

Nuclear Relaxation as a Probe of Electron Spin Correlation

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Adiabatic demagnetization of a nuclear spin system produces a state in which there is considerable correlation between neighboring spins. This correlation affects the nuclear relaxation rate and, in metals, where nuclei relax via interaction with conduction electrons, can be used as a probe of spin correlation in the *electronic* system. For a given lattice temperature the ratio δ of low- to high-field relaxation rates can be written in the form $\delta = 2 + \eta$, where η is essentially the electron spin correlation function at the nearest neighbor distance. η can also be related to the nonlocal electron spin susceptibility.

For noninteracting electrons, calculated values of η are more than an order of magnitude too small to explain the observations ($\eta \sim 0.2$ in the alkalis). The electronic spin correlation is considerably enhanced by exchange. Calculations which include this effect yield the value 0.1 for η .

I. INTRODUCTION

IN metals at low temperatures, nuclear spins come into thermal equilibrium with their surroundings by means of energy exchanges with conduction electrons. This process, called nuclear spin relaxation, results from the hyperfine interaction¹ between the conduction electron magnetic moments and those of the nuclei. The relaxation *rate* can be measured with nuclear magnetic resonance techniques. Such experiments are usually carried out in substantial magnetic fields, but it is also possible to measure the relaxation rate in zero (or small) field. Experiments of this type will concern us in the present paper.

The low-field experiment is complicated by the fact that the metal sample has no moment (and no resonance signal) in zero field. Thus one must proceed as follows. Nuclei are brought to equilibrium in a magnetic field at low temperature. The external field is then switched off adiabatically, but in a time short compared to the nuclear relaxation time T_1 . At this point the nuclei are in zero field and are there allowed to relax. Finally, the extent of the relaxation is determined by remagnetizing the sample (again adiabatically) and measuring the nuclear resonance signal.

For our purposes, the crucial feature of this experiment is the fact that the magnetizations are carried out in an isentropic way. This means that spin order, which is initially induced in the nuclei by the external field, must be preserved as one reduces the field to zero. The nuclei maintain the order by aligning themselves in each others' dipole fields, and the resultant state is one in which there is considerable spin correlation between neighboring nuclei. This correlation affects the nuclear relaxation rate and (since the nuclei relax via interactions with electrons) can be used as a probe to study correlation in the *electron* spin system. This possibility was first pointed out by Anderson and Redfield.² We here wish to explore the matter further, relating the relaxation rate to the susceptibility of the conduction electron spin system and studying the effect of exchange

enhancement of this susceptibility on the nuclear relaxation rate.

To use nuclear spin correlation as a probe of electronic structure one must, of course, know the degree of correlation in the nuclei. It is not possible to calculate this *ab initio*; instead, the assumption is commonly made that the nuclei in the demagnetized state are described by a spin temperature, even while relaxing. This hypothesis (which we also adopt) is a reasonable one and fairly well supported by experiment.^{2,3} It should be borne in mind, however, that the subsequent analysis explicitly depends upon its validity.

For cases in which the nuclear spin interactions are of a dipole-dipole character, the spin temperature theory predicts that the ratio (δ) of low- to high-field relaxation rates should be $\delta = 2 + \eta$, where η is a quantity that depends upon the degree of correlation between electron spins at neighboring nuclei. We shall show that η can be expressed in terms of the spin susceptibility of the electron system. Experimentally^{2,3} η , in the alkalis, is of the order of 0.2. Such a figure is too large, by about a factor of 20, to be explained by the susceptibility of a noninteracting electron gas. Exchange effects alter this susceptibility and bring the theoretical value into considerably closer agreement with experiment. A crude calculation yields a value $\eta = 0.1$, with a possibility that a more accurate computation would further improve the agreement.

II. THEORY OF SPIN TEMPERATURE

As was mentioned above, our analysis rests squarely upon the spin temperature hypothesis. Thus we begin our discussion by reviewing it, following closely the analysis of Hebel and Slichter.

The spin temperature theory makes the basic assumption that the nuclear spin system, as it relaxes in the demagnetized state, is describable by a temperature. That is, if "*m*" and "*n*" are any two nuclear spin states with energies ϵ_m and ϵ_n , their occupation probabilities, p_m and p_n , are in the ratio

$$(p_m/p_n) = e^{-(\epsilon_m - \epsilon_n)/k\theta_s}, \quad (1)$$

¹ See, for example, D. F. Holcomb and R. E. Norberg, *Phys. Rev.* **98**, 1074 (1955).

² A. G. Anderson and A. G. Redfield, *Phys. Rev.* **116**, 583 (1959).

³ L. C. Hebel and C. P. Slichter, *Phys. Rev.* **113**, 1504 (1959).

where k is Boltzmann's constant and θ_s the spin temperature. Such a distribution leads, at temperatures above those at which the nuclei become ferromagnetic, to a Curie law for the magnetization

$$M = CB/\theta_s, \quad (2)$$

where C is the nuclear Curie constant and B the external magnetic field.

As the nuclei relax, the magnetization approaches the value

$$M_0 = CB/\theta_L \quad (3)$$

appropriate to the lattice temperature, θ_L . Experimentally, the approach to equilibrium is described by the law

$$dM/dt = (M_0 - M)/T_1, \quad (4)$$

where T_1 is the nuclear relaxation time. We will see presently that this formula is also compatible with the spin temperature hypothesis. Assuming it to be correct, one may rewrite the formula [using Eqs. (2) and (3)] in the form

$$\frac{d}{dt} \left(\frac{1}{\theta_s} \right) = \left(\frac{1}{\theta_s} - \frac{1}{\theta_L} \right) \frac{1}{T_1}. \quad (5)$$

This is a convenient result, since the spin-temperature assumption permits one to make a rather straightforward calculation of $d\theta_s/dt$. It also gives some feeling for the meaning of nuclear relaxation in zero field. This is not apparent from Eq. (4) since M and M_0 are zero in the $B=0$ limit.

To calculate $d\theta_s/dt$, and thus determine T_1 from Eq. (5), one considers the time derivative of the total spin energy:

$$\frac{d\bar{\epsilon}}{dt} = \frac{\partial \bar{\epsilon}}{\partial \theta_s} \frac{d\theta_s}{dt} = \frac{d}{dt} \sum_n (\bar{p}_n \epsilon_n) = \sum_n \left(\epsilon_n \frac{d\bar{p}_n}{dt} \right). \quad (6)$$

This formula may be used to evaluate $d\theta_s/dt$ if one assumes that the time development of the occupation probabilities is governed by a transport equation of the form

$$d\bar{p}_m/dt = \sum_n [W_{mn}\bar{p}_n - W_{nm}\bar{p}_m]. \quad (7)$$

Here W_{mn} is the total transition rate, from state n to m , caused by the perturbation that gives rise to the nuclear spin relaxation. It is now a matter of algebra to combine Eqs. (5), (6), and (7) to obtain an expression for $d\theta_s/dt$. The analysis is given in detail in reference 3, so we only quote the final result which is

$$\frac{d}{dt} \left(\frac{1}{\theta_s} \right) = \left(\frac{1}{\theta_s} - \frac{1}{\theta_L} \right) \frac{1}{2} \sum_{n,m} [(\epsilon_n - \epsilon_m)^2 W_{mn}] / \sum_n (\epsilon_n^2). \quad (8)$$

This equation is compatible with Eq. (5) and enables us to write the following formula for the relaxation rate:

$$R = 1/T_1 = \frac{1}{2} \sum_{m,n} [(\epsilon_n - \epsilon_m)^2 W_{mn}] / \sum_n [\epsilon_n^2]. \quad (9)$$

To make explicit calculations of the temperature and field dependence of R , we calculate W_{mn} by perturbation theory. As was discussed in the introduction, nuclear relaxation in metals is caused by hyperfine interactions between conduction electrons and nuclear spins. The dominant part of this coupling is the contact interaction given by the well-known Fermi-Segrè formula:

$$H_1 = -\frac{8\pi\hbar^2}{3} \sum_i \{\gamma_i \gamma_e [\boldsymbol{\sigma}(\mathbf{r}_i) \cdot \mathbf{I}_i]\}. \quad (10)$$

Here γ_e and γ_i are, respectively, the gyromagnetic ratios of electron and nucleus, $\boldsymbol{\sigma}(\mathbf{r}_i)$ is the electron spin density at the position \mathbf{r}_i of the i th nucleus, and \mathbf{I}_i is the corresponding nuclear spin. The transition rate between two states, ψ_1 and ψ_2 , due to this interaction is given by first-order perturbation theory as

$$W_{12} = (2\pi/\hbar) |\langle \psi_1, H_1 \psi_2 \rangle|^2 \delta(E_1 - E_2), \quad (11)$$

where E_1 and E_2 are the energies of the two states. Since, to lowest order, the electrons and nuclei are uncoupled we may simplify this expression by factoring the wave functions into electronic and nuclear parts: $\psi_1 = \varphi_1 \chi_1$; $\psi_2 = \varphi_2 \chi_2$. After using Eq. (10) one finds

$$W_{12} = \left(\frac{2\pi}{\hbar} \right) \frac{64\pi^2}{9} (\hbar\gamma_e)^2 \sum_{ij, \alpha\beta} [(\hbar\gamma_i)(\hbar\gamma_j) \times (\varphi_1, \sigma_\alpha(\mathbf{r}_j) \varphi_2)(\varphi_2, \sigma_\beta(\mathbf{r}_i) \varphi_1) \times (\chi_1, I_j^\alpha \chi_2)(\chi_2, I_i^\beta \chi_1) \delta(E_1 - E_2)]. \quad (13)$$

An expression for the nuclear relaxation rate is obtained by substituting this expression into Eq. (9). If one neglects the very small nuclear energy change, the sum over states appearing there factors into two terms, one referring to the nuclei, the other to the electrons. The nuclear average reduces to a trace of known operators and can be calculated directly. That referring to the electrons is evaluated by averaging over a canonical ensemble with the temperature of the lattice. As will be seen in a moment, the resultant expression is directly related to the electron spin correlation function.

Since both Hebel and Slichter, and Anderson and Redfield have discussed this averaging process in detail, we will not repeat the analysis here but merely quote the pertinent results. The expression for the nuclear relaxation rate takes the form

$$\frac{1}{T_1} = \sum_{jk, \alpha\beta} [a_{jk}^{\alpha\beta} N_{jk}^{\alpha\beta}], \quad (14)$$

where

$$N_{jk}^{\alpha\beta} = -\frac{(\hbar\gamma_N)^2 \text{trace}\{[I_j^\alpha, \mathcal{H}][I_k^\beta, \mathcal{H}]\}}{2 \text{trace}\{\mathcal{H}^2\}} \quad (15)$$

is the average over nuclear configurations, and

$$a_{jk}^{\alpha\beta} = \left(\frac{2\pi}{\hbar} \right) \left(\frac{64\pi^2}{9} \right) (\hbar\gamma_e)^2 \sum_{1,2} \{\rho(E_1) \delta(E_1 - E_2) \times (\varphi_1, \sigma_\alpha(\mathbf{r}_j) \varphi_2)(\varphi_2, \sigma_\beta(\mathbf{r}_k) \varphi_1)\} \quad (16)$$

is the average over the electronic portion of the wave functions. In these formulas \mathcal{H} is the Hamiltonian of the nuclear system, ρ is the equilibrium density matrix for the electron system, and the square brackets in Eq. (15) indicate commutators. The expressions are written as tensors in the coordinate indices α and β . In many circumstances these tensors will be diagonal. To simplify the succeeding analysis we assume that this is the case and henceforth omit the indices α and β .

For a given nuclear Hamiltonian the quantity N_{jk} may be directly calculated. Assuming \mathcal{H} to consist of the Zeeman energy and a dipole-dipole interaction, one finds the formulas

$$N_{jj} = \left(\frac{B^2 + 2B_0^2}{B^2 + B_0^2} \right) (\hbar\gamma_N)^2, \quad (17)$$

$$N_{jk} (j \neq k) = (\hbar\gamma_N)^2 I(I+1) / (B^2 + B_0^2) (1/r_{jk}^6), \quad (18)$$

where r_{jk} is the distance between nuclei "j" and "k," B the external magnetic field, and

$$B_0 = (\hbar\gamma_N) \left[I(I+1) \sum_{(j \neq k)} \left(\frac{1}{r_{jk}^6} \right) \right]^{1/2} \quad (19)$$

the field due to dipole-dipole interactions. These formulas relate the equilibrium values of N_{jk} (large B) to those in the demagnetized state (B small compared to B_0). The terms $N_{jk} (j \neq k)$ describe correlation between nuclear spins located at sites "j" and "k". These are induced by the dipole fields, and are only important when these fields are not greatly exceeded by the external field. This result is clear from Eq. (18) which indicates $N_{jk} \rightarrow 0$ as (B/B_0) becomes large. Since we are hoping to use nuclear correlation as a probe of spin correlation in the electronic system, it is clearly essential to make use of data obtained in the demagnetized state.

It is of particular interest to calculate the ratio of the relaxation time at high field (where the nuclei are in equilibrium with the lattice) to that at zero field (where the effective nuclear temperature is well below that of the lattice). This ratio is given by

$$\delta = 2 + \left[\frac{\sum'_{jk} (K_{jk}/r_{jk}^6)}{\sum'_{jk} (1/r_{jk}^6)} \right], \quad (20)$$

where

$$K_{jk} = \frac{a_{jk}}{a_{jj}}$$

$$= \frac{\sum_{1,2} \{ \rho(E_1) \delta(E_1 - E_2) (\varphi_1, \boldsymbol{\sigma}(\mathbf{r}_j) \varphi_2) \cdot (\varphi_2, \boldsymbol{\sigma}(\mathbf{r}_k) \varphi_1) \}}{\sum_{1,2} \{ \rho(E_1) \delta(E_1 - E_2) (\varphi_1, \boldsymbol{\sigma}(\mathbf{r}_j) \varphi_2) \cdot (\varphi_2, \boldsymbol{\sigma}(\mathbf{r}_j) \varphi_1) \}} \quad (21)$$

As we shall see below, K_{jk} is directly related to the spin correlation function for the electrons. Its appearance

here is a direct consequence of correlation in the nuclear system.

The averages which appear in Eq. (21) may be related to spin correlation functions and the spin susceptibility. To demonstrate this point, we consider the quantity

$$b_{jk} = \sum_{1,2} \{ \rho(E_1) \delta(E_1 - E_2) (\varphi_1, \boldsymbol{\sigma}(\mathbf{r}_j) \varphi_2) \cdot (\varphi_2, \boldsymbol{\sigma}(\mathbf{r}_k) \varphi_1) \}. \quad (22)$$

The delta function in this expression may be rewritten as

$$\delta(E_1 - E_2) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(E_1 - E_2)t} dt. \quad (23)$$

If H_e is the Hamiltonian of the electron system, we then find

$$\begin{aligned} b_{jk} &= \sum_1 \left\{ \rho(E_1) \int_{-\infty}^{\infty} (\varphi_1, e^{iH_e t} \boldsymbol{\sigma}(\mathbf{r}_j) e^{-iH_e t} \cdot \boldsymbol{\sigma}(\mathbf{r}_k) \varphi_1) \frac{dt}{2\pi} \right\} \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \boldsymbol{\sigma}(\mathbf{r}_j t) \cdot \boldsymbol{\sigma}(\mathbf{r}_k 0) \rangle dt \end{aligned} \quad (24)$$

where we use the notation

$$\langle O \rangle = \text{trace}[\rho O]. \quad (25)$$

We see, therefore, that b_{jk} is the time integral of the temperature-dependent spin autocorrelation function. It may also be related to the spin susceptibility of the electron system. The susceptibility is determined by the response of the system to an infinitesimal external field.⁴ If we choose this field of the form

$$\mathbf{B} = \mathbf{B}_0 \delta(\mathbf{r} - \mathbf{r}_k) e^{i\omega t}, \quad (26)$$

we may easily verify that, to first order in \mathbf{B}_0 , the induced spin density at position \mathbf{r}_j is given by

$$\langle \sigma_\lambda(\mathbf{r}_j) \rangle = \left(\frac{1}{i} \right) \sum_{\mu} B_{0\mu} \int_0^{\infty} e^{(i\omega - \epsilon)t} \langle [\sigma_\lambda(\mathbf{r}_j t), \sigma_\mu(\mathbf{r}_k 0)] \rangle dt. \quad (27)$$

The susceptibility (which here is a nonlocal quantity) is given by

$$\begin{aligned} \chi_{\lambda\mu}(\mathbf{r}_j, \mathbf{r}_k; \omega + i\epsilon) \\ = \left(\frac{1}{i} \right) \int_0^{\infty} e^{(i\omega - \epsilon)t} \langle [\sigma_\lambda(\mathbf{r}_j t), \sigma_\mu(\mathbf{r}_k 0)] \rangle dt. \end{aligned} \quad (28)$$

Equations (24) and (28) involve similar, but slightly different temperature dependent Green's functions. The relations between such quantities have been extensively investigated by Zubarev⁵ and we may now

⁴ Such response functions are discussed by R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957); M. Lax, Phys. Rev. **109**, 1921 (1958); V. Galitskii and A. Migdal, Soviet Phys.—JETP **7**, 96 (1958).

⁵ D. N. Zubarev, Soviet Phys.—Uspekhi **3**, 320 (1960).

use his work to make a connection between Eqs. (24) and (28). Equation (28) is precisely his definition of the retarded Green's function so we write

$$\chi_{\lambda\mu}(\mathbf{r}_j\mathbf{r}_k; \omega+i\epsilon) = G_r^{\lambda\mu}(\mathbf{r}_j\mathbf{r}_k; \omega+i\epsilon). \quad (29)$$

By making the changes of variable $t \rightarrow -t$, $j \leftrightarrow k$, $\mu \leftrightarrow \lambda$ in Eq. (28) one may also relate the susceptibility to Zubarev's *advanced* Green's function. After some simple manipulations one finds

$$\chi_{\mu\lambda}(\mathbf{r}_k\mathbf{r}_j; -\omega+i\epsilon) = G_a^{\lambda\mu}(\mathbf{r}_j\mathbf{r}_k; \omega-i\epsilon). \quad (30)$$

We may now use Zubarev's work to relate χ to the Fourier transform of the autocorrelation function. Following his notation we write

$$\begin{aligned} b_{jk}^{\lambda\mu} &= J_{\lambda\mu}(\mathbf{r}_j\mathbf{r}_k; 0) \\ &= \lim_{\omega \rightarrow 0} \left\{ \left(\frac{i}{2\pi} \right) \left[\frac{\chi_{\lambda\mu}(\mathbf{r}_j\mathbf{r}_k; \omega+i\epsilon) - \chi_{\mu\lambda}(\mathbf{r}_k\mathbf{r}_j; -\omega+i\epsilon)}{(e^{\beta\omega} - 1)} \right] \right\}. \end{aligned} \quad (35)$$

In succeeding sections this relation between the correlation coefficient, $b_{jk}^{\lambda\mu}$, and the spin susceptibility will be used to make estimates of δ .

III. ELECTRON SPIN CORRELATION

In metals such as lithium and sodium the properties of the conduction electrons are, for many purposes, very well approximated by those of a free-electron gas. It is of interest, therefore, to consider the coefficients $b_{jk}^{\lambda\mu}$ for such a system. The free-electron gas is translationally and rotationally invariant so, for it, $b_{jk}^{\lambda\mu}$ is a multiple of the unit tensor (as far as the indices λ, μ are concerned) and a function of $\mathbf{r} = \mathbf{r}_j - \mathbf{r}_k$ alone. We denote this function by $b(\mathbf{r})$. In these circumstances it is usually simpler to work with the Fourier transform of Eq. (35) which takes the form

$$b(\mathbf{Q}) = \lim_{\omega \rightarrow 0} \left\{ \left(\frac{i}{2\pi} \right) \left[\frac{\chi(\mathbf{Q}, \omega+i\epsilon) - \chi(-\mathbf{Q}, -\omega+i\epsilon)}{(e^{\beta\omega} - 1)} \right] \right\}. \quad (36)$$

For the *noninteracting* electron gas $\chi(\mathbf{Q}, \omega)$ is easy to calculate. A straightforward generalization of the work of Ruderman and Kittel, and Yosida⁶ yields the formula⁷

$$\begin{aligned} \chi_0(\mathbf{Q}, \omega) &= \chi_0(-\mathbf{Q}, -\omega) \\ &= \sum_{\mathbf{k}} \left[\frac{n(\mathbf{k}+\mathbf{Q}) - n(\mathbf{k})}{(k^2/2m) - [(\mathbf{k}+\mathbf{Q})^2/2m] - \omega} \right] \end{aligned} \quad (37)$$

where $n(\mathbf{k})$ is the Fermi factor for the state of momentum \mathbf{k} . With this approximation for χ , $b(\mathbf{Q})$ takes

$$\langle \sigma_\lambda(\mathbf{r}_j) \sigma_\mu(\mathbf{r}_k) \rangle = \int J_{\lambda\mu}(\mathbf{r}_j\mathbf{r}_k; \omega) e^{-i\omega t} d\omega. \quad (31)$$

Zubarev's relations between G_r , G_a , and J are

$$G_r(\omega+i\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{(e^{\beta\omega'} - 1)J(\omega') d\omega'}{(\omega - \omega' + i\epsilon)} \quad (32)$$

and

$$G_a(\omega-i\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{(e^{\beta\omega'} - 1)J(\omega') d\omega'}{(\omega - \omega' - i\epsilon)}, \quad (33)$$

where $\beta = 1/kT$. Subtracting these equations gives the result

$$i[G_r(\omega+i\epsilon) - G_a(\omega-i\epsilon)] = (e^{\beta\omega} - 1)J(\omega). \quad (34)$$

Thus Eq. (14) for b_{jk} takes the form

the form

$$\begin{aligned} b(\mathbf{Q}) &= \lim_{\omega \rightarrow 0} \left\{ \left(\frac{kT}{\omega} \right) \sum [n(\mathbf{k}+\mathbf{Q}) - n(\mathbf{k})] \right. \\ &\quad \left. \times \delta \left[\frac{k^2}{2m} - \frac{(\mathbf{k}+\mathbf{Q})^2}{2m} - \omega \right] \right\} \\ &= [kT/(2\pi)^2] (m^2/Q) \quad \text{for } Q \leq 2k_F \\ &= 0 \quad \text{for } Q > 2k_F, \end{aligned} \quad (38)$$

where k_F is the Fermi momentum. Inversion of this formula gives the result

$$K_{jk} = \sin^2(k_F r_{jk}) / (k_F r_{jk})^2 \quad (39)$$

of references 2 and 3. The value of K_{jk} predicted by this equation is too small, by more than an order of magnitude, to explain the observed deviation of δ from 2. We may conclude, therefore, that electron-electron interactions induces considerably more spin correlation than that predicted by the free-electron model.

At least two authors⁸ have studied the effects of electron-electron interactions on the spin susceptibility of an electron gas. These investigations are carried out within the Hartree-Fock approximation (which, for this problem, is the same as the generalized random phase approximation) and yield equivalent results. The susceptibility is determined by the solution of an integral equation which, in general, is quite complicated. It can, however, be solved if one approximates the electron-electron interaction by a delta function. Since the effective interaction is actually a screened Coulomb potential this assumption is probably not badly in-

⁶ M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); K. Yosida, *ibid.* **106**, 893 (1957).

⁷ We set $\hbar = 1$ in these formulas.

⁸ A. W. Overhauser, Phys. Rev. Letters **3**, 414 (1959); P. A. Wolff, Phys. Rev. **120**, 814 (1960).

correct. The corresponding susceptibility is given by the formula

$$\chi(\mathbf{Q}, \omega) = \chi_0(\mathbf{Q}, \omega) / [1 - \bar{v}\chi_0(\mathbf{Q}, \omega)], \quad (40)$$

where $\chi_0(\mathbf{Q}, \omega)$ is the Ruderman-Kittel susceptibility of Eq. (37), and \bar{v} is a parameter that measures the strength of the delta-function interaction between electrons. We will later estimate \bar{v} by comparing the measured spin susceptibility of Li and Na to that calculated with the

free-electron model. In this way we force our formula for $\chi(\mathbf{Q})$ to be correct at $Q=0$, and only rely on it to determine the shape of the χ vs Q curve. This procedure will improve the reliability of Eq. (40), but it should be kept in mind that the formula is an approximate one.

We may now use Eq. (40) to obtain a formula for K_{jk} that takes account of exchange enhancement. As before $\chi(-\mathbf{Q}, -\omega) = \chi(\mathbf{Q}, \omega)$ so that Eq. (36) takes the form

$$\begin{aligned} b(\mathbf{Q}) &= \frac{ikT}{2\pi} \lim_{\omega \rightarrow 0} \left\{ \left(\frac{1}{\omega} \right) \left[\frac{\chi_0(\mathbf{Q}, \omega + i\epsilon)}{1 - \bar{v}\chi_0(\mathbf{Q}, \omega + i\epsilon)} - \frac{\chi_0(\mathbf{Q}, \omega - i\epsilon)}{1 - \bar{v}\chi_0(\mathbf{Q}, \omega - i\epsilon)} \right] \right\} \\ &\cong kT \lim_{\omega \rightarrow 0} \left\{ \left(\frac{1}{\omega} \right) \sum_{\mathbf{k}} [n(\mathbf{k} + \mathbf{Q}) - n(\mathbf{k})] \delta \left[\frac{\hbar^2}{2m} \frac{(\mathbf{k} + \mathbf{Q})^2}{2m} - \omega \right] / [1 - \bar{v}\chi_0(\mathbf{Q}, 0)]^2 \right\} \\ &= \frac{kT}{(2\pi)^2} \frac{m^2}{Q} \left[\frac{1}{1 - \bar{v}\chi_0(Q)} \right]^2, \quad \text{for } Q \leq 2k_F \\ &= 0 \quad \text{for } Q > 2k_F. \end{aligned} \quad (41)$$

This is just the result for the free-electron gas multiplied by a factor $[1 - \bar{v}\chi_0(Q)]^{-2}$. The inversion integral is

$$\begin{aligned} b(\mathbf{r}) &\sim \int \frac{e^{i\mathbf{Q} \cdot \mathbf{r}}}{Q} \frac{d^3Q}{[1 - \bar{v}\chi_0(Q)]^2} \\ &= \frac{4\pi}{r} \int_0^{2k_F} \frac{\sin(Qr) dQ}{[1 - \bar{v}\chi_0(Q)]^2}. \end{aligned} \quad (42)$$

This integral may be simplified by making the changes of variables $Q = 2k_F q$, $2k_F r = x$, becoming

$$\frac{4\pi(2k_F)^2}{x} \int_0^1 \frac{\sin(qx) dq}{[1 - \alpha f(q)]^2}, \quad (43)$$

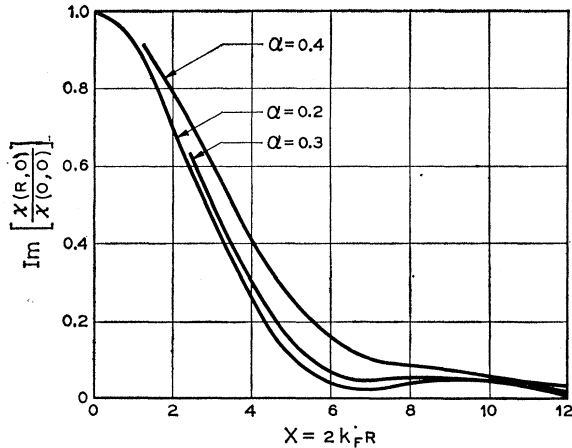


FIG. 1. Plots of spin density vs distance for various values of α .

where

$$f(q) = \left\{ 1 + \frac{(1-q^2)}{2q} \ln \left| \frac{1+q}{1-q} \right| \right\} \quad (44)$$

and α is a positive dimensionless constant proportional to \bar{v} . Since $f(0) = 2$, α must lie in the range $0.0 \leq \alpha < 0.5$. For $\alpha = 0.5$ the susceptibility goes to infinity at $Q = 0$. At this point, and for larger values of α , the electron gas is ferromagnetic and the calculations which lead to Eq. (41) are no longer valid.

If $\alpha = 0$ Eq. (43) may easily be evaluated. One obtains the formula for K_{jk} [Eq. (39)] quoted previously. For $\alpha \neq 0$ we have calculated the integral numerically. Curves of $K(\mathbf{r})$ vs $\mathbf{r} = (\mathbf{r}_j - \mathbf{r}_k)$ for the values $\alpha = 0.2, 0.3$, and 0.4 are shown in Fig. 1. The principal effect of the exchange term in the denominator of Eq. (43) is to fill in the zeros of Eq. (39). For monovalent metals (Li, Na, Cu) the quantity $(2k_F r)$ is close to 2π when r is the nearest neighbor distance. Thus, in the noninteracting electron model, K_{jk} is nearly zero for those nuclei which are most strongly correlated. As a consequence, exchange enhancement is important in just that portion of the $K(\mathbf{r})$ curve at which it can do most to improve agreement with experiment. We will use the result given above in the next section to make a comparison between theory and experiment.

IV. COMPARISON OF THEORY AND EXPERIMENT

Before using Eq. (43) to make numerical estimates of δ we must consider to what extent the free-electron gas may serve as a model for a real metal such as Li or Na. If one ignores electron-electron interactions the transition from plane to Bloch waves can be made quite easily and, if \mathbf{r}_j and \mathbf{r}_k are lattice vectors, one obtains (see reference 3) Eq. (39) for K_{jk} . It is not so clear,

however, that Eq. (42) will give the correct exchange enhancement in a real metal. We now consider this point.

In the alkalis the conduction electron wave functions are plane waves over the major part of the unit cell, but show large modulations near the nuclei. Correspondingly, the potential seen by a conduction electron is uniform over most of the cell with a small, strongly attractive region near the core. These wave functions are perturbed by the hyperfine interaction which produces a weak delta-function source term in the Schrödinger equation. To calculate the exchange-enhanced spin density one must (in principle at least) integrate this inhomogeneous equation—taking into account all modifications of the self-consistent field—from the source to that point in the crystal at which one wishes to know the spin density. If this point is at a lattice site different from that at which the source is located, much of the integration of the Schrödinger equation proceeds through a part of the lattice in which the crystal potential is nearly constant. In this range, exchange enhancement of the induced spin density should arise in much the same way that it does in a free-electron gas. Thus, we may anticipate that at these lattice sites Eq. (42) will give a fair estimate of the induced moment. This will not be the case at the central site, however. The induced spin density there is determined by the behavior of the conduction electron wave functions near the nucleus where the crystal potential is large and highly singular, and far outweighs the exchange field of the conduction electrons. The perturbation in this wave function will be peaked at the origin (as the zero order wave function is) but this peak will *not* be amplified by exchange. It is only as one proceeds away from the origin through regions in which the crystal potential is uniform that the modification of the exchange energy can produce enhancement of the type predicted by Eq. (42). Thus, in using this formula to make comparison with experiment we will set $\alpha=0$ in computing the spin density at the central lattice site.

This state of affairs may be viewed from another point of view. Imagine that we apply a small, sinusoidal magnetic field, $B=B_0 e^{i\mathbf{Q}\cdot\mathbf{r}}$, to the metal and seek, by perturbation theory, to compute the response. The interaction Hamiltonian is of the form

$$H_1 = \int \bar{\psi}(\mathbf{r})(\boldsymbol{\sigma}\cdot\mathbf{B}_0)e^{i\mathbf{Q}\cdot\mathbf{r}}\psi(\mathbf{r})d^3r, \quad (45)$$

where, in the usual way, we may expand the electron field operator, $\psi(\mathbf{r})$, in the form

$$\psi(\mathbf{r}) = \sum_{\mathbf{k},\mu} [a_{\mathbf{k},\mu}\varphi_{\mathbf{k}\mu}(\mathbf{r})]. \quad (46)$$

Here the $\varphi_{\mathbf{k},\mu}$'s are Bloch functions and the $a_{\mathbf{k},\mu}$'s the corresponding annihilation operators. If the wave vector Q is small the important matrix elements that appear in Eq. (45) are diagonal in band indices and H_1 takes the

form

$$H_1 \simeq \sum_{\mu,\mathbf{k}} [\bar{a}_{\mathbf{k}+\mathbf{Q},\mu} a_{\mathbf{k},\mu} \langle \boldsymbol{\sigma}\cdot\mathbf{B}_0 \rangle]. \quad (47)$$

In this limit we have essentially a single band problem and one may derive a formula exactly analogous to Eq. (42) for the spin susceptibility. On the other hand, for large Q (that is, for short distances) there are important interband matrix elements of H_1 that couple wave functions that differ by energies large compared to the conduction electron exchange energy. Thus, this energy becomes relatively less important and we expect a smaller exchange enhancement of the susceptibility.

The arguments given above are qualitative in nature. A detailed integration of the perturbed Schrödinger equation (taking account of modifications of the self-consistent potential) would be required to make them quantitative. This is a formidable task and, in view of the many uncertainties involved in our considerations, hardly seems warranted at the present. We will be content, therefore, to accept Eq. (42) as correct for lattice sites other than the central one, but will set $\alpha=0$ in computing spin density at the origin.

We are now in a position to calculate δ from Eq. (42). For this purpose one must know α . As indicated above, we will obtain its value by comparing Eq. (40) (for $Q=\omega=0$) with the measured spin susceptibility of the alkali metals. Measurements of spin susceptibility for Li and Na have been made by Schumacher, Carver, and Slichter.⁹ Comparison of their results with the free-electron values indicates that for both metals $\alpha \simeq 0.2$. The corresponding value of δ , calculated according to the scheme outlined above, is $\delta=2.1$. This is to be compared with the experimental value which, in both cases, is about 2.2. Thus the calculated correlation correction is about a factor of 2 too small to explain the observed value. A possible reason for this discrepancy can be seen from Eq. (43). As mentioned earlier, at the nearest-neighbor distance x is close to 2π and the integral is carried over one full cycle of the sine function. If all values of q were equally weighted, the result would be zero (or nearly so). It differs from this—though not greatly—because the denominator of Eq. (43) is smaller near $q=0$ than at $q=1$. We have seen, however, that this formula is incorrect, in a real metal, for large q . For $q \simeq 1$ the exchange enhancement should be even smaller than that predicted by Eq. (41). This effect will further reduce the cancellation which leads to a small value of $b(r)$ at the nearest neighbor distance.

Finally, a word should be said about the measurements in Al and Cu. Here the δ values are of order 2.5. No spin susceptibility measurements have been made on these metals so it is not possible to carry out the above analysis for them. Nevertheless, it seems very unlikely that the exchange enhancement would be sufficiently big to explain a δ of 2.5. We must look

⁹ R. Schumacher, T. Carver, and C. P. Slichter, Phys. Rev. **95**, 1089 (1954).

elsewhere for an explanation of the large values of δ in these metals.

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Elastic Constants of Strontium Titanate*

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The elastic constants c_{11} , c_{12} , and c_{44} of single-crystal strontium titanate have been measured as a function of temperature from 300 to 108°K by determining the velocity of an ultrasonic wave. At 108°K the strontium titanate undergoes a phase transition to a tetragonal structure which causes a marked change of the elastic properties and the appearance of a domain structure, but does not cause a discontinuity of the dielectric constant. The phase transition is free of hysteresis. The dependence of the elastic properties on a dc electric field parallel to the velocity of sound propagation was measured and found independent of the dielectric properties. The implications of this result are discussed.

I. INTRODUCTION

STRONTIUM titanate is a cubic material above 108°K with the perovskite structure which exhibits paraelectric properties. Its dielectric constant follows a Curie-Weiss law and is dependent on an external electric field.¹ It has been suggested by Cochran² and verified by Barker and Tinkham³ that the high dielectric constant in SrTiO₃ is connected with a "soft mode," an optically active lattice vibration which has a temperature-dependent resonance frequency. The assignment of this mode to a specific type of vibration is still debated.^{4,5} The temperature dependence of the effective spring constant for this $k=0$ mode is believed to be connected with the near cancellation of the short-range repulsive forces with the long-range Coulomb interaction; thus both the long-range and short-range forces are equally important.

For this reason we measured the elastic properties and their field dependence in SrTiO₃ to obtain more information about the short-range forces. As a consequence of the small effective spring constant for the soft

mode, the pertinent ions can move relatively large distances under an external electric field. The ions move into new equilibrium positions with different effective spring constants because of anharmonicities. This is apparent from the nonlinear dielectric behavior. The dielectric constant decreases with electric field,¹ indicating a stiffening of the effective spring constant of the soft mode. Since sound velocity measurements can be carried out relatively accurately, a measurable effect on the elastic properties through the influence of an electric field may be expected although in this case only the short-range forces are involved.

II. MEASUREMENTS

The elastic constants of a cubic material can be characterized by three stiffness constants, c_{11} , c_{12} , and c_{44} .⁶ These constants are related to the velocity of propagation for longitudinal and transverse waves along various crystallographic directions, so that by measuring velocities for various orientations the elastic constants may be determined. In Table I the equations relating velocities of propagation and elastic constants used for the measurements on strontium titanate are given.

At 108°K where the strontium titanate becomes tetragonal,^{7,8} six elastic constants are needed to specify all the elastic properties. When the strontium titanate passes into the tetragonal phase, however, it breaks up into domains which are the order of the wavelength of

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