The NMR spectrum is obtained from polycrystalline material and presents a means of detecting such transformations in cases where single crystals are not available. We have been able to determine that no comparable distortion occurs in V_3Ga.

The unexpectedly large changes in electric field gradient which occurred in the transformation indicate that effects of uniaxial stress could be observed in the NMR of single crystals of the vanadium β-tungsten-structure compounds. Such measurements would be useful in establishing a firmer correlation between the density of conduction-electron states at the Fermi energy and the electric field gradients in metals.

The changes in EFG found in the present work are of a magnitude which demonstrates that conduction electrons contribute dominantly to the vanadium quadrupole interaction in V_3Si and that a significant change in electronic band structure occurs in the transformation. The changes found in the Knight shift also reflect the change in the electronic band structure.

Dynamic Effects in Paramagnetic Resonance of Magnetic Ions in Metals*

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The transverse susceptibility, which determines the paramagnetic resonance behavior, is studied for paramagnetic ions coupled by an effective scalar exchange interaction to the conduction electrons of a host metal. By means of a temperature Green's-function technique for ionic spins, it is found that the dynamical behavior of the conduction electrons influences the ionic resonance if the relaxation rate of the conduction electrons is not large compared to their resonance frequency. The predicted effects, namely, a broadening at low temperature, a shift around the Curie temperature, and a diminished broadening at high temperature, are compared with experimental data. The last effect can also be seen in nuclear resonance, whereas, the other effects appear only in ionic resonance experiments, since only the ionic Zeeman energy is comparable with the Zeeman energy of the conduction electrons. The theory suggests a possibility for distinguishing between direct and indirect exchange coupling of ions in metallic solutions, since in the first case the resonance signals are exchange-narrowed, whereas, in the second case they are broadened by a dissipative contribution of the conduction electrons.

1. INTRODUCTION

THE magnetic resonance of paramagnetic ions in metals has been studied by several authors.[1-3] It is well known that the resonance frequency in these experiments is given by[2]

$$\omega_H = \omega_i + \bar{J}\chi_z{}^{el}(H_z/\mu N) \equiv \omega_i + \delta\omega, \qquad (1.1)$$

where $\chi_z{}^{el}$ is the static paramagnetic susceptibility of the conduction electrons, $\bar{J}$ is the effective exchange parameter[4] between ions and conduction electrons, H_z is the applied static field, ω_i is the resonance frequency of the free ions, μ is the Bohr magneton, and N is the number of lattice points per unit volume. We wish to point out here that this relation holds only in the limits where $\omega_i \ll \omega_{el}$, or where the relaxation rate of the conduction electrons $\Delta \gg \omega_{el}$ (ω_{el} is the resonance frequency of the conduction electrons), or finally where $kT \gg \hbar\omega_i$.

If none of these conditions are fulfilled, then the dynamical effects of the conduction electrons become important and the g shift and broadening in ionic resonance experiments are no longer analogous to the Knight shift and Korringa broadening known from nuclear resonance. Some anomalous observations on

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electron paramagnetic resonance (EPR) of ions in metals can be explained by these effects.

The following model was adopted for our discussion: The magnetic ions and the conduction electrons are coupled by the interaction

$$\mathcal{3C}_{ei} = -N^{-1} \bar{J} \sum_{nq} e^{i\mathbf{q}\cdot\mathbf{R}_n} \{ S_z{}^n(\rho_\uparrow(\mathbf{q}) - \rho_\downarrow(\mathbf{q}))$$
$$+ S_+{}^n\rho_-(\mathbf{q}) + S_-{}^n\rho_+(\mathbf{q}) \} , \quad (1.2)$$

where the sum runs over all $\mathbf{q}$ and the paramagnetic-ion sites $\mathbf{R}_n$, and

$$\rho_\uparrow(\mathbf{q}) = \sum_k a_+{}^\dagger(\mathbf{k}-\mathbf{q})a_+(\mathbf{k}),$$
$$\rho_\downarrow(\mathbf{q}) = \sum_k a_-{}^\dagger(\mathbf{k}-\mathbf{q})a_-(\mathbf{k}),$$
$$\rho_\pm(\mathbf{q}) = \sum_k a_\pm{}^\dagger(\mathbf{k}-\mathbf{q})a_\mp(\mathbf{k}).$$

S^n is the spin operator of the ion on lattice site n, and $a_\pm{}^\dagger(\mathbf{k})$ are the conduction-electron creation operators of spin $+$ or $-$. The magnetic ions at the lattice points $\mathbf{R}_n$ polarize the conduction electrons, and these electrons react on the ions. Hasegawa[5] has given a discussion of this model and has shown that in the case where the conduction electrons follow the *instantaneous* ionic polarization, they will give no second-order effects on the resonance of the magnetic ions, but there will be such an effect if the conduction electrons follow only the *average* polarization. Peter showed that there will in general be second-order effects if different ionic species are present, since these different species see only each other's average polarizations.[2] In this paper we study the effects of conduction electrons on one species if the hypothesis of very fast relaxation is not imposed. By this we understand that the relaxation rate of the conduction electrons is not necessarily fast compared to the resonance frequency of the ions. However, we still impose the condition that this relaxation must be fast compared to the relaxation rate of the ions.

This is done by extension to nonzero temperature of the theory developed earlier[6,7] to describe EPR in metals at zero temperature. Nonzero-temperature theory is quite difficult to set up generally for spin systems. It was however possible to make explicit second-order calculations using the extension of Wick's theorem to spin operators[6] and the temperature Green's-function technique.[8]

In Secs. 2 and 3, we present briefly the general frame of the theory, in Sec. 4 we give a short account of first- and second-order calculations, and in Sec. 5 the results are discussed and compared with experimental data.

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2. TEMPERATURE GREEN'S FUNCTIONS OF SPINS

The temperature Green's function for spins is defined by

$$\mathcal{D}_{nn'}(\tau) = -\langle T_\tau\{S_-{}^n(\tau)S_+{}^{n'}(0)\}\rangle , \quad (2.1)$$

where $\langle \cdots \rangle$ means an average over a canonical ensemble,[9] i.e.,

$$\langle A \rangle = \mathrm{Tr}(e^{-\beta H + \beta\Omega}A), \quad \beta = 1/T$$

with

$$e^{-\beta\Omega} = \mathrm{Tr}(e^{-\beta H})$$

and

$$A(\tau) = e^{H\tau}Ae^{-H\tau}.$$

Nonzero-temperature perturbation theory is then constructed in the usual way[8] and leads to the equations

$$\mathcal{D}_{nn'}(\tau) = -\frac{\langle T_\tau\{S_-{}^n(\tau)S_+{}^{n'}(0)\mathcal{L}(\beta)\}\rangle_0}{\langle\mathcal{L}(\beta)\rangle_0}, \quad (2.2)$$

where

$$\langle A \rangle_0 = \mathrm{Tr}(e^{-\beta\mathcal{3C}_0 + \beta\Omega_0}A),$$
$$e^{-\beta\Omega_0} = \mathrm{Tr}\,e^{-\beta\mathcal{3C}_0},$$

and

$$\mathcal{L}(\beta) = T_\tau \exp\left\{ -\int_0^\beta \mathcal{3C}_{\mathrm{int}}(\tau')d\tau' \right\}$$

$$= \sum_{n=0}^\infty \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 d\tau_2 \cdots d\tau_n$$
$$\times T_\tau\{\mathcal{3C}_{\mathrm{int}}(\tau_1)\cdots\mathcal{3C}_{\mathrm{int}}(\tau_n)\} \quad (2.3)$$

and the operators are now written in the "interaction representation," i.e.,

$$A(\tau) = e^{\mathcal{3C}_0\tau}Ae^{-\mathcal{3C}_0\tau}.$$

$\mathcal{3C}_0$ is defined in the next section.

One can show[8] that

$$\mathcal{D}_{nn'}(\tau < 0) = \mathcal{D}_{nn'}(\tau + \beta) \quad (2.4)$$

and, if we introduce

$$\mathcal{D}_{nn'}(\omega_m) = \frac{1}{2}\int_{-\beta}^\beta e^{i\omega_m\tau}\mathcal{D}_{nn'}(\tau)d\tau,$$

it follows from Eq. (2.4) that

$$\mathcal{D}_{nn'}(\omega_m) = \int_0^\beta e^{i\omega_m\tau}\mathcal{D}_{nn'}(\tau)d\tau, \quad \omega_m = 2m\pi/\beta. \quad (2.5)$$

The inverse transformation is given by

$$\mathcal{D}_{nn'}(\tau) = (1/\beta)\sum_m \mathcal{D}_{nn'}(\omega_m)e^{-i\omega_m\tau}. \quad (2.6)$$

3. SUSCEPTIBILITY OF A SPIN SYSTEM

The Kubo formula for the response to an external magnetic field perpendicular to the z axis leads to the

[9] We work in units defined by $\hbar = 1$, $k = 1$.

following expression for the transverse susceptibility[10]:

$$\chi_{\mp}(t-t') = \tfrac{1}{2} i g_i^2 \mu^2 \sum_{nn'} \langle [S_{\mp}{}^n(t), S_{\pm}{}^{n'}(t')] \rangle \vartheta(t-t').$$

If one defines

$$D_{nn'}{}^R(t) = -i \langle [S_-{}^n(t), S_+{}^{n'}(0)] \rangle \vartheta(t),$$

one can show[8] that its Fourier transform $D_{nn'}{}^R(\omega)$ can be written

$$D_{nn'}{}^R(\omega) = \sum_{xx'} e^{(\Omega-E_x)\beta} t_{xx'}{}^{nn'} \frac{1-e^{\beta(E_x-E_{x'})}}{\omega + E_x - E_{x'} + i\delta} \quad (3.1)$$

with

$$\delta = 0+,$$

$$\mathcal{3C}|x\rangle = E_x|x\rangle,$$

$$t_{xx'}{}^{nn'} = \langle x | S_-{}^n | x' \rangle \langle x' | S_+{}^{n'} | x \rangle.$$

Similarly,

$$\mathfrak{D}_{nn'}(\omega_m) = \sum_{xx'} e^{(\Omega-E_x)\beta} t_{xx'}{}^{nn'} \frac{1-e^{\beta(E_x-E_{x'})}}{i\omega_m + E_x - E_{x'}}. \quad (3.2)$$

It follows that

$$D_{nn'}{}^R(i\omega_m) = \mathfrak{D}_{nn'}(\omega_m) \quad \text{for} \quad \omega_m > 0.$$

As $D_{nn'}{}^R(\omega)$ is analytic in the upper half-plane one can always construct $\mathfrak{D}_{nn'}(\omega_m)$ from $D_{nn'}{}^R(\omega)$. The inverse problem is fundamentally more difficult,[8] but practically knowing $\mathfrak{D}_{nn'}(\omega_m)$, we obtain

$$D_{nn'}{}^R(\omega) = \mathfrak{D}_{nn'}(-i\omega+\delta).$$

The calculation of the susceptibility of the spin impurities reduces therefore to the calculation of $\mathfrak{D}_{nn'}(\tau)$ defined by Eq. (2.1).

4. CALCULATION OF $\mathfrak{D}_{nn'}(\tau)$ UP TO SECOND ORDER

As in Ref. (7) the Hamiltonian of the system is given by

$$\mathcal{3C} = \mathcal{3C}_0 + \mathcal{3C}_{\text{int}},$$

$$\mathcal{3C}_0 = \mathcal{3C}_{0i} + \mathcal{3C}_{0 \text{ el}}, \quad (4.1)$$

$$\mathcal{3C}_{\text{int}} = \mathcal{3C}_{1 \text{ el}} + \mathcal{3C}_{ei},$$

$$\mathcal{3C}_{0i} = \omega_i \sum_n S_z{}^n,$$

$$\mathcal{3C}_{0 \text{ el}} = \sum_{k\sigma} \mathcal{E}(k) a_\sigma{}^\dagger(\mathbf{k}) a_\sigma(\mathbf{k})$$

$$+ \tfrac{1}{2} \omega_{\text{el}} \{ \rho_\uparrow(\mathbf{q}=0) - \rho_\downarrow(\mathbf{q}=0) \}. \quad (4.2)$$

$\mathcal{3C}_{ei}$ is given by (1.2) and $\mathcal{3C}_{1 \text{ el}}$ contains electron-electron and electron-lattice interactions. The form of $\mathcal{3C}_{1 \text{ el}}$ is not specified. Formally our perturbation series is in powers of $\mathcal{3C}_{\text{int}}$, but $\mathcal{3C}_{1 \text{ el}}$ is taken into account implicitly by the renormalization of "bare" electron bubbles by "dressed" bubbles.

To the zeroth order then

$$\mathfrak{D}_{nn'}{}^{(0)}(\tau>0) = -e^{-\omega_i\tau} \langle S_-{}^n S_+{}^n \rangle_0 \delta_{nn'}.$$

From Eq. (2.5) it follows that

$$\mathfrak{D}_{nn'}{}^{(0)}(\omega_m) = -\langle S_-{}^n S_+{}^n \rangle_0 \frac{e^{-\beta\omega i}-1}{i\omega_m - \omega_i} \delta_{nn'}. \quad (4.3)$$

From Eq. (2.4) we see that

$$\langle S_+{}^n S_-{}^n \rangle_0 = e^{-\beta\omega i} \langle S_-{}^n S_+{}^n \rangle_0.$$

So

$$\mathfrak{D}_{nn'}{}^{(0)}(\omega_m) = -2 \langle S_z \rangle_0 \delta_{nn'} / (i\omega_m - \omega_i) \quad (4.4)$$

($\langle S_z{}^n \rangle_0$ is independent of n) or

$$D_{nn'}{}^{(0)R}(\omega) = (-2\langle S_z \rangle_0 \delta_{nn'}) / (\omega - \omega_i + i\delta). \quad (4.5)$$

The last result can also be calculated directly from the definition of $D^R(\omega)$.

It follows that

$$\chi_-{}^{(0)}(\omega) = cNg^2\mu^2 \langle S_z \rangle_0 / (\omega - \omega_i + i\delta),$$

where c is the ionic concentration. To calculate the first- and second-order corrections[11] to $\mathfrak{D}_{nn'}(\tau)$, we must calculate (2.2) up to second order. The procedure is the following:

(a) In order to take the denominator of (2.2) into account, the development of the numerator of (2.2) is written as

$$\{ \mathfrak{D}_{nn'}{}^{(0)}(\tau) + \mathfrak{D}_{nn'}{}^{(1)}(\tau) + \cdots \}$$

$$\times \{ 1 + \langle \mathcal{L}^{(1)}(\beta) \rangle_0 + \langle \mathcal{L}^{(2)}(\beta) \rangle_0 + \cdots \}, \quad (4.6)$$

where $\mathcal{L}^{(i)}(\beta)$ is the ith-order[11] term in the expansion (2.3). Equation (4.6) defines the quantity $\mathfrak{D}_{nn'}{}^{(i)}(\tau)$. Then

$$\mathfrak{D}_{nn'}(\tau) = \sum_{i=0}^{\infty} \mathfrak{D}_{nn'}{}^{(i)}(\tau).$$

(b) Using the fact that different sites are statistically independent if the trace is taken over $e^{-\beta\mathcal{3C}_0}$, one can decouple the average of products of spin operators for different indices (e.g., $\langle S_+{}^n S_-{}^n S_z{}^{n'} \rangle_0 = \langle S_+{}^n S_-{}^n \rangle_0 \langle S_z{}^{n'} \rangle_0$ for $n \neq n'$).

(c) The remaining terms are averages of time-ordered products of spin operators with the same indices. The time-ordered products are transformed with the help of the generalized Wick's theorem[6] and generate terms which can all be calculated explicitly.

(d) The results of first- and second-order calculations appear as the sum of two terms: The first, proportional to $\mathfrak{D}_{nn'}{}^{(0)}(\omega_m)$, is interpreted as a renormalization of the amplitude $cNg^2\mu^2\langle S_z \rangle_0$ of the resonance line and does not interest us directly here. The second, proportional to $[\mathfrak{D}_{nn'}{}^{(0)}(\omega_m)]^2$, appears as a natural extension of the first- and second-order results at zero temperature given in Ref. 7. These results, extended to a partial infinite series, gave contributions to the shift and width of the resonance lines. The nonzero-temperature calculations are more tedious than their zero-temperature

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[10] g_i is the g factor of the ions, i.e., if ω_i is the resonance frequency, $\omega_i = |\mu| g_i H_z$.

[11] In powers of H_{ei}.

counterpart because of the finite integrals, and because the spins of the unperturbed states are no longer aligned all in the same direction. The relevant result is that correction terms are added to the ionic resonance frequency

$$\chi_-(\omega) = A/[\omega - \omega_i - \delta\omega + K^{(2)}(\omega)].\qquad(4.7)$$

The first-order contribution is the Knight shift:

$$\delta\omega = -N^{-1}\bar{J}(n_+ - n_-),\qquad(4.8)$$

$$n_{+,-} = \mathrm{Tr}\,e^{-\beta(\mathcal{K}_0\,\mathrm{el}+\mathcal{K}_1\,\mathrm{el})}\rho_{\uparrow,\downarrow}.$$

The polarization bubble is here "renormalized."
The second-order contribution, $K^{(2)}(\omega)$ is given by

$$K^{(2)}(\omega) = -\frac{\bar{J}^2\langle S_z\rangle_0}{N^2\mu^2}\sum_{\mathbf{R}_n\neq 0}\{\chi_-^{\mathrm{el}}(\omega,\mathbf{R}_n)-\chi_z^{\mathrm{el}}(\omega=0,\ \mathbf{R}_n)\}+\frac{\bar{J}^2}{2N^2N^2\mu^2\langle S_z\rangle_0}\{(e^{-\omega i\beta}-1)(2\langle S_z^2\rangle_0-\langle S_+S_-S_z\rangle_0)-\langle S_+S_-\rangle_0\}$$

$$\times\{\chi_-^{\mathrm{el}}(\omega,\ \mathbf{R}=0)-\chi_z^{\mathrm{el}}(\omega=0,\ \mathbf{R}=0)\}+\frac{\bar{J}^2(n_+-n_-)^2\beta}{2N^2N^2\langle S_z\rangle_0}\{(1-e^{-\omega i\beta})(2\langle S_z^2\rangle_0-\langle S_+S_-S_z\rangle_0)+\langle S_+S_-\rangle_0-2\langle S_z\rangle_0^2)\}$$

$$+\frac{\bar{J}^2\langle S_+S_-\rangle_0}{2\mu^2N^2\langle S_z\rangle_0}\{\chi_z^{\mathrm{el}}(\omega-\omega_i,\ \mathbf{R}=0)-Re\chi_-^{\mathrm{el}}(\omega=\omega_i,\ \mathbf{R}=0)\}+\frac{\bar{J}^2\langle S_-S_+\rangle_0(1-e^{-\omega i\beta})}{2\mu^2N^2\langle S_z\rangle_0}$$

$$\times\{Re\tilde{\chi}_-^{\mathrm{el\ adv}}(\omega=\omega_i,\ \mathbf{R}=0)-\tilde{\chi}_z^{\mathrm{el\ ret}}(\omega-\omega_i,\ \mathbf{R}=0)\},\qquad(4.9)$$

where χ^{el} are the electronic susceptibility functions defined by

$$\chi_z^{\mathrm{el}}(t,\mathbf{q})=i\mu^2\langle[\rho_\uparrow(\mathbf{q}t)-\rho_\downarrow(\mathbf{q}t),$$
$$\rho_\uparrow(-\mathbf{q}0)-\rho_\downarrow(-\mathbf{q}0)]\rangle\vartheta(t),\qquad(4.10)$$

$$\chi_-^{\mathrm{el}}(t,\mathbf{q})=2i\mu^2\langle[\rho_-(\mathbf{q}t),\rho_+(-\mathbf{q}0)]\rangle\vartheta(t),\qquad(4.11)$$

and $\tilde{\chi}_-^{\mathrm{el\ adv}}$ and $\tilde{\chi}_z^{\mathrm{el\ ret}}$ are defined by

$$\tilde{\chi}_z^{\mathrm{el\ ret}}(t\mathbf{q})\equiv i\mu^2\langle T\{(\rho_\uparrow(\mathbf{q}t)-\rho_\downarrow(\mathbf{q}t))$$
$$\times(\rho_\uparrow(-\mathbf{q}0)-\rho_\downarrow(-\mathbf{q}0))\}\rangle\vartheta(t)$$

and

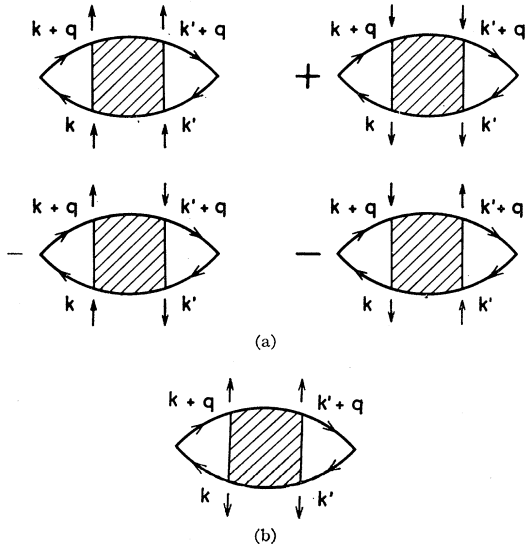$$\tilde{\chi}_-^{\mathrm{el\ adv}}(t\mathbf{q})\equiv 2i\mu^2\langle T\{\rho_-(\mathbf{q}t)\rho_+(-\mathbf{q}0)\}\rangle\vartheta(-t).$$

The functions χ_z^{el} and χ_-^{el} can be calculated in perturbation theory with help of temperature Green's functions. They are represented by the bubbles given in Fig. 1.

The expression (4.9) looks rather horrible, but only the two first terms are important, and will be discussed in the next section. The third term can easily be shown to be small. In particular, for $\omega_i\ll T$, it is proportional to $(\delta\omega)^2/T$. The fourth term is small because $Re\chi_-^{\mathrm{el}}\times(\omega_i,\ \mathbf{R}=0)$ and $\chi_z^{\mathrm{el}}(\omega=0,\ \mathbf{R}=0)$ nearly cancel. The last term has already been found in the zero-temperature limit, and is negligible for similar reasons. For the details of this discussion, we refer to Ref. 12.

5. DISCUSSION

The dynamical effects described by the first two terms of Eq. (4.9) are essentially given by the difference between the susceptibility χ_z^{el} and the transverse susceptibility χ_-^{el}. The reason for this is that the applied magnetic field H_z transforms the simple interionic scalar coupling given by Kasuya[13] into a more complicated frequency-dependent interaction (including also damping effects), which can be characterized by a tensor, the coupling being different in the z direction and in the x-y plane. This modified coupling gives rise to the effects to be discussed in this section.

The two first terms of Eq. (4.9) give rise to a shift (given by the real part) and a broadening (given by the imaginary part). First we discuss the susceptibility functions of the conduction electrons, χ_z^{el} and χ_-^{el}

FIG. 1. Diagrammatic representation of $\chi_z^{\mathrm{el}}(\omega,\mathbf{q})$ (a) and $\chi_-^{\mathrm{el}}(\omega,\mathbf{q})$ (b). To get these functions, one must multiply the expression one gets from the diagram by $i\mu^2$ (a) or $2i\mu^2$ (b) and integrate over frequency and momentum variables. (k,q stands for $\mathbf{k}\omega',\mathbf{q}\omega$). If no spin-flip mechanism is included in $\mathcal{K}_1\,\mathrm{el}$, the two last diagrams of (a) give zero contribution.

[12] B. Giovannini, Ph.D. thesis, University of Geneva, 1966 (unpublished).
[13] T. Kasuya, Progr. Theoret. Phys. (Kyoto) 16, 45 (1956), Sec. 3, Eq. 16.

defined by (4.10) and (4.11). These functions are known in the free-electron limit,[7,14] and their real parts differ only for small values of $|\mathbf{q}|$ ($|\mathbf{q}| \lesssim m\omega_{el}/k_f$), so we can set

$$\mathrm{Re} \sum_n \{\chi_{-}{}^{el}(\omega, \mathbf{R}_n) - \chi_z{}^{el}(\omega=0, \mathbf{R}_n)\}$$
$$\simeq Nc\{\mathrm{Re}\chi_{-}{}^{el}(\omega, \mathbf{q}=0) - \chi_z{}^{el}(\omega=0, \mathbf{q}=0)\}, \quad (5.1)$$

where c is the ionic concentration, and neglect the contribution from $\mathrm{Re}[\chi_{-}{}^{el}(\omega, \mathbf{R}=0) - \chi_z{}^{el}(\omega=0, \mathbf{R}=0)]$.[12] To discuss this expression in a realistic way, one must take into account the relaxation of the conduction electrons; we take for $\chi_{-}{}^{el}(\omega, \mathbf{q}=0)$ the following Lorentzian form[15]:

$$\chi_{-}{}^{el}(\omega, \mathbf{q}=0)$$
$$= \chi_z{}^{el}(\omega=0, \mathbf{q}=0)\left\{1 - \frac{\omega}{\omega - \omega_{el}' + i\Delta}\right\}, \quad (5.2)$$

where Δ is a linewidth and ω_{el}' a shifted resonance frequency. For any value of Δ, this form goes to $\chi_z{}^{el}(\omega=0, \mathbf{q}=0)$ for $\omega \to 0$ and satisfies the sum rule

$$\int \frac{d\omega'}{\omega'} \mathrm{Jm}\chi_{-}{}^{el}(\omega', \mathbf{q}=0) = \pi\chi_z{}^{el}(\omega=0, \mathbf{q}=0).$$

For $\Delta \to 0$, $\chi_{-}{}^{el}(\omega, \mathbf{q}=0)$ goes over into the expression for the undamped free electron gas[7] if one sets $\omega_{el}' = \omega_{el} - \Delta^2/\omega_{el}$ ($\omega_{el} = -2\mu H_z$).

The difference $\mathrm{Re}\chi_{-}{}^{el}(\omega, \mathbf{r}) - \chi_z{}^{el}(\omega=0, \mathbf{r})$ which enters in Eq. (5.1) becomes appreciable at a range $k_f/m\omega_{el}$. This is a large distance on the atomic scale, and the question arises whether the conduction electrons can traverse such a distance without being submitted to damping effects. It is interesting to note however that the mean free path for electron-spin relaxation is of the order $k_f/m\Delta$ and that therefore this free path exceeds the characteristic distance mentioned above as soon as $\Delta \lesssim \omega_{el}$. We shall see that this is also the condition for appreciable dynamical effects to occur.

In order for $\mathrm{Jm}\chi_{-}(\omega)$ to become maximal (resonance), ω must satisfy

$$\omega - \omega_i - \delta\omega = -\mathrm{Re}K^{(2)}(\omega) = B \cdot \frac{\omega(\omega - \omega_{el}')}{(\omega - \omega_{el}')^2 + \Delta^2},$$
$$B = -\frac{c \cdot \bar{J}^2 \langle S_z \rangle_0}{N \cdot \mu^2}\chi_z{}^{el}(\omega=0, \mathbf{q}=0). \quad (5.3)$$

The solution of this equation is represented graphically in Fig. 2. We find that ω_i is pushed away from the resonance frequency of the damped electrons. If $\omega_{el}' \simeq \omega_i$, this effect is only effective if $\Delta \simeq \omega_i$ or smaller. It completely disappears for $\omega_i \ll \omega_{el}'$, for $\omega_i = \omega_{el}'$, or for $\Delta \gg \omega_{el}'$. (Note that when c increases, B increases, but

Δ is expected to increase also. The variation of shift with concentration is therefore difficult to predict.)

The last case ($\Delta \gg \omega_{el}'$) has already been discussed by Shaltiel et al.[2]: the electrons follow at all times the instantaneous polarization of the ionic spins and therefore produce no torque on these spins, hence no second-order effect. The same is true for $\omega_i \ll \omega_{el}'$: the electrons again follow the spins. If $\omega_i \gg \omega_{el}'$, the electrons cannot follow the ions and undergo a polarization only in the z direction; they then produce the second-order effect mentioned by Kittel and Mitchell.[16] We shall see below that the onset of ferromagnetic ordering favors strongly the appearance of the second order effect described by our equation.

For intermediate values of ω_i the resonant behavior of the conduction electrons gives rise to a shift which is negative for $\omega_i < \omega_{el}'$, changes sign at $\omega = \omega_{el}'$, and is positive for $\omega_i > \omega_{el}'$. This shift is proportional to $\langle S_z \rangle$, and hence to T^{-1} for $\omega_i \ll T$, and should become large at low temperature. It should change rapidly when the ionic spins undergo a ferromagnetic transition.[17] This may be the explanation of the sudden change of the g value of the Gd^{3+} ions at the Curie point for metallic Gd, observed by Rodbell et al.[18] It is furthermore to be expected that the relaxation rate Δ of the conduction electrons diminishes at the Curie point, which would also contribute to this observed change. The imaginary part of $K^{(2)}(\omega)$ gives rise to a broadening, and consists of two terms of different temperature behavior. The first term is the imaginary part of the term producing the shift just discussed; this broadening will be inversely proportional to temperature for $\omega_i \ll T$ and increase with ionic concentration c. Below T_c, one should observe an increase of the linewidth correlated with the magnetization.[17] Physically this term is due to the damping of spin waves by the conduction electrons. In Fig. 5 of Ref. 1 an anomalous increase of the linewidth of the paramagnetic resonance of Gd ions in Pd metals was indeed observed, which has the indicated characteristics. This behavior is interesting, because it shows that indirect exchange between identical ions contains a damping term which does not occur for direct exchange. The measurements of linewidth should therefore provide a way to decide which interaction is relevant. We did not calculate the exchange-narrowing term in our formalism, since it is of higher order, but this term should be taken into account for appreciable values of the concentration. At high temperature, the imaginary part of the second term of $K^{(2)}(\omega)$, which is proportional to $\mathrm{Jm}\chi_{-}{}^{el}(\omega, \mathbf{R}=0)$ [since $\mathrm{Jm}\chi_z{}^{el}(\omega=0, \mathbf{r})=0$], predominates as this part is proportional to T. The half-width–half-power broadening goes in the low-temperature

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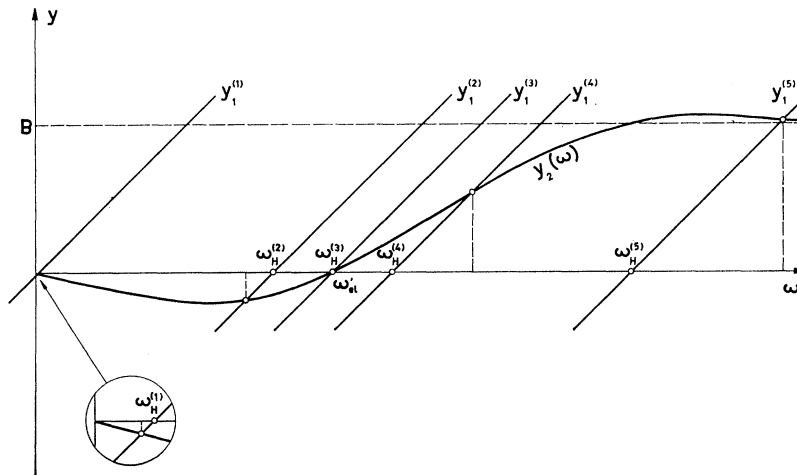
[16] C. Kittel and A. H. Mitchell, Phys. Rev. **101**, 1611 (1956).

[17] To predict this we must replace $\langle S_z \rangle_0$ by a more realistic average $\langle S_z \rangle$, making sure that we do not double-count terms in the perturbation series.

[18] T. S. Rodbell and T. W. Moore, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1965), p. 427.

FIG. 2. Graphical determination of ω_{res} from Eq. (5.3), which is written in the form $y_1^{(i)}(\omega) = y_2(\omega)$, where $y_1^{(i)}(\omega)$ $= \omega - \omega^{(i)} - \delta\omega = \omega - \omega_H^{(i)}$. ($\omega_H^{(1)}$ corresponds to nuclear resonance, the values $\omega_H^{(2)}$, $\omega_H^{(3)}$, and $\omega_H^{(4)}$ are in the neighborhood of ω_{el}', and $\omega_H^{(5)}$ illustrates the Kittel-Mitchell limit.) $y_2(\omega) = B[\omega(\omega - \omega_{el}')]/$ $[(\omega - \omega_{el}')^2 + \Delta^2]$ with the values $\omega_{el}' = \Delta = 2B$.

limit into the value previously found at zero temperature.[7] At high temperatures and in the free-electron approximation, we get

$$\Delta\omega_{T\to\infty} = 2\pi(\bar{J}^2/N^2)T\rho^2(E_f), \qquad (5.4)$$

where $\rho(E_F)$ is the density of states of one spin at the Fermi surface. This is just one-half the value Korringa found for the broadening in the nuclear case. The origin of this difference is at present not understood.

Going beyond the free-electron approximation, one can see that for the case of strong enhancement of the susceptibility[19] the imaginary part of $\chi_-^{el}(\omega, \mathbf{R}=0)$ becomes

$$\sum_{\mathbf{q}} \mathrm{Im}\chi_-^{el}(\omega,\mathbf{q}) \approx \sum_{\mathbf{q}} \frac{\mathrm{Im}\chi_-^{0\ el}(\omega,\mathbf{q})}{(1 - \bar{v}\rho(E_f)P(\mathbf{q}))^2}, \qquad (5.5)$$

where $\chi_-^{0\ el}$ is the free-electron function, $P(\mathbf{q})$ is the Ruderman-Kittel potential

$$P(\mathbf{q}) = \frac{1}{2}\left\{1 + \frac{1 - (|\mathbf{q}|/2k_f)^2}{|\mathbf{q}|/k_f} \ln\frac{|1 + |\mathbf{q}|/2k_f|}{|1 - |\mathbf{q}|/2k_f|}\right\},$$

and $\bar{v}$ is the electron-electron screened interaction (assumed independent of $\mathbf{q}$). Moriya[20] has carried through a numerical calculation of the integral (5.5), and has already suggested that this correction could account for the relatively small broadening observed for the EPR of Gd in Pd. Indeed, Gd in Pd should undergo a broadening of $DH = 100T$ gauss (T in °K) according to (5.4). But, as the reduction factor

$(1 - \rho(E_f)\bar{v})$ is about $\frac{1}{8}$ for Pd,[15] DH is reduced to $DH \simeq 6T$ gauss, which is the experimental value.

6. CONCLUSION

In conclusion, we can state that it has been possible to treat a dynamical problem involving spins at nonzero temperature by means of the temperature Green's-function technique adapted to spins with the help of the extended Wick's theorem (6). This encourages the hope that more involved problems such as ferromagnetism and transport phenomena can also be attacked by this technique. In the case treated here the results obtained can be understood intuitively by imagining the system of ionic spins coupled to the system of conduction electrons in such a way that the dynamical behavior of the conduction electrons influences the resonance behavior of the ions. From the experimental point of view the most interesting effects are the possibility of a change of the g value near the Curie temperature and the appearance of damping effects in the case of indirect exchange coupling via conduction electrons between ions in metallic solution. This latter effect should provide a qualitative criterion to distinguish direct from indirect exchange in certain cases. Both effects may have already been observed, but further experimentation will have to show how well the effects predicted here can be identified in actual metals. The theory was developed with the free-electron model and extended in a semi-phenomenological way to include the effects of electronic damping and of correlation. The established formalism should permit one to pursue these studies in a more precise manner and to include also the effects of band structure.

[19] B. Giovannini, M. Peter, and J. R. Schrieffer, Phys. Rev. Letters 12, 736 (1964).
[20] T. Moriya, Technical Report of the Institute for Solid State Physics, University of Tokyo, A67, 1963 (unpublished).