Ising Chain with a Spin Impurity*

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Consider a closed, linear chain of N localized spins (each $s=\frac{1}{2}$) with nearest-neighbor Ising interaction. Such a chain, exposed to a uniform external magnetic field, will be called the pure host. Replace a single spin in the pure host by an impurity spin which is also subjected to nearest-neighbor Ising interaction and to the external field. The magnitude of the impurity spin, the magnitude of its magnetic moment, and the magnitude and sign of its interaction with the host are allowed to differ from the corresponding values characterizing the host. For the bulk system ($N\to\infty$, for constant linear density of spins), the thermodynamic properties, such as the impurity magnetization, the (position-dependent) magnetization of the impurity-host system and the impurity-host spin correlation functions, are obtained exactly in terms of conventional, tabulated functions. Numerical results are presented for impurity spins of magnitude $S=\frac{3}{2}$, $\frac{5}{2}$.

1. INTRODUCTION

FOR the linear Ising chain in a uniform external magnetic field, the canonical partition function and the magnetization in the bulk limit were calculated by Ising[1] as part of his dissertation. He found that for any positive temperature T_{abs}, the magnetization $\to 0$ as the external field $H\to 0$. That result is independent of the sign of the nearest-neighbor interaction parameter, and led Ising to the correct conclusion that the linear model with short-range interactions does not provide a basis for the Weiss molecular field. On the other hand, the model is mathematically tractable for arbitrary fields and temperatures and is certainly a source of qualitative insight[2] into the noncritical behavior of more complicated spin systems. An additional positive feature is the ease of generalizing the model so as to include spin-$\frac{1}{2}$ impurities with interaction parameters and magnetic moments which may differ from those of the host. Edelstein[3] has discussed such generalized Ising models with spin-$\frac{1}{2}$ impurities and has been able to achieve favorable comparison with observed magnetic behavior of certain organic free radicals.

Incisive observation of the behavior of magnetic impurities is provided by Mössbauer techniques, and experiments have, in part, motivated a recent approximate calculation[4] which deals mainly with the thermodynamic properties of a single, spin-S impurity in a simple-cubic Heisenberg ferromagnet. For reference it seems worthwhile to obtain the exact thermodynamic properties of a spin-S impurity in an Ising chain with either ferromagnetic or antiferromagnetic nearest-neighbor interactions. Such is the purpose of the present paper. The results follow in a straightforward manner on the basis of transfer-matrix methods.[5] The impurity magnetization and the (position-dependent) magnetization of the impurity-host system and the impurity-host spin correlation functions are expressed in terms of conventional, tabulated functions (e.g., Brillouin functions). For certain selected fields and temperatures, the magnetic properties are displayed graphically for various cases, e.g., (1) a spin-$\frac{3}{2}$ antiferromagnetic impurity imbedded in an antiferromagnetic host; (2) a spin-$\frac{3}{2}$ antiferromagnetic impurity imbedded in a ferromagnetic host, etc.

2. PARTITION FUNCTION

Consider a linear chain of N lattice points labeled $1, 2, \cdots, N$, successively, and associate with each point a localized spin. Let all the spins except that at point $N/2$ (N even) have magnitude $\frac{1}{2}$. The spin at point $N/2$ has magnitude S to be selected from the possible values $\frac{1}{2}, 1, \frac{3}{2}, 2\cdots$. The chain is closed so that the ordered points lie on a circle, and a periodic boundary condition is thereby imposed. The z axis is defined by a uniform magnetic field H perpendicular to the plane of the circle. With s_i^z denoting the z component of the spin at point i, and μ denoting the Bohr magneton, the Hamiltonian of the system being considered is

$$\mathcal{H}=\sum_{i=1}^{N}\mathfrak{h}(s_i^z,s_{i+1}^z)\,,\quad (s_{N+1}^z\equiv s_1^z)\,,$$

where

$$\begin{aligned}\mathfrak{h}(s_i^z,s_{i+1}^z)&=2\epsilon J s_i^z s_{i+1}^z+g\mu H[(s_i^z+s_{i+1}^z)/2]\,,\quad \text{for}\quad i=1,2,\cdots,N/2-2,N/2+1,\cdots,N;\\&=2\bar{\epsilon}\bar{J}s_{N/2-1}^z s_{N/2}^z+\mu H[(g s_{N/2-1}^z+\bar{g}s_{N/2}^z)/2]\,,\quad \text{for}\quad i=N/2-1;\\&=2\bar{\epsilon}\bar{J}s_{N/2}^z s_{N/2+1}^z+\mu H[(\bar{g}s_{N/2}^z+g s_{N/2+1}^z)/2]\,,\quad \text{for}\quad i=N/2.\end{aligned}$$

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The nearest-neighbor interaction parameter J for the host is defined to be non-negative so that ϵ is $+1$ for an antiferromagnetic host and -1 for a ferromagnetic host. The Landé factor is denoted by g, and the quantities $\bar{J}$, $\bar{\epsilon}$, and $\bar{g}$ are defined analogously for the impurity.

The computation of the partition function is readily accomplished in terms of the following quantities. Let $\beta=1/$(the Boltzmann constant k_B times the absolute temperature T_{abs}), and introduce the matrices

$$T_i=[\exp\{-\beta\mathfrak{h}(s_i^z,s_{i+1}^z)\}]\equiv \begin{array}{c} \\ s_i^z=-\frac{1}{2} \\ s_i^z=+\frac{1}{2}\end{array}\!\!\begin{array}{c} \begin{array}{cc} s_{i+1}^z=-\frac{1}{2} & s_{i+1}^z=+\frac{1}{2}\end{array} \\ \begin{bmatrix} \exp\{-\beta\mathfrak{h}(-\frac{1}{2},-\frac{1}{2})\} & \exp\{-\beta\mathfrak{h}(-\frac{1}{2},+\frac{1}{2})\} \\ \exp\{-\beta\mathfrak{h}(+\frac{1}{2},-\frac{1}{2})\} & \exp\{-\beta\mathfrak{h}(+\frac{1}{2},+\frac{1}{2})\}\end{bmatrix}\end{array}$$

for $i=1, 2, \cdots, N/2-2, N/2+1, \cdots, N$. Clearly, the 2×2 matrix is symmetric and independent of i (note: $i\neq N/2-1$ or $N/2$), and may be written

$$T=e^{K\epsilon}\begin{pmatrix}\phi_- & 1\\ 1 & \phi_+\end{pmatrix},$$

where

$$K\equiv\beta J/2,\quad h\equiv g\mu H/(2J),$$

and

$$\phi_\pm\equiv\exp[-2K(\epsilon\pm h)].$$

For future discussion I now introduce $\theta\equiv1/(4K)$.

The $2\times(2S+1)$ matrix $\bar{T}$ is defined by

$$\bar{T}=[\exp\{-\beta\mathfrak{h}(s_{N/2-1}^z,s_{N/2}^z)\}]$$

$$\equiv \begin{array}{c} \\ s_{N/2-1}^z=-\frac{1}{2} \\ s_{N/2-1}^z=+\frac{1}{2}\end{array}\!\!\begin{array}{c} \begin{array}{cccc} s_{N/2}^z=-S & s_{N/2}^z=-S+1 & \cdots & s_{N/2}^z=+S\end{array} \\ \begin{bmatrix} \exp\{-\beta\mathfrak{h}(-\frac{1}{2},-S)\} & \exp\{-\beta\mathfrak{h}(-\frac{1}{2},-S+1)\} & \cdots & \exp\{-\beta\mathfrak{h}(-\frac{1}{2},+S)\} \\ \exp\{-\beta\mathfrak{h}(+\frac{1}{2},-S)\} & \exp\{-\beta\mathfrak{h}(+\frac{1}{2},-S+1)\} & \cdots & \exp\{-\beta\mathfrak{h}(+\frac{1}{2},+S)\}\end{bmatrix}\end{array},$$

and the $(2S+1)\times2$ matrix

$$\bar{T}^{\mathcal{T}}=[\exp\{-\beta\mathfrak{h}(s_{N/2}^z,s_{N/2+1}^z)\}],$$

defined by obvious analogy, is seen to equal the transpose of $\bar{T}$. It is helpful to express $-\beta\mathfrak{h}(s_i^z,s_{i+1}^z)$ in terms of the parameters

$$\rho\equiv\bar{J}/J,\quad \lambda\equiv\bar{g}/g,$$

and K; the result is

$$\begin{aligned}-\beta\mathfrak{h}(s_i^z,s_{i+1}^z)&=-4K\epsilon s_i^z s_{i+1}^z-4Kh[s_i^z+s_{i+1}^z)/2],\quad\text{for}\quad i=1,2,\cdots,N/2-2,N/2+1,\cdots,N;\\ &=-4K\bar{\epsilon}\rho s_{N/2-1}^z s_{N/2}^z-4Kh[(s_{N/2-1}^z+\lambda s_{N/2}^z)/2],\quad\text{for}\quad i=N/2-1;\\ &=-4K\bar{\epsilon}\rho s_{N/2}^z s_{N/2+1}^z-4Kh[(\lambda s_{N/2}^z+s_{N/2+1}^z)/2],\quad\text{for}\quad i=N/2.\end{aligned}$$

The partition function

$$Z=\sum_{\substack{\text{all states}\\ \{s_1^z,\cdots,s_N^z\}}}\exp(-\beta\mathcal{H})$$

is simply[2]

$$\begin{aligned}&=\operatorname{tr}(T^{N/2-2}\bar{T}\bar{T}^{\mathcal{T}}T^{N/2})\\ &=\operatorname{tr}(T^{N-2}\bar{T}\bar{T}^{\mathcal{T}})\\ &=\operatorname{tr}(T_{\text{diag}}{}^{N-2}U^{-1}\bar{T}\bar{T}^{\mathcal{T}}U),\end{aligned}$$

where the orthogonal matrix U transforms T to a diagonal matrix

$$T_{\text{diag}}=U^{-1}TU.$$

The eigenvalues of T are readily found to be

$$\omega_\pm=e^{-K\epsilon}[\cosh(2Kh)\pm(\sinh^2(2Kh)+e^{4K\epsilon})^{1/2}]$$

with corresponding orthonormal eigenvectors

$$\begin{pmatrix}a_+\\ b_+\end{pmatrix}=\begin{pmatrix}\cos\delta\\ \sin\delta\end{pmatrix},$$

$$\begin{pmatrix}a_-\\ b_-\end{pmatrix}=\begin{pmatrix}-\sin\delta\\ \cos\delta\end{pmatrix},$$

where

$$\cos\delta\equiv-\alpha_+/(1+\alpha_+^2)^{1/2},$$
$$\sin\delta\equiv1/(1+\alpha_+^2)^{1/2},$$

and

$$\alpha_+\equiv-e^{-2K\epsilon}[\sinh(2Kh)+(\sinh^2(2Kh)+e^{4K\epsilon})^{1/2}].$$

Since $|\omega_-/\omega_+|<1$ (and $\omega_-<\omega_+$) for all positive temperatures, ω_+ will be referred to as the maximum eigenvalue, and its corresponding eigenvector as the maximum eigenvector of the host transfer matrix T.

The orthogonal matrix U is written

$$U=\begin{pmatrix}\cos\delta & -\sin\delta\\ \sin\delta & \cos\delta\end{pmatrix},$$

and, by definition, U^{-1} is the transpose of U.

The computation of the matrix product $\bar{T}T^{T}$ leads to a concise result, since the sums which appear are all of the form[6]

$$\sum_{j=-S}^{+S} e^{-2jx}=\sinh[(2S+1)x]/\sinh x.$$

It is therefore convenient to introduce the function

$$G_S(x)\equiv\sinh[(2S+1)x]/[(2S+1)\sinh x].$$

Then

$$\bar{T}T^{T}=(2S+1)\begin{pmatrix}Y_+ & Y_0\\ Y_0 & Y_-\end{pmatrix},$$

where

$$Y_\pm\equiv e^{\pm 2Kh}G_S(\eta_\pm),$$
$$Y_0\equiv G_S(\eta_0),$$
$$\eta_\pm\equiv 2K(\mp\bar{\epsilon}\rho+h\lambda),$$

and

$$\eta_0\equiv 2Kh\lambda.$$

In terms of the above notation, the exact partition function for the N-spin impurity-host system is

$$Z=(2S+1)\omega_+^{N-2}\,\mathrm{tr}\left[\begin{pmatrix}1 & 0\\ 0 & (\omega_-/\omega_+)^{N-2}\end{pmatrix}\begin{pmatrix}a_+ & b_+\\ a_- & b_-\end{pmatrix}\times\begin{pmatrix}Y_+ & Y_0\\ Y_0 & Y_-\end{pmatrix}\begin{pmatrix}a_+ & a_-\\ b_+ & b_-\end{pmatrix}\right].$$

For positive temperatures the magnitude of $(\omega_-/\omega_+)^{N-2}$ diminishes exponentially with increasing N; consequently, for positive temperatures and N large

$$Z\cong(2S+1)\omega_+^{N-2}D, \tag{1}$$

where

$$D\equiv a_+^2Y_++2a_+b_+Y_0+b_+^2Y_-.$$

In the bulk limit the quantities computed with (1) will be exact, and, unless otherwise stated, all succeeding ensemble averages are considered only in that limit.

[6] J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders, Company, Philadelphia, 1966).

3. MAGNETIZATION

The impurity magnetization[7] in the bulk limit is here defined by the canonical ensemble average

$$\sigma_{N/2}\equiv\langle s_{N/2}^z\rangle/S\equiv(ZS)^{-1}\sum_{\text{all states}} s_{N/2}^z\exp(-\beta\mathcal{H})$$
$$=-(4KhS)^{-1}(\partial/\partial\lambda)\ln Z,$$

but $(2S+1)\omega_+^{N-2}$ is independent of λ; so that

$$\sigma_{N/2}=-(4KhS)^{-1}(\partial/\partial\lambda)\ln D.$$

Now the only dependence of D on λ is implicit through $G_S(\eta_\pm)$ and $G_S(\eta_0)$; therefore by using the relation

$$\partial G_S(x)/\partial x=2SG_S(x)B_S(2Sx),$$

where $B_S(y)$ is the familiar[6] Brillouin function defined by

$$B_S(y)=[(2S+1)/(2S)]\coth[(2S+1)y/(2S)]-[1/(2S)]\coth[y/(2S)],$$

one finds

$$\sigma_{N/2}=-(a_+^2Y_+B_++2a_+b_+Y_0B_0+b_+^2Y_-B_-)/D, \tag{2}$$

with

$$B_\pm\equiv B_S(2S\eta_\pm),$$
$$B_0\equiv B_S(2S\eta_0).$$

It is readily verified that $\sigma_{N/2}=0$ for $h=0$, $T_{\text{abs}}>0$; and that for $\rho=0$ the magnetization of the uncoupled impurity spin is $\sigma_{N/2}=-B_S(4SKh\lambda)$, as expected.

It is interesting to compare the impurity magnetization with the magnetization of the uncontaminated (pure) host. In the bulk limit the pure-host magnetization is given by

$$\sigma_{\text{host}}=-(2K)^{-1}(\partial/\partial h)\ln\omega_+$$
$$=-\sinh(2Kh)/(\sinh^2(2Kh)+e^{4K\epsilon})^{1/2}, \tag{3}$$

i.e., the well-known[1] expression which vanishes as $h\to 0$ for all $T_{\text{abs}}>0$. It is apparent that for $T_{\text{abs}}=0$,

$$\sigma_{\text{host}}=0 \quad\text{for}\quad h<1,\quad \epsilon=1 \text{ (antiferromagnetic case)};$$
$$=-1 \quad\text{for}\quad h>1,\quad \epsilon=1 \text{ (antiferromagnetic case)};$$
$$=-1 \quad\text{for}\quad h>0,\quad \epsilon=-1 \text{ (ferromagnetic case)}.$$

Of future use will be the following simply derived relation between the pure-host magnetization and the components of the maximum eigenvector of the host transfer matrix:

$$\sigma_{\text{host}}=b_+^2-a_+^2=1-2a_+^2. \tag{3'}$$

Figure 1 shows the magnetization of an antiferromagnetic pure host, and the magnetization of a spin-$\frac{3}{2}$ impurity imbedded in an antiferromagnetic host. The host-impurity coupling is also taken to be antiferromag-

[7] In the following, the term, magnetization, will be used interchangeably with the phrase, average spin projection. These quantities will frequently refer to a particular lattice point, since the impurity-host system is not homogeneous.

netic with $\bar{J}=J$, and the Landé factor $\bar{g}$ is put equal to g; therefore $\rho=\lambda=1$. For $h<1$ and low temperatures,[8] neighboring pure-host spins have essentially antiparallel alignment. As the temperature is increased for a fixed value of $h<1$, the Zeeman term begins to dominate and the field begins to overcome the antiferromagnetic alignment. The resultant magnetization achieves a maximum magnitude and then decreases with increasing temperature. For $h>1$ the Zeeman term dominates for all non-negative temperatures, and the pure-host spins behave like those of a ferromagnetic pure host exposed to a field of magnitude $h-1$. It is clear that even for large fields ($h=\frac{4}{3}$), the impurity magnetization does not quantitatively follow the pure-host magnetization for $T_{\text{abs}}>0$.

Figure 2 indicates a quite different situation for a spin-$\frac{3}{2}$ impurity antiferromagnetically coupled to a ferromagnetic host. For $h\lambda<\rho$ (in this example $\rho=\lambda=1$) and low temperatures, the impurity spin orients opposite to the other spins, but as the temperature increases, the impurity wilts and submits to the increasing influence of the field which tends to align the impurity parallel to the other spins. For $h\lambda>\rho$ the Zeeman term dominates for all $T_{\text{abs}}\geqq 0$, and the impurity magnetization follows closely the pure-host magnetization.

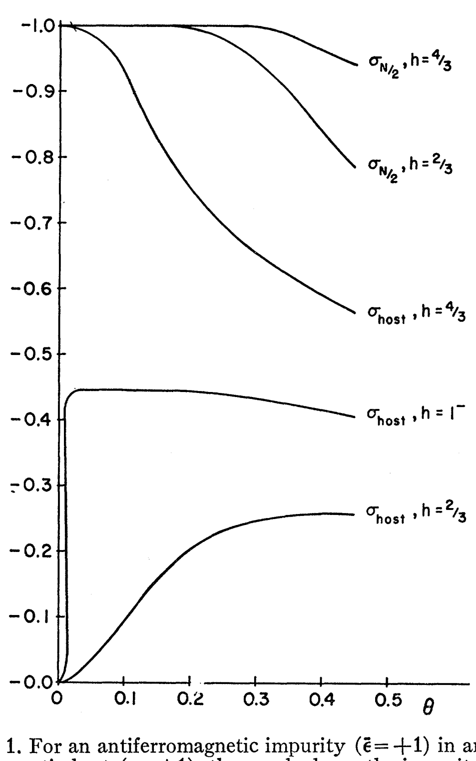

FIG. 1. For an antiferromagnetic impurity ($\bar{\epsilon}=+1$) in an antiferromagnetic host ($\epsilon=+1$), the graph shows the impurity magnetization $\sigma_{N/2}$ and the pure—host magnetization σ_{host} versus temperature ($\theta\equiv k_BT_{\text{abs}}/(2J)$) for selected fields ($h\equiv g\mu H/(2J)$). The impurity spin has magnitude $S=\frac{3}{2}$, and the parameters J and g have been taken equal to $\bar{J}$ and $\bar{g}$, respectively. The symbol $1^-\equiv 1-\delta$, where $0<\delta\ll 1$.

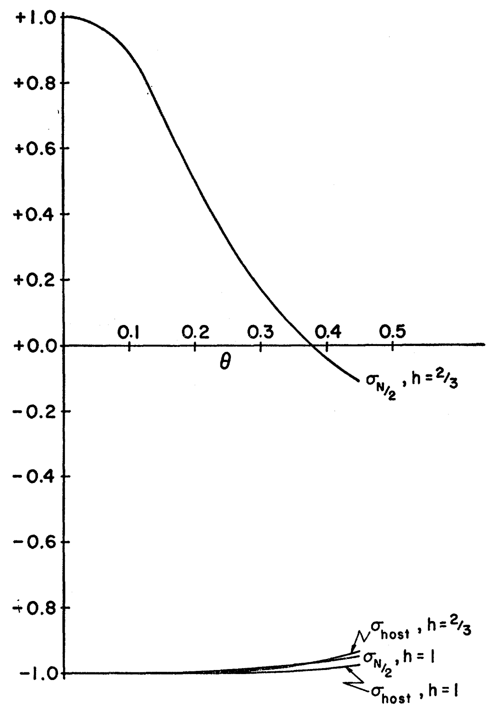

FIG. 2. Same as Fig. 1 except that the host is ferromagnetic ($\epsilon=-1$).

A better understanding of the above behavior is approached by considering the (position-dependent) magnetization of the impurity-host system. One then sees how the spins of the host are influenced by the presence of the impurity. The quantity of interest is the bulk-limit magnetization

$$\sigma_{N/2-t}\equiv\langle s_{N/2-t}{}^z\rangle/\tfrac{1}{2}=(-4KhZ/2)^{-1}[(\partial/\partial v)\times\mathrm{tr}(T_{\text{diag}}{}^{N-t-2}U^{-1}T(v)T^{\mathcal{T}}(v)UT_{\text{diag}}{}^{t-2}U^{-1}\bar{T}\bar{T}^{\mathcal{T}}U)]_{v=1}$$

for $t=2, 3, \cdots, N/2-1$. The matrices $T(v)$ and $T^{\mathcal{T}}(v)$ are defined in Appendix A, where it is apparent that $\sigma_{N/2-t}$ is implicitly obtained in the process of calculating $\langle s_{N/2-t}{}^z s_{N/2}{}^z\rangle$. Thus

$$\sigma_{N/2-t}=(-4KhZ/2)^{-1}(2S+1)(2Kh)\omega_+{}^{N-2}\{D(a_+{}^2-b_+{}^2)+(\omega_-/\omega_+)^{t-1}(a_+a_--b_+b_-)\times[a_+a_-Y_++(a_+b_-+b_+a_-)Y_0+b_+b_-Y_-]\},$$

which, with (1) and (3′), is put into the form

$$\sigma_{N/2-t}=\sigma_{\text{host}}-(\omega_-/\omega_+)^{t-1}(a_+a_--b_+b_-)\times\{[a_+a_-Y_++(a_+b_-+b_+a_-)Y_0+b_+b_-Y_-]/D\},\quad(4)$$

where $t=2, 3, \cdots, N/2-1$. Now only the bulk limit is being considered; so that there is essentially symmetry about the impurity spin, and $(\omega_-/\omega_+)^{t-1}$ could be replaced by $(\omega_-/\omega_+)^{|t|-1}$ in (4) which would then obtain for $t=\pm 2, \pm 3, \cdots, \pm N/2-1$. Recall that the periodic boundary condition ensures that $\sigma_{N+1}=\sigma_1$.

[8] In the present context, the temperature will be referred to as high or low in accord with whether $\theta\equiv k_BT_{\text{abs}}/(2J)$ is $\gg\frac{1}{2}$ or $\ll\frac{1}{2}$, respectively.

To compute $\sigma_{N/2-1}$, which is equal to $\sigma_{N/2+1}$ by symmetry in the bulk limit, replace the product $h\lambda$ by h' and then replace h by h'' in the arguments of the elements of $\bar{T}$ and $\bar{T}^{\mathcal{T}}$. Then

$$\sigma_{N/2-1}=\sigma_{N/2+1}=(-4KZ/2)^{-1}[(\partial/\partial h'')\times\mathrm{tr}(T_{\mathrm{diag}}{}^{N-2}U^{-1}\bar{T}(h',h'')\bar{T}^{\mathcal{T}}(h',h'')U)]_{\substack{h''=h\\ h'=h\lambda}}$$

$$=-(a_+{}^2Y_+-b_+{}^2Y_-)/D. \quad (5)$$

The following checks have been performed: for $h=0$, $\sigma_{N/2-t}=\sigma_{N/2\pm 1}=\sigma_{\mathrm{host}}=0$; and for $\epsilon=\bar{\epsilon}$ and $\rho=\lambda=2S=1$, $\sigma_{N/2-t}=\sigma_{N/2\pm 1}=\sigma_{\mathrm{host}}$, as expected, since the impurity spin has completely lost its identity and the impurity-host system becomes indistinguishable from the pure host.

Now the definitions of ω_+ and ω_- lead to the formula

$$\omega_-/\omega_+=-2(\sinh 2K\epsilon)/\omega_+{}^2, \quad \text{for} \quad h\geqq 0;$$
$$=-\tanh K\epsilon, \quad \text{for} \quad h=0,$$

which indicates that the impurity adds to the antiferromagnetic host magnetization a term whose sign alternates as t changes by an odd integer. Recall that for positive temperatures $|\omega_-/\omega_+|<1$; so that $(\omega_-/\omega_+)^{|t|}$ decreases in magnitude with increasing $|t|$. Clearly, as $|t|$ becomes very large, the average spin projection $\sigma_{N/2-t}$ will tend to approach the value of σ_{host}. For nontrivial ($\rho>0$) impurity-host coupling, how large must $|t|$ be before the presence of the impurity is not significantly reflected in the value of $\sigma_{N/2-t}$; i.e., what is the size of the domain of influence of the impurity. To roughly answer this question, observe that

$$\omega_-/\omega_+\sim e^{-4Kh}+O(e^{-4K(h+1)}), \quad \text{for} \quad 0<h,\ \epsilon=-1;$$
$$\sim -e^{-4K(h-1)}+O(e^{-8K(h-1)}), \quad \text{for} \quad 1<h,\ \epsilon=+1;$$
$$\sim -1+e^{-2K(1-h)}+O(e^{-4K(1-h)}+e^{-4Kh}), \quad \text{for} \quad 0<h<1,\ \epsilon=+1.$$

For the ferromagnetic case ($\epsilon=-1$) at low temperatures and $0<h$, the domain of influence of the impurity is, thus, crudely measured by the distance (in number of lattice spacings)

$$l\sim 1/(4Kh)=k_BT_{\mathrm{abs}}/(g\mu H), \quad \text{for} \quad e^{-4K(h+1)}\ll 1,\ 0<h,\ \epsilon=-1;$$

whereas for the antiferromagnetic case ($\epsilon=+1$),

$$l\sim 1/[4K(h-1)]=k_BT_{\mathrm{abs}}/(g\mu H-2J), \quad \text{for} \quad e^{-8K(h-1)}\ll 1,\ 1<h,\ \epsilon=+1;$$
$$\sim e^{2K(1-h)}, \quad \text{for} \quad (e^{-4K(1-h)}+e^{-4Kh})\ll 1,\ 0<h<1,\ \epsilon=+1.$$

In particular, notice that for the antiferromagnetic host, the polarizing influence of the impurity extends over a large number of spins for a significant region of the $H-T_{\mathrm{abs}}$ plane. Physically, at low temperatures, the ferromagnet in a moderate field and the antiferromagnet in a large field ($1<h$) are both "frozen" by the field and only spins adjacent to the impurity sense the impurity. But at low temperatures and $0<h<1$, the antiferromagnet is highly energetically degenerate, and the presence of the impurity tends to stabilize the system.

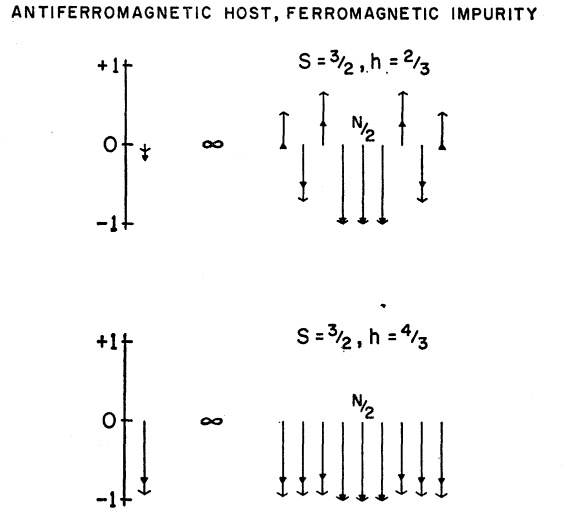

FIG. 3. The vectors represent the average spin projections (magnetization) $\sigma_{N/2-t}$ for $t=0, \pm 1, \pm 2, \pm 3, \pm 4$. The impurity is at site $N/2$, and the vector on the far left represents the pure-host magnetization for the same field and temperature. Open arrows are used for a temperature $\theta=0.1$, and closed arrows are used for $\theta=0.2$.

The above very qualitative discussion is reinforced by numerical results displayed in Figs. 3, 4, 5, and 6, which, unless specified, are essentially unchanged for a spin-$\frac{5}{2}$ impurity. It is helpful to know that for this model: the configuration[9] $|\cdots -\frac{1}{2}, +S, -\frac{1}{2}\cdots\rangle$ is energetically

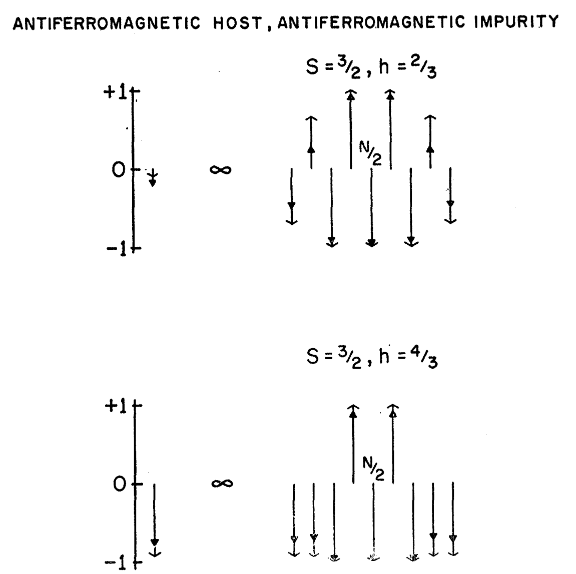

FIG. 4. See caption for Fig. 3.

[9] The symbol $|\rangle$ denotes a state of the many-spin system. In comparing two states, spins which are both irrelevant and have fixed orientation are simply indicated by dots.

favored over $|\cdots -\frac{1}{2}, -S, -\frac{1}{2}\cdots\rangle$ if and only if $h\lambda<\rho$, independent of S; and the configuration $|\cdots -\frac{1}{2}, -\frac{1}{2}, +S, -\frac{1}{2}, -\frac{1}{2}\cdots\rangle$ is energetically favored over $|\cdots -\frac{1}{2}, +\frac{1}{2}, -S, +\frac{1}{2}, -\frac{1}{2}\cdots\rangle$ if and only if $\epsilon<(2-2S\lambda)h$; furthermore $|\cdots -\frac{1}{2}, +\frac{1}{2}, -S, +\frac{1}{2}, -\frac{1}{2}\cdots\rangle$ is energetically favored over $|\cdots -\frac{1}{2}, -\frac{1}{2}, -S, -\frac{1}{2}, -\frac{1}{2}\cdots\rangle$ if and only if $h<(\epsilon/2+\bar{\epsilon}\rho S)$.

4. CORRELATION

The correlation[10] between spins is conveniently discussed in terms of the canonical ensemble average $(\langle s_f^z s_g^z\rangle - \langle s_f^z\rangle\langle s_g^z\rangle)$. The first correlation to be calculated is that between the impurity spin $s_{N/2}^z$ and the nearest-neighbor host spins $s_{N/2-1}^z$ and $s_{N/2+1}^z$. By referring back to the derivation of (1), one sees that in the bulk limit,

$$\begin{aligned}\langle s_{N/2-1}^z s_{N/2}^z\rangle/\tfrac{1}{2}S &= \langle s_{N/2}^z s_{N/2+1}^z\rangle/\tfrac{1}{2}S\\ &= (1/2)(S/2)^{-1}(-4K\rho)^{-1}(\partial/\partial\bar{\epsilon})\ln Z\\ &= (-4K\rho S)^{-1}(\partial/\partial\bar{\epsilon})\ln D\\ &= (a_+^2 Y_+ B_+ - b_+^2 Y_- B_-)/D. \end{aligned}\qquad(6)$$

For $h=0$ the situation is simplified, since

$$\left.\begin{aligned} &Y_+=Y_-=G_S(2K\bar{\epsilon}\rho)\,,\\ &B_+=-B_-=-B_S(2S\times 2K\bar{\epsilon}\rho)\,,\\ &a_+=b_+=-a_-=b_-=1/\sqrt{2}\,,\end{aligned}\right\}\quad\text{for}\quad h=0$$

and one has

$$\sigma_{N/2-1}=\sigma_{N/2+1}=\sigma_{N/2}=0\,;$$

therefore, with $\sigma_{N/2-t;N/2}\equiv\langle s_{N/2-t}^z s_{N/2}^z\rangle/\frac{1}{2}S$,

$$\sigma_{N/2-1;N/2}-\sigma_{N/2-1}\sigma_{N/2}=-B_S(2S\times 2K\bar{\epsilon}\rho)/[1+(1/G_S(2K\bar{\epsilon}\rho))],\quad\text{for}\quad h=0.\qquad(6.1)$$

Now the Brillouin function $B_S(y)=-B_S(-y)$; whereas $G_S(x)=G_S(-x)$. It follows that for $h=0$, the sign of the correlation between the impurity spin and a neighboring host spin is opposite to the sign of $\bar{\epsilon}$; i.e., antiferromagnetic impurity-host coupling ($\bar{\epsilon}=+1$) implies antiparallel nearest-neighbor impurity-host order for $h=0$, $T_{\text{abs}}\geqq 0$; etc. Notice that

$$\begin{aligned} G_S(x)&\sim 1\quad\text{for}\quad (2S+1)|x|\ll 1\,;\\ &\sim\frac{e^{2S|x|}}{2S+1}\quad\text{for}\quad |x|\gg 1\,;\end{aligned}$$

consequently, the nearest-neighbor correlation (6.1) is dominated by the behavior of the Brillouin function. For conditions such that $4SK\rho\gg 1$, the magnitude of (6.1) is close to unity and the impurity is strongly correlated with its nearest neighbors. At the other extreme $4SK\rho\ll 1$, and the magnitude of (6.1)$\sim 2SK\rho$.

One may put $\epsilon=\bar{\epsilon}$ and $\rho=\lambda=2S=1$ to recover from (6.1) the well-known, nearest-neighbor, pure-host correlation function

$$\begin{aligned}\langle s_i^z s_{i+1}^z\rangle/\tfrac{1}{4}-\langle s_i^z\rangle\langle s_{i+1}^z\rangle/\tfrac{1}{4}&\equiv\langle s_i^z s_{i+1}^z\rangle/\tfrac{1}{4}-\sigma_{\text{host}}^2\\ &=-\tanh K\epsilon,\quad\text{for}\quad h=0\quad\text{and}\quad i=1,2,\cdots,N-1.\end{aligned}\qquad(7)$$

For arbitrary fields $h\geqq 0$ and $i=1, 2, \cdots, N-1$, the nearest-neighbor, pure-host correlation function

$$\begin{aligned}\langle s_i^z s_{i+1}^z\rangle/\tfrac{1}{4}-\sigma_{\text{host}}^2&=(-K)^{-1}(\partial/\partial\epsilon)\ln\omega_+-\sigma_{\text{host}}^2\\ &=(1-\sigma_{\text{host}}^2)-[2e^{3K\epsilon}/[\omega_+(\sinh^2(2Kh)+e^{4K\epsilon})^{1/2}]].\end{aligned}\qquad(8)$$

In the bulk limit the correlation between the impurity-spin $s_{N/2}^z$ and the spin $s_{N/2-t}^z$ for $t=2, 3, \cdots, N/2-1$ is discussed in terms of

$$\begin{aligned}&\langle s_{N/2-t}^z s_{N/2}^z\rangle/\tfrac{1}{2}S-\langle s_{N/2-t}^z\rangle\langle s_{N/2}^z\rangle/\tfrac{1}{2}S\\ &\equiv\sigma_{N/2-t;N/2}-\sigma_{N/2-t}\sigma_{N/2}=(\sigma_{\text{host}}-\sigma_{N/2-t})\sigma_{N/2}\\ &\qquad+2(\omega_-/\omega_+)^{t-1}a_+a_-[a_+a_-Y_+B_+\\ &\qquad+(a_+b_-+b_+a_-)Y_0B_0+b_+b_-Y_-B_-]/D.\end{aligned}\qquad(9)$$

The derivation is given in Appendix A, and the reader should note that the term $(\sigma_{\text{host}}-\sigma_{N/2-t})$ is contained in (4); in fact the symmetry argument given after (4) applies as well to (9). For all positive temperatures, the impurity spin and any spin at "infinite separation" on

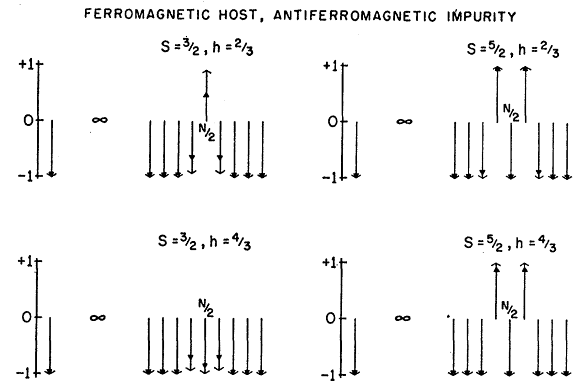

FIG. 5. See caption for Fig. 3.

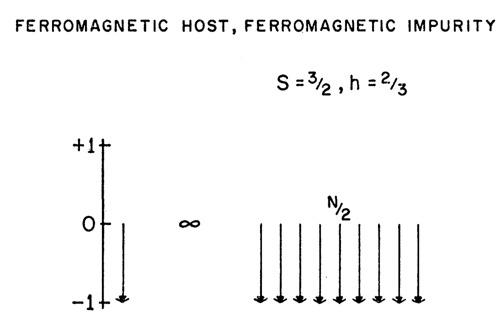

FIG. 6. See caption for Fig. 3.

[10] According to the conventional statistical definition of a correlation coefficient, one could consider

$$\begin{aligned}&\langle(s_f^z-\langle s_f^z\rangle)(s_g^z-\langle s_g^z\rangle)\rangle/[\langle(s_f^z-\langle s_f^z\rangle)^2\rangle^{1/2}\langle(s_g^z-\langle s_g^z\rangle)^2\rangle^{1/2}]\\ &\quad=(\langle s_f^z s_g^z\rangle-\langle s_f^z\rangle\langle s_g^z\rangle)/[(\langle(s_f^z)^2\rangle-\langle s_f^z\rangle^2)^{1/2}(\langle(s_g^z)^2\rangle-\langle s_g^z\rangle^2)^{1/2}].\end{aligned}$$

Our present interests are satisfied by a slightly different quantity which is adopted for simplicity.

the chain are manifestly statistically uncorrelated; thus there is absence of impurity-host long-range correlation.[11]

The latter result is not a surprise in view of rigorous arguments (see Domb, Ref. 2) about the absence of long-range order in one-dimensional classical systems with finite-range interactions. It should perhaps be iterated that there presently appears to be an absence of published rigorous arguments about the absence of long-range order in one-dimensional quantum-mechanical[12] systems with finite-range interactions.

For the special case of $h=0$, (9) reduces to

$$\sigma_{N/2-t;N/2}-\sigma_{N/2-t}\sigma_{N/2}=-(-\tanh K\epsilon)^{t-1}B_S(2S\times 2K\bar{\epsilon}\rho)/[1+(1/G_S(2K\bar{\epsilon}\rho))] \quad (9.1)$$

which, due to (6.1), is valid for $t=1, 2, \cdots, N/2-1$. For the antiferromagnetic host ($\epsilon=1$), the zero-field, impurity-host correlation alternates in sign and decreases in magnitude by factors of $\tanh K$ as t increases from unity by successive integers. One derives the pure-host correlation function

$$\langle s_i^z s_{i+t}^z\rangle/\tfrac{1}{4}-\sigma_{\text{host}}^2=(-\tanh K\epsilon)^t \quad \text{for } h=0 \text{ and } t=1, 2, \cdots, N-1, \quad (10)$$

from (9.1) by putting $\epsilon=\bar{\epsilon}$ and $\rho=\lambda=2S=1$ and using the translational invariance of the pure host. On the basis of previous discussion, one is able to think of following the correlation along the lattice. The initial "amplitude" transmitted from the impurity to its nearest neighbor is essentially a Brillouin function of index and argument appropriate to the parameters which characterize the impurity. From that point on, the amplitude is diminished by a "transfer coefficient" $|\tanh K\epsilon|$ which is simply the Brillouin function ($s=\frac{1}{2}$) which characterizes the pure-host, nearest-neighbor correlation—all for $h=0$.

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It is a pleasure to acknowledge the singular insight and kindness of Professor Robert Griffiths. I would also like to thank Professor Frederic Keffer and his students, Freddie Ninio and Paulo Silva, for informative discussions.

APPENDIX A

The computation of $\langle s_{N/2-t}^z s_{N/2}^z\rangle$ is accomplished by introducing a parameter v into the Hamiltonian in such a way that differentiation of the resulting $\ln Z(v)$ generates the desired ensemble average. Write

$$\begin{aligned}-\beta\mathfrak{h}(s_i^z,s_{i+1}^z;v)&=-4K\epsilon s_i^z s_{i+1}^z-4Kh[(s_i^z+s_{i+1}^z)/2], \quad \text{for } i\in Q\equiv\{1, 2, \cdots, N/2-t-2, N/2-t+1, \cdots, N/2-2, N/2+1, \cdots, N\};\\ &=-4K\epsilon s_{N/2-t-1}^z s_{N/2-t}^z-4Kh[(s_{N/2-t-1}^z+vs_{N/2-t}^z)/2], \quad \text{for } i=N/2-t-1;\\ &=-4K\epsilon s_{N/2-t}^z s_{N/2-t+1}^z-4Kh[(vs_{N/2-t}^z+s_{N/2-t+1}^z)/2], \quad \text{for } i=N/2-t;\\ &=-4K\bar{\epsilon}\rho s_{N/2-1}^z s_{N/2}^z-4Kh[(s_{N/2-1}^z+\lambda s_{N/2}^z)/2], \quad \text{for } i=N/2-1;\\ &=-4K\bar{\epsilon}\rho s_{N/2}^z s_{N/2+1}^z-4Kh[(\lambda s_{N/2}^z+s_{N/2+1}^z)/2], \quad \text{for } i=N/2,\end{aligned}$$

with $t=2, 3, \cdots, N/2-1$, and $s_0^z\equiv s_N^z$. Define

$$\mathfrak{H}(v)\equiv\sum_{i=1}^{N}\mathfrak{h}(s_i^z,s_{i+1}^z;v),$$

and denote the associated partition function by $Z(v)$; the original Hamiltonian and partition function are simply related to the newly defined quantities by $\mathfrak{H}=\mathfrak{H}(1)$, $Z=Z(1)$. Thus

$$\begin{aligned}\langle s_{N/2-t}^z s_{N/2}^z\rangle&=(-4Kh)^{-2}Z^{-1}(\partial/\partial\lambda)[(\partial/\partial v)Z(v)]_{v=1}\\ &=(16K^2h^2Z)^{-1}(\partial/\partial\lambda)[(\partial/\partial v)\\ &\quad\times\operatorname{tr}(T_{\text{diag}}^{N-t-2}U^{-1}T(v)T^{\mathcal{T}}(v)\\ &\quad\times UT_{\text{diag}}^{t-2}U^{-1}\bar{T}\bar{T}^{\mathcal{T}}U)]_{v=1},\end{aligned}$$

where the quantities have all been previously defined except

$$T(v)=[\exp\{-\beta\mathfrak{h}(s_i^z,s_{i+1}^z;v)\}]\equiv e^{K\epsilon}\begin{pmatrix}\gamma_-(v)\phi_- & \gamma_+(v)\\ \gamma_-(v) & \gamma_+(v)\phi_+\end{pmatrix},$$

and $T^{\mathcal{T}}(v)$ which is the transpose of $T(v)$. In the definition of $T(v)$ take $i\in Q$ and

$$\gamma_\pm(v)\equiv e^{\mp Kh(v-1)}, \quad (A1)$$

and notice that the original transfer matrix $T=T(1)$.

The calculation of

$$U^{-1}T(v)T^{\mathcal{T}}(v)U=(U^{-1}T(v)U)(U^{-1}T(v)U)^{\mathcal{T}}$$

is greatly facilitated by using the equations for the eigenvectors of T; namely,

$$(\phi_--\rho_\pm)a_\pm+b_\pm=0,$$

and

$$a_\pm+(\phi_+-\rho_\pm)b_\pm=0,$$

where $\rho_\pm\equiv e^{-K\epsilon}\omega_\pm$. With the definitions of $a_\pm$ and $b_\pm$

[11] The absence of long-range correlation follows from the vanishing of $\lim_{|t|\to\infty}(\omega_-/\omega_+)^{|t|}$, for all $T_{\text{abs}}>0$. One should distinguish that result from the vanishing of $\sigma_{N/2-t}$ and $\sigma_{N/2}$ as $h\to 0^+$ for $T_{\text{abs}}>0$; the latter being a statement about the absence of spontaneous magnetization. In this context long-range is synonymous with infinite-range.

[12] It is not here intended to construct sharp definitions of "classical" and of "quantum mechanical" as applied to one-dimensional systems. However, in the present discussion a classical one-dimensional system is one described by a Hamiltonian composed of commuting operators for which Domb's discussion (Ref. 2, p. 173) certainly obtains.

given in Sec. 2, it follows from inspection that

$$a_\pm^2+b_\pm^2=a_+^2+a_-^2=b_+^2+b_-^2=1\,,$$

and

$$a_+a_-+b_+b_-=a_+b_++a_-b_-=0\,.$$

With the above information one obtains

$$U^{-1}T(v)U=\begin{pmatrix}\tau_{11}(v) & \tau_{12}(v)\\ \tau_{21}(v) & \tau_{22}(v)\end{pmatrix},$$

where

$$\begin{aligned}\tau_{11}(v)&=\gamma_-\omega_+a_+^2+\gamma_+\omega_+b_+^2\,,\\ \tau_{12}(v)&=\gamma_-\omega_+a_+a_-+\gamma_+\omega_+b_+b_-\,,\\ \tau_{21}(v)&=\gamma_-\omega_-a_+a_-+\gamma_+\omega_-b_+b_-\,,\\ \tau_{22}(v)&=\gamma_-\omega_-a_-^2+\gamma_+\omega_-b_-^2\,.\end{aligned} \tag{A2}$$

By using the fact that in the bulk limit $(\omega_-/\omega_+)^{N-t-2}\rightarrow 0$ for positive temperatures and $t=2, 3, \cdots, N/2-1$, one finds

$$\begin{aligned}\langle s_{N/2-t}{}^z s_{N/2}{}^z\rangle &=(2S+1)\omega_+^{N-4}(16K^2h^2Z)^{-1}(\partial/\partial\lambda)\{(\partial/\partial v)[(\tau_{11}{}^2(v)\\ &\quad+\tau_{12}{}^2(v))D+(\omega_-/\omega_+)^{t-2}(a_+a_-Y_++(a_+b_-+b_+a_-)Y_0\\ &\quad+b_+b_-Y_-)(\tau_{11}(v)\tau_{21}(v)+\tau_{12}(v)\tau_{22}(v))]\}_{v=1}.\end{aligned} \tag{A3}$$

From (A1) and (A2)

$$\begin{aligned}\partial\tau_{11}(v)/\partial v|_{v=1}&=\omega_+Kh(a_+^2-b_+^2)\,,\\ \partial\tau_{12}(v)/\partial v|_{v=1}&=\omega_+Kh(a_+a_--b_+b_-)\,,\\ \partial\tau_{21}(v)/\partial v|_{v=1}&=\omega_-Kh(a_+a_--b_+b_-)\,,\\ \partial\tau_{22}(v)/\partial v|_{v=1}&=\omega_-Kh(a_-^2-b_-^2)\,,\\ \tau_{11}(1)&=\omega_+\,,\\ \tau_{12}(1)&=\tau_{21}(1)=0\,,\\ \tau_{22}(1)&=\omega_-\,;\end{aligned}$$

consequently

$$(\partial/\partial v)(\tau_{11}{}^2(v)+\tau_{12}{}^2(v))|_{v=1}=2\omega_+^2Kh(a_+^2-b_+^2)\,,$$

and

$$\begin{aligned}(\partial/\partial v)(\tau_{11}(v)\tau_{21}(v)+\tau_{12}(v)\tau_{22}(v))|_{v=1}\\ =2\omega_+\omega_-Kh(a_+a_--b_+b_-)\,.\end{aligned}$$

After referring back to (1), (3′), and the derivation of (2) one arrives at (9) by differentiating with respect to λ in (A3) and substituting

$$\begin{aligned}Z&=(2S+1)\omega_+^{N-2}D\,,\\ \sigma_{N/2}&=(-4KhS)^{-1}D^{-1}\partial D/\partial\lambda\,,\\ \sigma_{\text{host}}&=b_+^2-a_+^2\,.\end{aligned}$$

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Orthorhombic and Trigonal Electron-Spin-Resonance Spectra of Ce^{3+} Ions in CaF_2

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Two new electron-spin-resonance spectra, one having trigonal and the other having orthorhombic symmetry, have been observed in CaF_2 doped with small amounts of CeO_2. The x and y axes of the orthorhombic spectrum lie in the (110) plane and are tilted by an angle $\delta=13.8\pm0.2°$ from the [$\bar{1}$10] and the [001] axes, respectively, and the z axis lies along the [110] axis. The components of the g tensor for the two spectra are: orthorhombic, $g_x=0.844\pm0.001$, $g_y=0.22\pm0.05$, $g_z=3.286\pm0.001$; trigonal, $g_{\parallel}=3.673\pm0.002$, $g_\perp\leq0.3$.

1. INTRODUCTION

Single crystals of CaF_2 containing trace impurities of paramagnetic ions often exhibit electron-spin resonance (ESR) spectra with symmetry lower than cubic. Such spectra arise because of the proximity of compensating charges which lower the point symmetry at the sites of the impurity ions. In previous papers,[1–3] we described spectra having orthorhombic symmetry which were observed in crystals of CaF_2 containing rare-earth (RE) ions which had been introduced into the crystals in the form of the RE oxides. In the present paper, results on Ce^{3+} ions in CaF_2 doped with CeO_2 are described; in this system, two spectra of approximately equal intensity are observed, one having trigonal and the other having orthorhombic symmetry. Previous ESR studies of Ce^{3+} ions in CaF_2 have revealed ions situated in purely cubic sites,[4] and ions having tetragonal[5] and trigonal[6] symmetries, but the trigonal spectrum which we have observed is different from the one previously reported.

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