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Green's-Function Theory of an Induced-Moment System Containing Impurities. II. Vacancy Impurities*

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The bulk susceptibility of an induced-moment system containing substitutional vacancy impurities is studied in the low-impurity-concentration limit, utilizing a Green's-function method in the random-phase approximation. It is found that the variation of the inverse susceptibility with the impurity concentration is strongly temperature dependent, in contrast to the temperature-independent result predicted by the simple molecular-field theory in which the exchange interaction is merely scaled by the factor $1-c$. At low temperatures the deviation can be up to 35% for a simple cubic lattice. A further investigation shows that a refined molecular-field theory taking account of the nonuniform distribution of the magnetization in the impure crystal recovers most of the features predicted by the Green's-function theory. However, no molecular-field theory can account for the behavior of systems of small energy gap, or systems of low ordering temperature. In these systems the contribution of the collective excitations greatly alters the results at low temperatures not only quantitatively but also qualitatively.

I. INTRODUCTION

The study of the effects of impurities in an otherwise perfect crystal has been of considerable theoretical and experimental interest in recent years. In a previous paper[1] (referred to as I hereafter) we discussed the impurity modes and local susceptibilities of an induced-moment magnetic system containing a single substitutional impurity. The system was studied in the paramagnetic phase. Two singlet energy levels were assumed for all ions and explicit results were given for a simple cubic crystal lattice with nearest-neighbor-only exchange interactions. In particular, we showed that there exist two impurity modes and they are of S type. This remains true for impure induced-moment paramagnets of other geometry with only nearest-neighbor exchange interaction. As in an ordinary ferromagnet,[2] the impurity modes can become localized, appearing above the energy band and/or in the gap. Local susceptibilities on the impurity ions were also calculated and remarkable differences were found between the Green's-function results and the prediction of molecular-field theory (which ignores the collective excitations of the system).

In this paper we extend the Green's-function calculation in I to the case of vacancy impurities, that is, when the impurity ions are nonmagnetic or are actually vacancies. We still choose a two-level paramagnetic induced moment system as the host in this calculation. Instead of the local susceptibility on the impurity ion, which is zero for a vacancy impurity, we discuss the bulk susceptibility of the impure crystal. To study the depression of the bulk susceptibility by addition of vacancy impurities, we plot the inverse susceptibility per magnetic ion versus the impurity concentration. At low impurity concentration a straight line is obtained, the slope of which describes the effect of the dilution. We find, in the Green's-function calculation, that the effect of dilution is temperature dependent, and is most pronounced as the energy gap of the excitations of the pure host crystal vanishes. In the random-phase approximation (RPA) this is the case at the critical temperature T_c for systems with $kT_c/\Delta < 0.1$.[3] But even for a system with sizable energy gap in the excitation spectrum, say, a third of the crystal field splitting of the two levels, 20% change in the slope is observed (for a simple cubic lattice) as temperature increases. This phenomenon is not expected in the simple molecular-field theory in which the exchange interaction is simply scaled linearly according to the concentration of the vacancies; in this case the dilution effect can be easily shown to be temperature independent. (We shall call this theory MT1.) A closer investigation, however, shows that despite the fact that the excitation waves are important in the determination of the detailed behavior of the temperature dependence of the dilution effect, it is possible to develop a molecular-field theory (MT2) to account largely for the temperature behavior. What is missing in MT1 is a consideration of the nonuniform distribution of the magnetization (or the susceptibility) in an impure crystal, or the cluster effect. In MT2 we recover the major features. However, for an induced-moment system with small energy gap in the collective excitations, the theory is still inadequate in describing the low-temperature behavior of the system; and the Green's-function theory should be used.

Recently, Fulde and Peschel[4] have discussed the same system using Abrikosov's diagrammatic technique. The static susceptibility function they obtained is reproduced here by the molecular-field theory MT2, which, in a certain way, shows more explicitly the physical picture of the impure system. Like MT2, the theory of Fulde and Peschel failed to include the effect of the collective excitations in the crystal. This is achieved in the Green's-function theory.

In the experimental aspect, problems of vacancy impurities in a paramagnetic induced-moment system have been of interest recently in various laboratories. Wallace *et al.*[5] have measured the magnetic susceptibilities of Pr-La and Pr-Y alloys as the concentrations of the vacancy impurities La and Y vary. Unfortunately, because of the oxidization problem, the sample was not prepared as a real powder (nor a single crystal). The uncertainty in the susceptibility due to the crystalline field thus overshadowed the effect calculated in this paper. Two experiments, focusing on the transition of induced-moment systems from the ordered phase to the paramagnetic phase by diluting the ordered crystals with nonmagnetic ions, have been carried out. Cooper and Vogt[6] studied the decrease of ordering temperature of $Y_xTb_{1-x}Sb$ as the concentration of the nonmagnetic component Y increases. It becomes a paramagnet when $x \simeq 0.6$. The results were analyzed using a simple molecular-field theory (MT1) and the strength of the exchange interaction was scaled linearly according to the concentration of Y. The high impurity concentration in this case precludes us from using the results derived in this paper, which are valid to first order in the impurity concentration. At low concentrations of the vacancies, as will be shown later, the strength of the exchange interaction $\mathcal{J}$ is not scaled down linearly according to the concentration c, but rather that $\mathcal{J} \to \mathcal{J}[1 - c\,\overline{G}^{-1}(0)]$, where $\overline{G}(0)$ is the lattice Green's function. Bucher *et al.*[7] have also studied a related problem. They measured the susceptibility of Th-Pr alloy and found a steady decrease of the inverse susceptibility as the concentration of Th, a nonmagnetic ion, decreased. The alloy was in the paramagnetic state throughout the range of concentration of Th in the experiment. However, presumably because of the quite different sizes of Pr and Th ions, the crystal field interactions as well as the exchange interactions vary in a rather complicated way. A simple analysis does not appear likely. At present we do not seem to have a suitable experiment to test the theory. It is hoped that this calculation will stimulate some carefully prepared experiments in this direction. An interesting system for this purpose may be the Pr_3Tl compounds with La dilution recently studied by Bucher *et al.*[8] They have measured the susceptibilities of $La_xPr_{3-x}Tl$ compounds with various La concentrations at one temperature, 4.2 °K, which is below the magnetic ordering temperature of the pure-host compound (11 °K). To measure the susceptibilities at various temperatures above the ordering temperature, and observe the temperature-dependent depression upon adding the La impurity, would be of great interest. At the low-concentration limit, the temperature dependence of the depression of susceptibility should be described by our theory. For high concentration of the impurity, we do not have a suitable theory and it is not unreasonable to assume a more uniform distribution of the magnetization (upon applying a field), so perhaps the simple molecular-field theory (MT1) is not a bad one to use in this case.

In Sec. II the Green's-function formalism used in I will be modified to adapt to the present case of vacancy impurities by letting Δ_0, the energy gap between the two crystal field states on the impurity ion, approach infinity. This is not a trivial process and some caution needs to be exercised. The momentum Green's functions are then calculated and the results are extended to a small but finite concentration of impurities using Izyumov's procedure. Susceptibility as functions of concentration of impurities and temperature are then found from the momentum Green's functions and discussed in Sec. III.

II. GREEN'S-FUNCTION FORMALISM

To examine the behavior of susceptibilities we consider the following Green's functions:

$$G^{\pm}_{il}(t) = \langle\langle S^{\pm}_i(t); S^{-}_l(0)\rangle\rangle$$

$$\equiv -i\theta(t)\langle [S^{\pm}_i(t);\; S^{-}_l(0)]\rangle,$$

where $\theta(t)$ is the unit step function and the angular brackets denote the canonical thermal average. For an impure system with randomly distributed impurities, the Green's functions are to be averaged over all configurations of the random lattice. We shall follow the procedure of Izymov[9] to obtain the average accurate to the first order in the impurity concentration. We first consider the single-vacancy–impurity problem. To borrow the formulations of I, we recall that the Hamiltonian, in pseudospin variables, for an induced-moment host crystal in the paramagnetic phase containing a single substitutional impurity at the origin of the coordinates, assuming two energy levels for each ion and only nearest-neighbor exchange interaction, has the form

$$\mathcal{H} = -\Delta\sum_l S^z_l - (\Delta_0 - \Delta)S^z_0 - 4\mathcal{J}\alpha^2\sum_l\sum_\delta S^x_l S^x_{l+\delta}$$

$$- 8\alpha(\mathcal{J}_0\alpha_0 - \mathcal{J}\alpha)S^x_0\sum_\delta S^x_\delta, \qquad (2.1)$$

where Δ and Δ_0 are the host and impurity crystal field energy-level splittings, $\mathcal{J}$ and $\mathcal{J}_0$ are the host-host and impurity-host exchange coupling parameters, and α and α_0 are the matrix elements of the z component of angular momentum J^z between the crystal field ground state and the excited state for the host and the impurity ions, respectively. We have taken pseudospin component S^z equal to $\frac{1}{2}$ for an ion in its ground state and $-\frac{1}{2}$ for an ion in the excited state. The equation-of-motion method is used to study the Green's functions. As shown in I, the combined Green's functions in the energy Fourier space, $\mathcal{G}^{+}_{il}(E) \equiv G^{+}_{il}(E) + G^{-}_{il}(E)$, obey the following equation of motion:

$$\frac{1}{\Delta}\left(\frac{E^2}{\Delta_i} - \Delta_i\right)\mathcal{G}^{+}_{il} + \frac{8\mathcal{J}\alpha^2}{\Delta}\langle S^z_i\rangle\sum_\delta \mathcal{G}^{+}_{i+\delta,l}$$

$$- \frac{8\mathcal{J}\alpha^2}{\Delta}\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha} - 1\right)\sum_\delta\left(\langle S^z_\delta\rangle\mathcal{G}^{+}_{0l}\Delta_{i,\delta} + \langle S^z_0\rangle\mathcal{G}^{+}_{\delta l}\Delta_{i,0}\right)$$

$$= -\frac{1}{\pi\Delta}\left(1 + \frac{E}{\Delta_i}\right)\langle S^z_i\rangle\Delta_{i,l}. \qquad (2.2)$$

Here $\Delta_{i,l}$ is the Kronecker δ function. Taking $\Delta_0 = \Delta$ and $\mathcal{J}_0\alpha_0 = \mathcal{J}\alpha$ we solve for the pure-crystal Green's function,

$$\mathcal{G}^{0+}_{il} = \frac{\langle S^z\rangle(E+\Delta)}{\pi}\,\frac{1}{N}\sum_{\vec{k}}\frac{e^{i\vec{k}\cdot(\vec{i}-\vec{l})}}{E^2 - E^2_k}, \qquad (2.3)$$

where

$$E_k = \Delta(1 - 2\langle S^z\rangle A\gamma_{\vec{k}})^{1/2} \qquad (2.4)$$

is the energy dispersion relation for the magnetic excitons in the pure crystal, $A \equiv 4\mathcal{J}z\alpha^2/\Delta$, and z is the number of nearest neighbors to an ion.

For the case of a vacancy impurity we take $\mathcal{J}_0\alpha_0$ equal to zero since the impurity is not magnetically coupled to its surrounding ions, and take Δ_0 to approach infinity since only one energy level is involved at the impurity site. This procedure is different from that of Pink,[10] who has studied problems of impurities in an ordered induced-moment system and specialized the results to the case of vacancy impurities by taking $\Delta_0 = 0$. The spurious zero-energy mode is thus avoided. Fulde and Peschel[6] have employed the same procedure to obtain their results for the case of a vacancy impurity. The susceptibility function they have obtained agrees with ours in MT2.

Substituting $\mathcal{J}_0\alpha_0$ as zero and considering the limiting case of $\Delta_0 \to \infty$, we see from Eq. (2.2) that $\mathcal{G}^{+}_{0l} = 0$ for all l. That this must be true can be seen by interpreting $\mathcal{G}^{+}_{il}$ as a measurement of the response of the ith pseudospin to a small disturbance of frequency $E/\hbar$ applied at the lth pseudospin; because of a lack of coupling of the impurity ion at the origin with its neighboring host ions the response is obviously zero. On the other hand, the product $\Delta_0\mathcal{G}^{+}_{00}$ takes the value $-\langle S^z_0\rangle/\pi$ in the limit. $\langle S^z_0\rangle$ is $\frac{1}{2}$ exactly because of the infinite energy gap. If we take $\langle S^z_i\rangle = \langle S^z\rangle$ for all $i \neq 0$ as an approximation, we obtain the equation of motion of $\mathcal{G}^{+}_{il}$ as follows:

$$\left(\frac{E^2}{\Delta^2} - 1\right)\mathcal{G}^{+}_{il} + \frac{8\mathcal{J}\alpha^2\langle S^z\rangle}{\Delta}\sum_\delta \mathcal{G}^{+}_{i+\delta,l} = \frac{T_{il}}{\Delta}, \qquad (2.5)$$

where

$$T_{il} = 8\mathcal{J}\alpha^2\langle S^z\rangle\Delta_{i,0}\sum_\delta \mathcal{G}^{+}_{\delta l}$$

$$+ (1 - \Delta_{i,0})\Delta_{i,l}\langle S^z\rangle(1 + E/\Delta)/\pi. \qquad (2.6)$$

As in I, we can solve this equation to obtain

$$\mathcal{G}^{+}_{il} = \frac{\pi\Delta}{\langle S^z\rangle(E+\Delta)}\sum_j \mathcal{G}^{0+}_{ij}T_{jl}, \qquad (2.7)$$

which relates the Green's function $\mathcal{G}^{+}_{il}$ to a sum of Green's function, $\Sigma_\delta \mathcal{G}^{+}_{\delta l}$. We therefore find the Green's function easily:

$$\mathcal{G}^{+}_{il} = \mathcal{G}^{0+}_{il} - \mathcal{G}^{0+}_{i0}\mathcal{G}^{0+}_{0l}/\mathcal{G}^{0+}_{00} . \tag{2.8}$$

We note that Eq. (2.8) is a general result of models of nearest-neighbor coupling of ions in a Bravais lattice and is independent of the crystal symmetry. The only impurity mode is seen at $E = \Delta$, where $\mathrm{Re}\,\mathcal{G}^{0+}_{00} = 0$, and is within the host excitation band. The mode is of S symmetry and is spatially extended.

To facilitate the configuration averaging process for a finite impurity concentration, we consider the momentum Green's function $\mathcal{G}^{+}_{i}(\vec{k})$, defined, for $\vec{k}$ in the first Brillouin zone, as

$$\mathcal{G}^{+}_{i}(\vec{k}) = \sum_{l} \mathcal{G}^{+}_{il}\, e^{-i\vec{k}\cdot(\vec{i}-\vec{l})} . \tag{2.9}$$

We note that because of the lack of translational invariance of the system, $\mathcal{G}^{+}_{i}(\vec{k})$ still depends on a site index. For the single-vacancy–impurity problem,

$$\mathcal{G}^{+}_{i}(\vec{k}) = \mathcal{G}^{0+}(\vec{k})\,(1 - e^{-i\vec{k}\cdot\vec{i}}\,\mathcal{G}^{0+}_{i0}/\mathcal{G}^{0+}_{00}), \tag{2.10}$$

where

$$\mathcal{G}^{0+}(\vec{k}) = \frac{\langle S^z\rangle}{\pi}\left(\frac{E+\Delta}{E^2 - E_k^2}\right) \tag{2.11}$$

is the momentum Green's function for the pure host crystal. The configuration average is now taken on the momentum Green's function $\mathcal{G}^{+}_{i}(\vec{k})$. The process of averaging restores the translational invariance. We find for the single-vacancy problem,

$$\langle \mathcal{G}^{+}_{i}(\vec{k})\rangle = \frac{1}{N}\sum \mathcal{G}^{+}_{i}(\vec{k}) = \mathcal{G}^{0+}(\vec{k}) - \mathcal{G}^{0+}(\vec{k})\,(1/N)\,(\mathcal{G}^{0+}_{00})^{-1}\,\mathcal{G}^{0+}(\vec{k}), \tag{2.12}$$

$$\langle \mathcal{G}^{+}_{i}(\vec{k})\rangle = \frac{1}{[\mathcal{G}^{0+}(\vec{k})]^{-1} + (1/N)(\mathcal{G}^{0}_{00})^{-1}} \tag{2.13}$$

to order of $1/N$. More explicitly,

$$\langle \mathcal{G}^{+}_{i}(\vec{k})\rangle = \frac{\langle S^z\rangle}{\pi}\,\frac{(E+\Delta)(1 - D_s^{-1}/N)}{E^2 - \Delta^2 + 2\langle S^z\rangle A\Delta^2\gamma_k(1 - D_s^{-1}/N)} , \tag{2.14}$$

where

$$D_s = \pi(E-\Delta)\,\mathcal{G}^{0+}_{00}/\langle S^z\rangle . \tag{2.15}$$

For finite impurity concentration one may expect a simple extension of Eq. (2.14) by replacing $1/N$ with the impurity concentration c at the low-concentration limit. That this indeed is true can be shown in a way parallel to the derivation of Izyumov for a conventional impure ferromagnet. We sketch the proof in the Appendix. To first order in the impurity concentration,

$$\langle \mathcal{G}^{+}_{i}(\vec{k})\rangle = \frac{\langle S^z\rangle}{\pi}\,\frac{(E+\Delta)(1 - cD_s^{-1})}{E^2 - \Delta^2 + 2\langle S^z\rangle A\Delta^2\gamma_k(1 - cD_s^{-1})} . \tag{2.16}$$

We note that the excitation wave-energy spectrum is shifted as if the exchange interaction were weakened by a factor $1 - c\,\mathrm{Re}\,D_s^{-1}(E_k)$, instead of $1 - c$ as one would obtain based on a molecular-field–type reasoning. The excitation modes are also broadened, with a width proportional to c.

III. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility for the impure system can be found directly from the averaged momentum Green's function $\langle \mathcal{G}^{+}(\vec{k})\rangle$. We first note that the static longitudinal susceptibility is given by

$$\tilde{\chi} = -2\pi g^2\mu_B^2\,\langle\langle J^z;\ J^z\rangle\rangle_{E=0,\,k=0} , \tag{3.1}$$

and that the retarded Green's function $\langle\langle J^z; J^z\rangle\rangle$ is, in the pseudospin variables,

$$\langle\langle J^z;\ J^z\rangle\rangle = 4\alpha^2\,\langle\langle S^x;\ S^x\rangle\rangle . \tag{3.2}$$

This is because[3]

$$J^z = 2\alpha S^x \tag{3.3}$$

as the net magnetization $\langle J\rangle \to 0$, which is the pertinent limit in the calculation of the susceptibility at a vanishing field in the paramagnetic phase. Therefore

$$\frac{\tilde{\chi}}{g^2\mu_B^2} = -4\pi\alpha^2\,\mathcal{G}^{+}(k=0,\ E=0) \tag{3.4}$$

$$= \frac{2\alpha^2}{\Delta}\,\frac{[1 - c\,\bar{G}^{-1}(0)]\,2\langle S^z\rangle}{1 - 2\langle S^z\rangle A\,[1 - c\,\bar{G}^{-1}(0)]} . \tag{3.5}$$

Here we have made use of the fact that

$$\langle\langle S^x;\ S^-\rangle\rangle_{E=0} = \langle\langle S^x;\ S^+\rangle\rangle_{E=0} \tag{3.6}$$

and that

$$D_s(E=0) = \bar{G}(0) = \frac{1}{N}\sum_k \frac{1}{1 - 2\langle S^z\rangle A\gamma_K} , \tag{3.7}$$

This integral can be calculated numerically,[11] and the physics of its appearance in Eq. (3.5) will become clear later in the discussion of MT2.

The susceptibility per magnetic ion is $\chi = \tilde{\chi}/(1-c)$. We consider the inverse susceptibility per magnetic ion to the first order in c;

$$g^2\mu_B^2\,\chi^{-1}(c) = \frac{\Delta}{2\alpha^2}\left(\frac{1}{2\langle S^z\rangle} - A + \Phi c\right), \tag{3.8a}$$

where

$$\Phi = A - [1 - \bar{G}^{-1}(0)]/2\langle S^z\rangle . \tag{3.8b}$$

Higher-order terms may enter. However, the present calculation is accurate only to the first order in the impurity concentration; this prevents us from discussing the deviation from linearity in a plot of χ^{-1} vs c. On the other hand, a simple molecular-field theory (MT1), assuming simply a weakening of exchange field by a factor $1 - c$, would give

$$g^2\mu_B^2\,\chi^{-1} = \frac{\Delta}{2\alpha^2}\left(\frac{1}{2\langle S^z\rangle} - A + Ac\right), \tag{3.9}$$

which is an *exact* linear relationship between χ^{-1} and c. We see also that the intercept of the straight line on the ordinate axis [i.e., $\chi^{-1}(c=0)$]

is given by $(\Delta/2\alpha^2)(1/2\langle S^z\rangle - A)$ for both theories although the population factors $2\langle S^z\rangle$ may be quite different. A discussion of $\chi^{-1}(c=0)$ calculated in the Green's function theory (GFT) and in the molecular-field theory has been given by Wang and Cooper.[3] The slope of the straight line in the present GFT varies with temperature as both $\langle S^z\rangle$ and $\overline{G}(0)$ are functions of temperature. This is in contrast to the simple molecular-field theory which gives a temperature-independent slope $A\Delta/(2\alpha^2)$ or $2\mathcal{J}z$. At high temperatures or small exchange to crystal field ratio A, the slope given by the Green's function theory approaches that by the simple molecular-field theory.

As mentioned in Sec. I, it is possible to recover the main feature of the temperature behavior of Φ using a more careful molecular-field method. We sketch the theory in the following.

We consider a single substitutional vacancy impurity in an induced-moment system in the paramagnetic phase. In a small external field H applied along the z axis, the magnetic moments induced vary in space relative to the site of the impurity. A similar analysis briefed in I enables us to write the equations relating the induced magnetic moments (letting the impurity site be the origin),

$$\sum_{\eta} L_{mn} J_n = \sum_{\kappa} \delta L_{mk} J_k + h(1-\Delta_{m,0}), \tag{3.10}$$

where

$$L_{mn} = \Delta_{m,n} - \frac{a}{z}\sum_{\delta} \Delta_{m,n+\delta}, \tag{3.11a}$$

$$\delta L_{mk} = -\frac{a}{z}\left(\Delta_{m,0}\sum_{\delta}\Delta_{k,\delta} + \Delta_{k,0}\sum_{\delta}\Delta_{m,\delta}\right), \tag{3.11b}$$

$$h = \frac{2g^2\mu_B^2\,\alpha^2 H}{\Delta}\tanh\left(\frac{\Delta}{2kT}\right), \tag{3.11c}$$

and

$$a = A\tanh\left(\frac{\Delta}{2kT}\right). \tag{3.11d}$$

Also, in the equations we have used $\Delta_{m,n}$ for the Kronecker δ function and z to denote the number of nearest neighbors of an ion. A two-level system is assumed. A generalization to a system of more levels is straightforward. As in I, we define a lattice Green's function $\overline{G}_{lm}$ such that

$$\sum_{m} \overline{G}_{lm} L_{mn} = \Delta_{ln}. \tag{3.12}$$

This gives

$$\overline{G}_{lm} = \frac{1}{N}\sum_{k} \frac{e^{i\vec{k}\cdot(\vec{l}-\vec{m})}}{1-a\gamma_k}. \tag{3.13}$$

In terms of the Green's function $\overline{G}$, we rewrite Eq. (3.10) as

$$J_l = \sum_{m,k} \overline{G}_{lm}\,\delta L_{mk} J_k + h\sum_{m}\overline{G}_{lm}(1-\Delta_{m,0}). \tag{3.14}$$

We find

$$\frac{1}{N}\sum_{l} J_l = \frac{h}{1-a}\left(1-\frac{1}{N}\right) - \frac{1}{N}\frac{a}{1-a}J_1, \tag{3.15}$$

where $g\mu_B J_1$ is the magnetic moment of the nearest-neighbor ions of the impurity and can be found from Eq. (3.14) as

$$J_1 = [h/a(1-a)]\,[\overline{G}^{-1}(0) - (1-a)] \tag{3.16}$$

with

$$\overline{G}(0) = \frac{1}{N}\sum_{k}\frac{1}{1-a\gamma_k}. \tag{3.17}$$

In the dilute limit we replace $1/N$ by the concentration of the impurity c. The averaged susceptibility per magnetic ion is therefore

$$\chi = (2g^2\mu_B^2\alpha^2/\Delta)(1/1-a)\{1-(c/1-a) \times [\overline{G}^{-1}(0) - 1 + a]\}\tanh(\Delta/2kT) \tag{3.18}$$

or

$$g^2\mu_B^2\chi^{-1} = (\Delta/2\alpha^2)(\coth(\Delta/2kT) - A + c\{A - [1-\overline{G}^{-1}(0)]\coth(\Delta/2kT)\}). \tag{3.19}$$

A plot of $(2g^2\mu_B^2\alpha^2/\Delta)\chi^{-1}$ vs c gives a straight line with slope

$$\Phi = A - [1-\overline{G}^{-1}(0)]\coth(\Delta/2kT). \tag{3.20}$$

This result is similar to that given by Green's-function theory. The difference is in the population factor $2\langle S^z\rangle$. In the molecular-field theory,

$$2\langle S^z\rangle = \tanh(\Delta/2kT). \tag{3.21}$$

A comparison of the calculations of the GFT and MT2 is presented in Fig. 1 for a simple cubic lattice. The slope Φ is plotted against the reduced temperature k_BT/Δ for a choice of values of A. Results of GFT are represented by the solid curves and those of MT2 by dashed curves. As shown in the figure, the main feature of the temperature behavior of Φ in GFT is recovered in MT2 in most cases, especially for cases of small values of A. Even for $A = 0.9$, they are quite similar. The difference between the two curves is obviously due to the inclusion of the collective excitations in the GFT calculation and not in the MT2 calculation. The zero-point motion is also included in GFT only. This accounts for the difference of the two theories at zero temperature. For finite temperatures, it is seen that the lower-lying exciton states have caused Φ of GFT to start to rise at a lower temperature. The difference is not large because of the existence of a sizable energy gap (of about 0.3Δ) in the exciton spectrum. At low temperatures both GFT and MT2 show a 20% depression from the value given by MT1. As the critical condition of magnetic ordering is approached, the two theories show more deviations from each other. Since the critical condition given by GFT is different from that

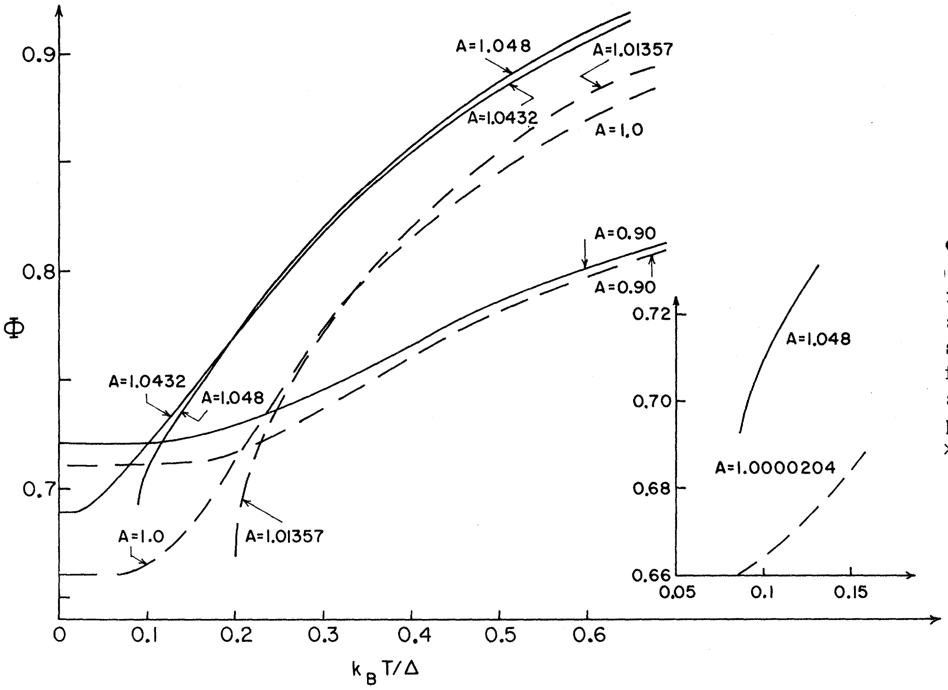

FIG. 1. Temperature dependence of $\Phi = 2g^2\mu_B^2\alpha^2/\Delta \times(\Delta\chi^{-1}/\Delta C)$. Solid curves represent results of GFT and dashed curves the results of MT2 (a molecular-field theory). The curves are labeled by their corresponding values of $A = \mathcal{J} \times z\alpha^2/\Delta$.

given by the molecular-field theory, we have plotted the GFT curve and the MT2 curve at their corresponding critical values of A, i.e., for the GFT, $A = 1.0432$ and for MT2, $A = 1$. Now the contribution of the low-lying collective excitation states manifests itself more dramatically. As shown in the same figure, at low temperatures Φ calculated in GFT rises much more rapidly than in MT2. Indeed, for k_BT between 0.025Δ and 0.1Δ, the GFT curve shows a rapid linear increase in Φ while the MT2 curve shows almost no increase. Thus for a nearly ordered induced-moment system the low-temperature behavior of Φ given by GFT is not only far from that given by MT1 (a 34% depression), but also at striking variance with that predicted by MT2. This is also true for ordered systems of low critical temperature. The case with $k_BT_c = 0.09\Delta$ is shown in Fig. 1 as an example. As the MT2 curve for this case is too close to the curve for $T_c = 0$, we show it in an insert. The steep rise of Φ just beyond the critical temperature is a rather general behavior. It shows up also in MT2 calculation, but only for systems of higher T_c (shown in the figure for a case with $k_BT_c = 0.2\Delta$). For the case of $k_BT_c = 0.09\Delta$, the MT2 curve rises with a positive curvature, in contrast to the negative curvature shown in the GFT curve.

In conclusion we remark on the possibility of observing experimentally the effects calculated in this paper. To do this we rewrite Eq. (3.19) in the following form:

$$[\chi(c)/\chi_0]^{-1} = [\chi(0)/\chi_0]^{-1} + c\Phi 2\langle S^z\rangle,$$

where

$$\chi_0 = (2g^2\mu_B^2\alpha^2/\Delta)\, 2\langle S^z\rangle$$

is the crystal-field-only susceptibility of the system assuming no exchange interaction. For 2% impurity, the cluster effect can be observed if $\chi(0)/\chi_0$ is greater than 20 which corresponds to $A = 0.95$ in a paramagnet. The condition for observing the collective excitation effect is more stringent. We note, however, that Pr_3Tl (a singlet-triplet system rather than the singlet-singlet system calculated here) is an induced-moment ferromagnet with Curie temperature $\approx 0.1\Delta$. As shown in Fig. 1, the collective excitation effect could be observed for systems with such a low ordering temperature. It is further noted that the possibility of observing these effects is greatly increased if a system of lower dimension is used because then the impurity concentration can be much higher. For lower-dimensional systems the effect calculated in this paper is even more pronounced, as can be seen by examining Φ with the lower-dimensional Watson integral $\overline{G}(0)$. Finally, we point out that for an ordinary magnetic system, the effect calculated in this paper certainly exists. It can be shown that the paramagnetic susceptibility for an ordinary spin system ($S = \frac{1}{2}$) containing a small concentration of nonmagnetic impurities is, according to MT2, given by

$$\chi^{-1} = (4k/g^2\mu_B^2)((T - T_c) + c\{T_c - T[1 - \overline{G}^{-1}(0)]\}), \tag{3.22}$$

where

$$G(0)=\frac{1}{N}\sum_{k}\frac{1}{1-(T_c/T)\gamma_k}\,. \qquad (3.23)$$

Here the collective excitations (spin waves) are heavily damped and we do not expect their contribution to be large enough to alter the result of MT2 too much, as compared to the case of induced-moment systems discussed in this paper. Work on impurities of general nature and of arbitrary concentration is in progress.

APPENDIX: GREEN'S FUNCTION FOR FINITE CONCENTRATION OF IMPURITIES

In a recent paper Izyumov[9] shows that, in extending a calculation of the momentum-dependent Green's function for a host ferromagnet containing a single isolated impurity to the case of a small finite concentration c of randomly distributed impurities, one may obtain a result correct to first order in c by replacing $1/N$ in the single-impurity result by c. We sketch here a similar diagrammatic technique for an induced-moment paramagnet containing a small but finite concentration of vacancies.

The Green's function $\mathcal{G}^{+}_{il}$ for our system with finite vacancy concentration obeys the matrix equation

$$\mathcal{G}^{+}=X+\mathcal{G}^{0+}V\mathcal{G}^{+}, \qquad (\mathrm{A1})$$

where $X_{il}=(1-\Sigma_\beta\,\Delta_{\beta l})\mathcal{G}^{0+}_{l}$, β is a vacancy-site index, and V is the block diagonal matrix (correct to first order in c),

$$V_{mn}=\sum_{\beta}\sum_{\sigma,\sigma'}V^{1}_{\sigma\sigma'}\,\Delta_{m,\beta+\sigma'}\,\Delta_{n,\beta+\sigma}\,. \qquad (\mathrm{A2})$$

σ and σ' are summed over *all* $z+1$ perturbed sites consisting of the impurity site and its nearest neighbors, and V^1 is the perturbation matrix for a single impurity, which has the dimensions $z+1$ by $z+1$. All elements of V^1 in the second through the last rows, and the first element in the first row, are zero; the remaining elements have the value $8\mathcal{J}\alpha^2(E+\Delta)/\pi\Delta$. Iteration of (A1) gives

$$\mathcal{G}^{+}_{jl}=\Big(1-\sum_{\beta}\Delta_{\beta l}\Big)(\mathcal{G}^{0+}+\mathcal{G}^{0+}V\mathcal{G}^{0+}+\mathcal{G}^{0+}V\mathcal{G}^{0+}V\mathcal{G}^{0+}+\dots). \qquad (\mathrm{A3})$$

We then Fourier transform to $\vec{k}$ space, defining $\mathcal{G}^{+}_{j}(\vec{k})$ as for the single-impurity problem, and average over all possible configurations of the cN impurities. We obtain for the configuration-averaged Green's function $\langle\mathcal{G}^{+}(\vec{k})\rangle$, where the lattice-site index j drops out as expected,

$$\langle\mathcal{G}^{+}(\vec{k})\rangle=\mathcal{G}^{0+}(\vec{k})+\frac{1}{N}\sum_{\vec{k}'}\sum_{\sigma,\sigma'}\mathcal{G}^{0+}(\vec{k}')V^{1}_{\sigma'\sigma}\,\mathcal{G}^{0+}(\vec{k})\,e^{-i(\vec{k}'\cdot\vec{\sigma}'-\vec{k}\cdot\vec{\sigma})}\langle\rho(\vec{k}'-\vec{k})\rangle+\cdots-\frac{1}{N}\sum_{\vec{k}'}\mathcal{G}^{0+}(\vec{k})\langle\rho(\vec{k}'-\vec{k})\rangle$$

$$-\frac{1}{N^2}\sum_{\vec{k}',\vec{k}''}\sum_{\sigma',\sigma}\mathcal{G}^{0+}(\vec{k}'')V^{1}_{\sigma'\sigma}\,\mathcal{G}^{0+}(\vec{k}')\,e^{-i(\vec{k}''\cdot\sigma'-\vec{k}'\cdot\vec{\sigma})}\langle\rho(\vec{k}''-\vec{k}')\rho(\vec{k}'-\vec{k})\rangle-\cdots, \qquad (\mathrm{A4})$$

where we have defined $\rho(\vec{k})=\Sigma_\beta\,e^{-i\vec{k}\cdot\vec{\beta}}$. The explicit expressions for the configuration averages of the products of $\rho(\vec{k})$ are discussed, for example, by Yonezawa.[12] Expression (A4) can then be expressed in diagrammatic form, as discussed, for example, in the work of Jones[13] on fixed-moment systems. We wish to consider, as does Jones, only those scattering processes which contribute to first order in the concentration; hence we retain only the terms of order c in the proper self-energy. We note that, since the perturbation is small in spatial extent but not small in magnitude, we may truncate the series in c but must keep all orders in the perturbation V^1. We obtain for $\langle\mathcal{G}^{+}(\vec{k})\rangle$,

$$\langle\mathcal{G}^{+}(\vec{k})\rangle=\frac{\pi^{-1}\langle S^z\rangle(E+\Delta)[1-cD_s^{-1}(E)]}{E^2-\Delta^2+2\langle S^z\rangle A\Delta^2\gamma_{\vec{k}}[1-cD_s^{-1}(E)]}\,. \qquad (\mathrm{A5})$$

The term $-cD_s^{-1}(E)$ in the numerator, analogous to that called L in Ref. 13, is the contribution from the terminal diagrams (called interference diagrams by Jones), and the term $-2c\langle S^z\rangle A\Delta^2\gamma_{\vec{k}}D_s^{-1}(E)$ in the denominator, called $\sigma(\vec{k},\omega)$ in the analogous result of Jones, is the self-energy correction, due to the impurities, to the dispersion relation of a pure crystal.

Comparing (A5) with (2.14), which is the Green's function, correct to order $1/N$ for the crystal containing a single impurity, we see that an extension to a finite concentration c, to first order in c, involves only the replacement of $1/N$ by c.

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Hall Effect in VO$_2$ near the Semiconductor-to-Metal Transition[*]

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Hall-effect measurements as a function of temperature have been made on single-crystal samples of VO$_2$ at temperatures both above and below the semiconductor-to-metal transition temperature; the Hall mobility in the semiconducting phase was approximately 0.5 cm^2/V sec and in the metallic phase approximately 0.35 cm^2/V sec.

INTRODUCTION

A number of transition-metal-oxide compounds exhibit large, nearly discontinuous decreases in their resistance at a specific temperature as their temperature is increased; the mechanism causing these semiconductor-to-metal transitions and its relationship to the unusual properties of both the semiconducting and metallic phases of these materials are not well understood at this time. Vanadium dioxide is a good example of such a material; good single-crystal samples of VO$_2$ have shown a semiconductor-to-metal transition at 67 °C at which their resistance decreased by as much as a factor of 10^5 in less than 0.1 °C with a hysteresis on cooling of about 1 °C.[1] This resistivity transition is accompanied by a structural transformation in which the tetragonal (rutile) high-temperature phase is converted into a related monoclinic low-temperature structure in which the vanadium atoms form alternate staggered pairs along the c_r axis.[2] Discontinuous changes in the magnetic susceptibility and optical properties and a latent heat of about 1020 cal/mole have also been observed at the semiconductor-to-metal transition.[3] Various theories which describe the semiconductor-to-metal transition make more or less specific statements concerning the change in electrical carrier density at the transition or the processes by which the electrical conduction occurs in the high- or low-temperature phase. The low mobility of the carriers in VO$_2$ makes measurement of their properties difficult. In spite of the difficulty of interpreting Hall-effect measurements in terms of carrier densities and carrier mobilities, it was felt that such measurements would be of some use in discussing the application of certain theories to VO$_2$.

EXPERIMENTAL DETAILS

Our samples were high-quality VO$_2$ single crystals grown by the slow cooling of VO$_2$ dissolved in a flux of V$_2$O$_5$ in a sealed fused-silica ampoule, in a manner similar to that of Ladd.[1] The best crystals were grown at a cooling rate of 3.6 °C/h, cooling from 1070 to 720 °C with about a 2.5 °C/cm temperature gradient, and starting from an initial mixture of VO$_2$ and V$_2$O$_5$ with a composition corresponding to VO$_{2.41}$.[4] The samples were approximately 5 mm long and 0.5×0.5 mm in cross section with their long axes in the c_r direction; all electrical measurements reported here were made parallel to this direction.

Hall-effect measurements were complicated by the unusually large amount of noise observed between the Hall contacts in the semiconducting phase which seems to be associated with strain in the sample arising from the discontinuous change of the lattice dimensions at the semiconductor-to-metal transition. For this reason, our Hall-effect measurements were made with a specially constructed Hall-effect apparatus which employs a dc electric current and an ac magnetic field.[4] An ac magnetic field at 35 Hz with an amplitude of 11 kG peak-to-peak was furnished by a small magnet with a 0.32-cm air gap driven through a resonant circuit by a modified 40-W ac power amplifier. In order to minimize inductive pickup from the magnetic field, all leads to the sample were formed as twisted