caused by the electrons's electric fields. Also, it has been shown that the first-order nature of the transition and several other experimental results can be explained in terms of nonlinear effects due to polarization of near-neighbor oxygen electronic charge.<sup>2</sup>

In conclusion, we have discussed how magnetite can be described as a degenerate system of polarons below  $T_v$ . To test these conclusions, it would be necessary to measure conductivity in doped systems of magnetite below  $T_v$  to see if the added carriers truly behave as polarons. The flatness of the lower two bands above  $T_v$  is purely a peculiarity of the near-neighbor tight-binding approximation. It would certainly not be true if next-nearest neighbors were included, but since they are far away, this should be a good approximation. The existence of small-polaron hopping conductivity above but not below  $T_v$  is borne out by Hall-effect experiments.<sup>22</sup>

#### APPENDIX A

We can see from Eqs. (4) that for  $\epsilon_0$  equal to 2, the system is not an insulator because the lowest-conduction and highest-valence bands cross at  $\vec{k} = (0, 0, \pi/a)$ . Let us see if the three-parameter ordering of Cullen and Callen can make the system an insulator. To investigate this possibility let us find the eigenvalues at the point  $\vec{k} = (0, 0, \pi/a)$ . At this point the secular determinant is found to be

$$\begin{vmatrix} \epsilon_1 - \lambda & 0 & 0 & 2 \\ 0 & \epsilon_2 - \lambda & 2 & 0 \\ 0 & 2 & \epsilon_3 - \lambda & 0 \\ 2 & 0 & 0 & \epsilon_4 - \lambda \end{vmatrix} = 0,$$

using Eq. (1) with

$$H_{\alpha\alpha}(\vec{k}) = \epsilon_\alpha.$$

The solutions are



$$\lambda = \frac{1}{2}(\epsilon_1 + \epsilon_4) \pm \left[ \frac{1}{2}(\epsilon_1 - \epsilon_4)^2 + 4 \right]^{1/2}$$

or

$$\lambda = \frac{1}{2}(\epsilon_2 + \epsilon_3) \pm \left[ \frac{1}{2}(\epsilon_2 - \epsilon_3)^2 + 4 \right]^{1/2}.$$

The  $\epsilon$ 's for the three-parameter ordering can always be written

$$\epsilon_1 = \epsilon_0 + \epsilon',$$

$$\epsilon_2 = -\epsilon_0 + \epsilon'',$$

$$\epsilon_3 = -\epsilon_0 - \epsilon'',$$

$$\epsilon_4 = \epsilon_0 - \epsilon'.$$

Then, the eigenvalues are

$$\lambda_1 = \epsilon_0 - [4 + (\epsilon')^2]^{1/2},$$

$$\lambda_2 = -\epsilon_0 - [4 + (\epsilon'')^2]^{1/2},$$

$$\lambda_3 = \epsilon_0 + [4 + (\epsilon')^2]^{1/2},$$

$$\lambda_4 = -\epsilon_0 + [4 + (\epsilon'')^2]^{1/2}.$$

The numbering of the levels corresponds to precisely the numbering in Eqs. (4). [This identification is made by examining these equations for  $\epsilon = \epsilon'' = 0$  and comparing with Eqs. (4) with  $k = \pi/a$ .] We find in this way that bands 1 and 4 are made to cross more by increasing  $\epsilon'$  and  $\epsilon''$  from zero; the bands are not split by the addition of two new parameters at point  $\vec{k} = (0, 0, \pi/a)$ . Of course, the addition of the two new order parameters could possibly introduce a gap at another point in the Brillouin zone. Nevertheless, the Verwey order

parameter chosen for the self-consistent calculation is the smallest parameter which will give an insulating Verwey state, and thus, we would assume that if three-parameter ordering was a more favorable situation, this would be a situation in which it should show itself; yet it does not.

#### APPENDIX B

We will show that the lower two bands are flat throughout the Brillouin zone. To find the eigenvalues, we must evaluate the secular determinant

$$\det |1 + a_{\alpha\beta} - \lambda \delta_{\alpha\beta}|,$$

where

$$a_{\alpha\beta} = e^{2i\vec{k}\cdot\vec{r}_{\alpha\beta}}$$

and  $\lambda = E + 2$  (energy defined as in the text). This may be written as a polynomial in  $\lambda$  as follows:

$$\det_{\alpha,\beta=1,4} |1 + a_{\alpha\beta} - \lambda \delta_{\alpha\beta}| = \det_{\alpha,\beta=1,4} |1 + a_{\alpha\beta}| - \lambda \det_{\alpha,\beta=2,4} |1 + a_{\alpha\beta}| + \text{higher order terms in } \lambda.$$

Using a well-known theorem for determinants,<sup>23</sup> each determinant may be written

$$\det |a_{\alpha\beta}|$$

plus all the determinants found by replacing a column of  $|a_{\alpha\beta}|$  by a column of ones. From the definition of  $a_{\alpha\beta}$ , these determinants can be shown to be equal to zero. Thus, the first two bands must be flat with  $E = -2$  throughout the Brillouin zone.

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PHYSICAL REVIEW B

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## Green's-Function Theory of an Induced Moment System Containing Impurities: Paramagnetic Phase\*

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An induced moment system containing a substitutional impurity is studied using the Green's-function method in the random phase approximation. All the ions are assumed to have a singlet crystal field ground state and a singlet excited state. We focus our attention on the paramagnetic phase, without local polarization, in this paper. Two *s*-type modes are predicted in a lattice with only nearest-neighbor exchange interactions. The energies of the impurity modes have been calculated as functions of the impurity parameters and the temperature for a simple-cubic lattice. Similar to an ordinary impure magnetic system, local modes can appear above the energy band of the host and/or in the energy gap. The spectral weight function at the impurity site is discussed. Local susceptibilities, which are proportional to the temperature-dependent part of the NMR Knight shift, are calculated and compared with predictions of the molecular-field theory. The experimental situation is also reviewed.

### I. INTRODUCTION

The problem of the effects of impurities in magnetic spin systems has been an active field of study in recent years. In particular, the localized excitations, the magnetization at the impurities, and the effects of impurities on the spin-wave spectrum of the host crystal are the central topics of discussions for impure magnetic insulators.<sup>1-3</sup> They are of interest both theoretically and experimentally, as the measurements of these quantities provide valuable information on the interactions of the impurity ions with the host ions. In this paper, we examine an induced moment system containing a substitutional impurity. Along with the behavior similar to an impure ordinary spin system, we also note the interesting features unique to the impure induced moment systems.

Induced moment systems with a singlet crystal-field ground state have been discussed by Trammel<sup>4</sup> and Bleaney<sup>5</sup> in the molecular-field approximation, and by Wang and Cooper<sup>6</sup> using a Green's-function method. It was shown that for rare-earth compounds with a singlet crystal field ground state for the rare-earth ions, the exchange interaction between neighboring ions must exceed a certain critical value relative to the crystal field to have magnetic ordering even at zero temperature. The magnetic moment which then occurs is essentially an induced moment corresponding to the Van Vleck susceptibility, where the exchange field takes the place of an applied magnetic field. When the ex-

change is less than the critical value the system is paramagnetic, as is a system with larger exchange above its critical temperature. Collective spin-wave-like exciton modes have been predicted in the ordered phase as well as in the paramagnetic phase.<sup>4,6-8</sup> Indeed, a large dispersion in the exciton energies in the paramagnetic phase has been observed recently by neutron inelastic scattering on praseodymium single crystals.<sup>9</sup>

In this calculation we consider an impure induced moment system in the paramagnetic phase. This requires not only that the pure host be a paramagnet, but also that the impurity be either a nonmagnetic ion or an ion with a nonmagnetic crystal field ground state. For the latter case we also assume that the local self-polarization centered at the impurity does not occur.<sup>10</sup> Localized excitations and local susceptibilities are of special interest as they are accessible to experimental measurements. Neutron inelastic scattering<sup>3</sup> and Raman scattering<sup>11</sup> are the well-known techniques used to probe the localized excitations of an impure system. Specific-heat measurement can also be a possibility, especially when the localized modes occur in the energy gap (as will be discussed later). To measure local susceptibilities, NMR or Mössbauer techniques can be used.

A method of thermal Green's functions is employed for the theoretical calculation. To simplify the algebra, we assume that each ion can be represented by a two energy-level system. That is, in the crystal field, each ion has a singlet ground