this T^6 term. Thus an analysis which does not include the direct phonon processes as contributors to the temperature variation of the spectral linewidth could not possible hope to obtain a good correlation between theory and experiment, even if there appears superficially to be correlation.

The obvious extension of this work is to carry out a similar analysis of ion-lattice interactions in magnetic materials, to see if analogous magnon relaxation processes are observable. As the phonon system surrounding an ion provides a ready reservoir and means of ion-lattice interaction, so too should the surrounding system in a magnetic lattice. The main problem is to obtain a system in which such processes will have measurable contributions to spectral linewidths. This has been discussed in a previous paper,[18] and we hope to carry out these and related studies on the systems $RbMnF_3:Pr^{3+}$, $RbMnF_3:Co^{2+}$, and $YIG:Tb^{3+}$.

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Temperature Dependence of the Electronic Structure of Solid and Liquid Copper–An NMR Study

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The Knight shift and spin-lattice relaxation rate in copper metal were measured using pulsed-NMR methods. The temperature range of the measurements extends in the solid from room temperature to the melting point (1083 °C), and in the liquid from 875 (supercooled phase) to 1250 °C. From these measurements the temperature dependence of $\mathcal{K}(\alpha)$, the reciprocal enhancement factor of the Korringa relation, is obtained. The recent developments in the theory of exchange enhancement of the Pauli susceptibility in metals are used to interpret this temperature dependence of $\mathcal{K}(\alpha)$. Thus the temperature dependence of the band effective mass m^* and of the conduction-electron spin density at the nucleus, $\langle|\psi(0)|^2\rangle$, is derived. It is shown that these quantities are strongly influenced by s-d hybridization, and their temperature dependence is explained as being due to the volume dependence of the hybridization. Similarly, the change in both m^* and $\langle|\psi(0)|^2\rangle$ on melting is shown to be caused by the accompanying volume change, and to be only weakly influenced by loss of structure and order.

I. INTRODUCTION

In a previous paper[1] (referred to henceforth as I) we presented measurements of Knight shift K and spin-lattice relaxation T_1 in copper, both in the solid and liquid states. We have tried to explain the temperature dependence of these quantities in terms of copper band structure.

An appreciable progress has been made recently in the theory of electron susceptibility and the many-body mechanisms of its enhancement.[2] This progress might have been used to produce a more sophisticated interpretation of the results presented in I. However, the accuracy of the measurements was insufficient for this purpose. Moreover, we have found that there was some instrumental contribution to the measured Knight shift, which was caused by a residual magnetism of the high-temperature probe. Therefore, we carried out a new set of experiments in which we measured the Knight shift and spin-lattice relaxation of copper with far greater accuracy than in I. This was achieved by improving the experimental setup, and by ensuring that the high-temperature probe was free of any magnetic materials. Using our latest results we were able to obtain a better understanding of the K and T_1 behavior of copper.

In Sec. II we describe the experimental details; the results of the measurements are presented in Sec. III. In Sec. IV we give a very brief summary of the theoretical background needed to interpret the results. In Sec. V we obtain the dependence on temperature of two quantities: the effective mass m^* and the conduction-electron spin density at the nucleus, $\langle|\psi(0)|^2\rangle$. These are explained in Sec. VI by making use of the known band structure of copper, the main characteristic of which is the hybridization between a $3d$ band and a conduction band.

II. EXPERIMENTAL DETAILS

The experimental setup was fundamentally the same as in I. The main improvement over the previous system was a new high-temperature probe, built of carefully chosen materials. Thus its relative contribution to the magnetic field at the site of the sample was less than 5×10^{-7}.

The pulsed-NMR spectrometer was similar to that described by Clark.[3] However, we preferred a single-coil configuration with dynamic switching between transmitting and receiving modes. This configuration was more convenient to use in the limited space of the high-temperature probe.

The center of the NMR line was defined, using a boxcar integrator,[4] by recording the Fourier transform of the free-induction decay as a function of magnetic field. We chose to record the sinus Fourier transform (dispersion mode) rather than the cosine transform (absorption mode). Accuracy in locating the line center in the former case was higher than in the latter, and was equal to the linewidth divided by the signal-to-noise ratio. This point is exemplified in Fig. 1, which shows a recording of both modes of integration of the Cu^{63} NMR line at room temperature.

The accuracy of measurement of the line center up to 700 °C was 5×10^{-6} of the resonance field. The accuracy at temperatures above 800 °C, after motional narrowing took place,[1] was about 1×10^{-6}.

The samples used in this work were chemically

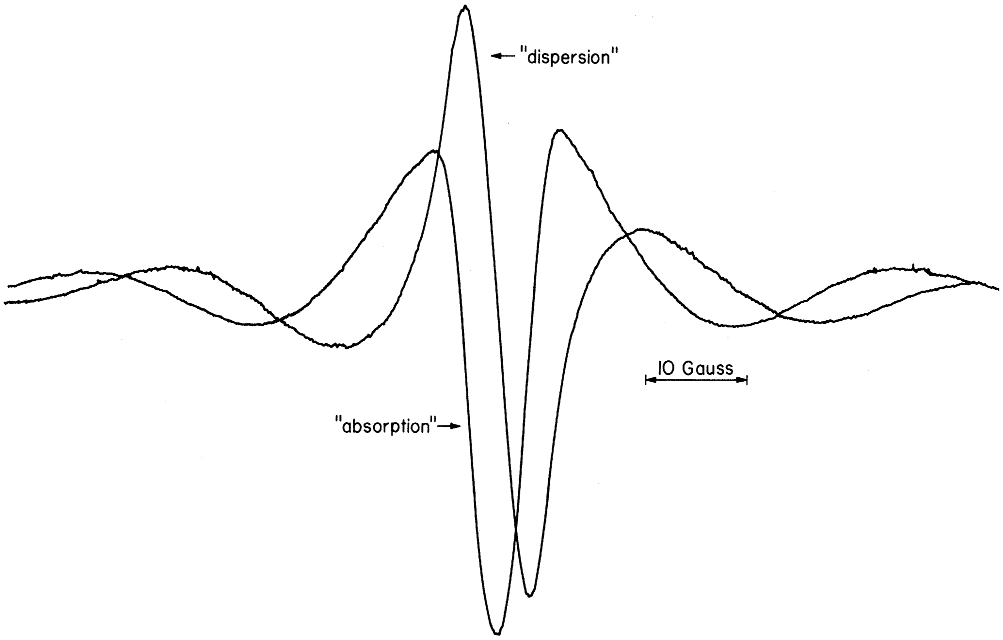

FIG. 1. Boxcar integrations of Cu^{63} free-induction decay at room temperature. Both modes were recorded with time constant of 3 msec and with boxcar gating width of 200 μsec (sample was about 1 g of metallic copper and the resonance frequency—22 MHz).

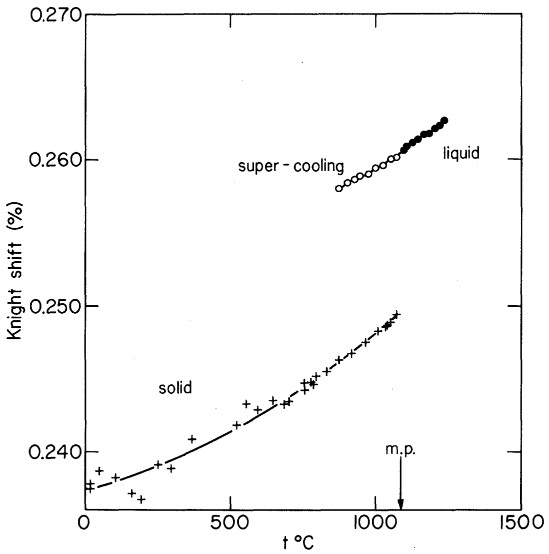

FIG. 2. Knight shift of Cu^{63} in copper as function of temperature.

prepared as described in I. We used two different sources[5] for preparing the copper samples. The purity in both cases was 99.999%.

Spin-lattice relaxation times were measured with π-τ-$\pi/2$ pulse sequences. The amplitude of the free-induction decay following the $\pi/2$ pulse was measured with a boxcar integrator, as a function of τ. It can be shown that the boxcar opening must be about T_2 in order to get maximum signal-to-noise ratio for a specific learning time. The data were fitted by a least-squares computer program to $M = M_0(1 - A\, e^{-\tau/T_1})$. This method brings both convenience and accuracy in deriving T_1 from the experimental data.[6]

All the measurements were made at a frequency of 22 MHz, with an H_1 field in the rotating frame of 60 Oe. The magnetic field was measured by a proton magnetometer with accuracy of 5×10^{-7} at a field of 20 kG.

III. EXPERIMENTAL RESULTS

A. Knight Shift

The Cu^{63} Knight shift K was measured in solid copper from room temperature to the melting point (1083 °C), and in the liquid from 875 (supercooled liquid) to 1240 °C. The data are given in Fig. 2, where the solid line is the best fit. We see that in the solid, K increases from a room-temperature value of $K(20\,°\mathrm{C}) = (2.375 \pm 0.004)\times10^{-3}$ to its melting-point value of $K(\mathrm{sol.}\ 1083\,°\mathrm{C}) = (2.496 \pm 0.001)\times10^{-3}$ and increases on melting to $K(\mathrm{liq.}\ 1083\,°\mathrm{C}) = (2.605 \pm 0.001)\times10^{-3}$. The accuracies quoted are not absolute, as they do not include the systematic error arising from measurement of the reference compound. The absolute value of K when measured relative to a reference of CuBr was at room temperature $K(20\,°\mathrm{C}) = (2.375 \pm 0.012)\times10^{-3}$. CuBr was selected as a reference because it is the least covalent among the cuprous halides.[7] It seems that the difference between our value and the value of $K(23\,°\mathrm{C}) = (2.34 \pm 0.02)\times10^{-3}$, measured by Warren and Clark,[8] is because they used CuCl as a reference.

In Table I we compare the relative changes in K, as measured in this work, with earlier results. Our results fall within the experimental errors of the previous works. As to the jump on melting, our results in the present work agree, within experimental accuracy, with those in I. However, they do not exhibit the anomalous increase in the Knight shift from 700 to 800 °C measured there. This instrumental effect was caused by the temperature-dependent residual magnetism of the probe used in I. Due to the method of measuring described in I, this magnetism influenced both the sample and the Hall probe stabilizing the magnet. Thus, it induced an artificial line shift, especially in the region where the line is motionally narrowed. Unfortunately, the method of calibration of the probe in I was not sufficiently sensitive to detect such an effect.

B. Spin-Lattice Relaxation

Spin-lattice relaxation time T_1 for both Cu^{63} and Cu^{65} was measured in the same temperature range in which the Knight shift was measured. The experimental data are presented in Fig. 3, where the solid lines are best fits for the data. We see that $(T_1T)^{-1}$ of Cu^{63} increases by (24.5 ± 0.7)% from room temperature to the melting point, and jumps by (17.5 ± 0.7)% on melting. These results are in agreement, within experimental error, with the measurements in I. However, the accuracy in the present work is far higher than that in I, and it includes measurements of T_1 in the supercooled phase, which were not included in I. Warren and Clark[8] have also measured T_1 but their results disagree with the present results, especially in the solid before melting. This disagreement is explained by the large quadrupole contribution to relaxation in their sample, which was caused by

TABLE I. Relative changes of the Knight shift in copper.

Reference	Increase in solid from room temperature to melting temperature	Change on melting
Odle and Flynn (Ref. 9)	(5±1.5)%	(5.1 ±0.3)%
Warren and Clark (Ref. 8)	(6.8±1.6)%	(3.6 ±1.6)%
Present work	(5.15±0.15)%	(4.37±0.08)%

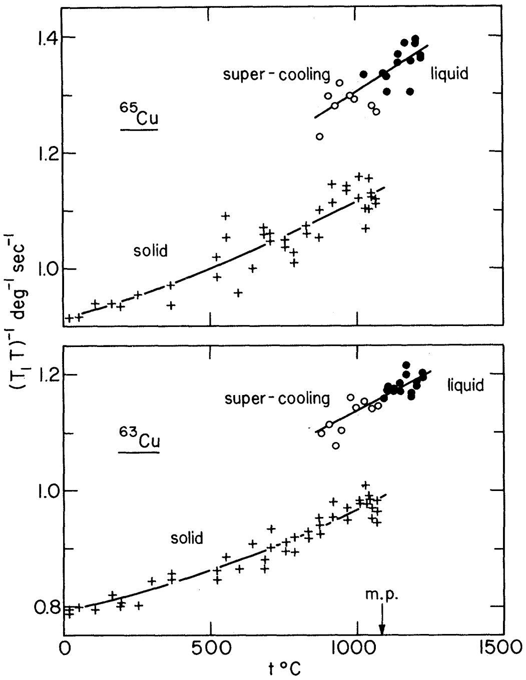

FIG. 3. Spin-lattice relaxation of Cu^{63} and Cu^{65} as a function of temperature.

diffusing impurities.[8]

In our samples there was no quadrupole contribution to relaxation, as was proved by the accurate measuring of the ratio of spin-lattice relaxation times T_1^{63}/T_1^{65}. In the solid, this ratio was between 1.150(8) and 1.160(8), whereas in the liquid it was between 1.141(8) and 1.151(8). However, spin-lattice relaxation caused solely by magnetic processes should satisfy the condition $T_1^{63}/T_1^{65} = (\gamma^{65}/\gamma^{63})^2 = 1.1477(6)$, while spin-lattice relaxation caused by quadrupole processes should satisfy $T_1^{63}/T_1^{65} = (Q^{65}/Q^{63})^2 = 0.856(5)$.[10] Therefore, the measured ratio of spin-lattice relaxation proves that in the solid this quadrupole contribution is at most 2% of the total relaxation, whereas in the liquid it is $(2 \pm 2)\%$ only.

Thus we can safely say that the measured spin-lattice relaxation in copper is a result of magnetic hyperfine interaction only.

IV. THEORETICAL BACKGROUND

A. Hyperfine Interaction in Metals

In most nontransition metals the dominant mechanism which couples nuclear spins with the conduction electrons is the contact hyperfine interaction. Such interaction gives rise to a Knight shift[11]

$$K_s = (8\pi/3)\,\Omega P_F\, \chi_p\,, \tag{1}$$

where χ_p is the Pauli susceptibility of the conduction electrons (per unit volume), Ω is the atomic volume, and $P_F \equiv \langle |\psi(0)|^2 \rangle_F$ is the conduction-electron spin density at the nucleus, averaged over all the Fermi-surface states. The subscript s in K_s emphasizes that only conduction electrons with s character contribute to this shift.

The same interaction gives rise to spin-lattice relaxation[12]

$$(1/T_1)_s = \pi k T\, (\gamma_e \gamma_n)^2 \left[(8\pi/3)\,\Omega P_F\, N(E_F)\right]^2 , \tag{2}$$

where γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, respectively, and $N(E_F)$ is the density of states at the Fermi energy.

For independent electrons, that is, assuming there is no electron-electron interaction, one gets $\chi_p = \frac{1}{2}(\hbar\gamma_e)^2 N(E_F)$. One might expect, then, that K_s and $(1/T_1)_s$ would satisfy the Korringa relation[12]:

$$K_s^2\, T_{1s}\, T = (\hbar/4\pi k)\,(\gamma_e/\gamma_n)^2 \equiv \eta\,. \tag{3}$$

The Pauli spin density interacts with the nucleus not only *directly*, as presented by (1) and (2), but also *indirectly* through core polarization. When the polarizing Fermi electrons have only s character, this interaction enhances P_F and therefore Eq. (3) is still satisfied. Thus, when non-s core polarization and orbital contributions may be neglected, the Korringa relation is obeyed. We shall show later that this is true in the case of copper.

In fact, experimental values of $K^2 T_1 T$ almost never obey the Korringa relation. This discrepancy is due to electron-electron interactions which were disregarded while deriving Eq. (3). This interaction enhances the independent electron susceptibility χ_p^0 so that the Pauli susceptibility is rather[13]

$$\chi_p = \chi_p^0/(1-\alpha)\,, \tag{4}$$

and the Knight shift, which is proportional to χ_p, is enhanced similarly. When the electron-electron interaction can be represented by an effective potential $V(\vec{q})$, then the enhancement parameter is $\alpha = V(0)\,N(E_F)$. This interaction has been calculated for a free-electron gas at metallic densities in various many-body techniques.[14,15]

The spin-lattice relaxation rate is also enhanced by electron-electron interactions, though less than K^2. Moriya[16] has shown that

$$(1/T_1) = (1/T_1^0)\left\langle \left[1 - \alpha F(\vec{q})\, V(\vec{q})/V(0)\right]^{-2} \right\rangle , \tag{5}$$

where $F(\vec{q})$ is the static response function of the noninteracting electrons, and the outer brackets indicate averaging over all the momenta $\vec{q}$ connecting states on the Fermi surface. Thus the Korringa relation will have a new form [see Eqs. (4) and (5)]:

$$K^2 T_1\, T = \eta/\mathcal{K}(\alpha)\,, \tag{6}$$

where $\mathcal{K}(\alpha)$ is a complicated function of α and is dependent on the band structure of the metal.

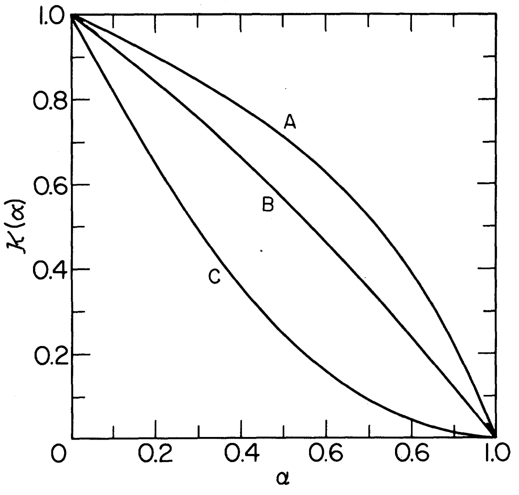

FIG. 4. Reciprocal enhancement factor of the Korringa relation $\mathcal{K}(\alpha)$, as against the enhancement parameter α. The different calculations were made assuming for the interaction (A) δ-like behavior (Ref. 17), (B) short but finite range (Ref. 2), and (C) long range.

Narath and Weaver[17] have calculated $\mathcal{K}(\alpha)$ assuming a spherical Fermi surface and $V(\vec{q}) = \text{const}$, which means that V is a δ function in real space. The result of this calculation is presented by curve A of Fig. 4. One of the main conclusions of Narath and Weaver's work was that a zero-range electron-electron interaction potential [that is, $V(\vec{q}) = \text{const}$] is not realistic, and should be replaced by $V(\vec{q})$, which is momentum dependent. However, the approximations made by these authors limited their calculation to momentum-independent potentials only.

The recent work of Shaw and Warren[2] extended Moriya's theory to include interaction potentials which are momentum dependent. Their calculation of $\mathcal{K}(\alpha)$ is presented by curve B in Fig. 4 and is based on recent theoretical studies of electron-gas response, which are reviewed in their paper. They have shown that the enhancement of the Korringa relation in alkali metals is explained by this $\mathcal{K}(\alpha)$. Therefore we have chosen to use Shaw and Warren's $\mathcal{K}(\alpha)$ throughout this work.

Curve C of Fig. 4 is $\mathcal{K}(\alpha)$, calculated under the assumption of a long-range interaction potential, in which case the relaxation rate is not enhanced and $\mathcal{K}(\alpha) = (1-\alpha)^2$. Thus, curves A and C represent $\mathcal{K}(\alpha)$ calculated under different extreme assumptions for the electron-electron interaction range.

The calculation of α [14,15] has been made for a gas of free electrons. We shall include band-structure effects in the method used by Silverstein,[14] namely,

$$\alpha = \alpha_f (m^*/m) , \qquad (7)$$

where the subscript f stands for a free-electron model, and (m^*/m) is the band effective-mass ratio, excluding electron-phonon effects. The independent electron susceptibility χ_p^0 is also dependent on the effective mass

$$\chi_p^0 = \chi_f^0 (m^*/m) , \qquad (8)$$

where χ_f^0 is the independent free-electron susceptibility. Thus, from Eqs. (4), (7), and (8) the dependence of the susceptibility on density of states may be obtained at the Fermi level, because $m^*/m = N(E_F)/N_f(E_F)$.

B. NMR and Electronic Structure of Liquid Metals

We have seen that Knight shift and spin-lattice relaxation depend directly on electronic quantities such as $N(E_F)$ and P_F. It has therefore been argued[18,19] that NMR measurements in metals should be very sensitive to changes in electronic structure accompanying melting. However, Knight shift for most metals changes only slightly upon melting, which indicates that almost no change of $N(E_F)$ and P_F takes place.[19]

This conclusion seems to contradict the information received from transport and optical measurements in liquid metals.[19–21] Hall coefficient and optical properties change considerably upon melting and show free-electron-like characteristics in the liquid,[19] whereas in the solid they seem to be influenced strongly by band-structure effects.

This apparent contradiction has been a challenge for a long time. Some[18,19] have explained the fact that the Knight shift does not change upon melting as being due to preservation of short-range order from solid to liquid. This explanation does not seem plausible, as short-range order is not preserved, even on melting of close-packed metals. The structure of most liquid metals is rather that of "random close-packed liquid" suggested by Bernal.[22]

Another explanation has been offered by Ziman,[23] that K does not change on melting because the susceptibilities of both solid and liquid metals are free-electron-like. This explanation also seems inadequate, at least for some metals, such as lithium, which is certainly not free-electron-like in the solid, and nevertheless shows no change in K upon melting.[24]

In the case of copper metal we shall show that its electronic structure, both in the solid and the liquid, is strongly influenced by nonstructural effects. Thus, the main effect of melting will be explained by the accompanying volume change, while there is almost no effect brought about by loss of order.

V. INTERPRETATION

It can be shown that in copper the only important contribution to the hyperfine field is due to contact interaction. In the atomic $3d^{10}4s^1$ configuration this contribution of the one 4*s* electron produces a hyperfine field of about 1600 kOe.[25] The indirect contribution of this electron, via core polarization, is evaluated as 10–50% of the direct contribution.[26] A value of 2600 kOe for the total hyperfine field was obtained from atomic-beam measurement in copper.[27] However, this contribution of the *s* core polarization to the spin density has no effect on the value of the Korringa relation, and therefore will not hinder the interpretation of the experimental data (see Sec. II).

On the other hand, the *d* core polarization may change the value of the Korringa relation. It can be shown to be negligible in the case of copper, in which the hyperfine field induced by an unpaired 3*d* electron through core polarization is about −125 kOe.[26] As we shall see later, there is at most 30% of 3*d* character in the Fermi electrons of copper, and therefore the contribution of the *d* core polarization to the Knight shift, K_d, is no more than 2% of the total *K*. The *d* contribution to the spin-lattice relaxation, $(1/T_1)_d$, is even smaller, as it is proportional to K_d^2.

Similarly, the contributions of the orbital interaction both to *K* and $1/T_1$ are estimated to be very small in copper; they may be large in heavy metals,[28] or in transition metals having half-filled narrow bands. Thus, we shall assume that there is only *s* contact contribution to the hyperfine field in copper metal.

Under this assumption, we used Eq. (6) to derive $\mathcal{K}(\alpha)$ from the measurements of *K* and T_1. We present $\mathcal{K}(\alpha)$ in Fig. 5 as function of volume, utilizing thermal expansion data in copper.[29] We preferred to plot it thus, rather than as function of temperature, as the temperature dependence of *K* and T_1 is not intrinsic and is due chiefly to effects of thermal expansion. This point will be discussed in greater detail in the course of this paper.

In Fig. 6 there is a plot of the Knight shift, this time as a function of volume. The points were measured by Benedek and Kushida[30] as a function of pressure, thus giving the explicit volume dependence $(\partial K/\partial v)_T$. The solid line, on the other hand, presents our measurements, which were carried out as function of temperature, thus giving $(\partial K/\partial T)_P$. Comparison of both these independent measurements shows that the explicit temperature dependence of the Knight shift $(\partial K/\partial T)_v$ is quite negligible.

This point is also proved by direct estimation, using the semiquantitative model of Benedek and Kushida.[30] From the volume dependence of P_F (derived later), we obtained for $(\partial K/\partial T)_v$ an upper limit of 20% of the total temperature dependence $(\partial K/\partial T)_P$.

As we see in Fig. 5, $\mathcal{K}(\alpha)$ changes considerably over the present volume and temperature range. We used the dependence of $\mathcal{K}(\alpha)$ on α, calculated by Shaw and Warren[2] (graph B of Fig. 4), and thus obtained the volume dependence of α.

This volume dependence of α may be brought about by both α_f and m^* [see Eq. (7)]. However, the dependence of α_f on volume, no matter how it is calculated, is negligible in comparison to that of α. For instance, according to Rice's calculation,[15] $\alpha_f = 0.27$ for a free-electron gas, the density of which is that of copper, ($\Omega = 80$ a.u.), and its volume dependence is $(d\ln\alpha_f/d\ln\Omega) \sim 0.2$ only.

Thus we assumed that the whole volume dependence of α is brought about by m^*/m. Using Eqs. (1) and (4) we obtained also the volume dependence of ΩP_F.

Both these dependences are plotted in Fig. 7. The heavy drawn graphs of m^*/m and ΩP_F were derived using $\mathcal{K}(\alpha)$ according to Shaw and Warren.[2] The upper and lower graphs, in each case, are obtained assuming δ-function-type and long-range electron-electron interactions, respectively. It is interesting to note that the relative behaviors of both these functions, referred to their room-temperature value, are not too sensitive to the model assumed for $V(\vec{q})$. Their derived absolute values, on the other hand, do depend strongly on $\mathcal{K}(\alpha)$.

VI. DISCUSSION

We shall show now that the volume dependence of m^* and P_F can be explained by the band structure of copper.

Copper has an atomic configuration $3d^{10}4s^1$. Its band structure in the solid consists of a wide nearly-free-electron conduction band, intersected by

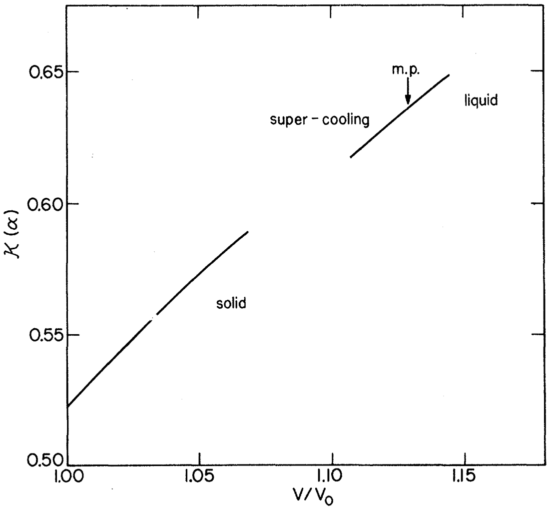

FIG. 5. Reciprocal enhancement factor of the Korringa relation $\mathcal{K}(\alpha)$ in copper metal, as function of volume.

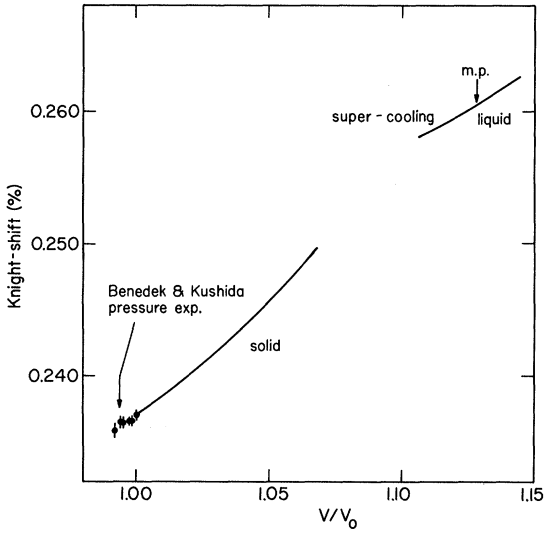

FIG. 6. Knight shift of copper as a function of volume. The points present the results of Benedek and Kushida (Ref. 30), whereas the solid line is the least-squares fit to our measurements.

a full $3d$ band. The $3d$ band is about 3.2 eV wide, and its center of gravity is about 3.7 eV below the Fermi level E_F.[31,32] The Fermi surface of copper is contained in the first Brillouin zone, and touches its face by the so-called "necks" in the $\langle 111 \rangle$ directions.[33,34]

Let us analyze a simple model of a free-electron band, intersected by a d level. We shall see that such a simple model explains semiquantitatively the dependence of m^* on volume derived from our measurements.

Both the free-electron band $\hbar^2k^2/2m$, and the d level E_d are presented in Fig. 8 by the dashed lines. Such a system is described using a 2×2 model Hamiltonian[35,36]

$$\mathcal{H} = \begin{vmatrix} \hbar^2k^2/2m & V_{sd} \\ V_{ds}^* & E_d \end{vmatrix} , \tag{9}$$

where V_{sd} is a hybridization matrix element arising from the distortion of the atomic d state in the metallic state.

The solution of $\det \| \mathcal{H}_{ij} - E\delta_{ij} \| = 0$ is

$$E = \tfrac{1}{2}\{E_d + \hbar^2k^2/2m \pm [(E_d - \hbar^2k^2/2m)^2 + 4V_{sd}^2]^{1/2}\} , \tag{10}$$

which is described by the solid line in Fig. 8, for a special case of $V_{sd} = \frac{1}{4}E_d$. At the intersection point K_d there is an energy gap of $2V_{sd}$. Far from K_d, that is, for $\hbar^2k^2/2m - E_d \gg V_{sd}$, there is a second-order shift of the free-electron energy:

$$\delta E \sim \frac{V_{sd}^2}{\hbar^2k^2/2m - E_d} . \tag{11}$$

Such a shift will influence the density of states at the Fermi level. The general expression for the density of states is

$$N(E_F) = \frac{1}{(2\pi)^3} \int \frac{d^2k}{(dE/dK)_{E_F}} , \tag{12}$$

where the integration is over the whole Fermi surface. In the case of copper metal, a good approximation for the Fermi surface is a sphere with eight necks. Thus, Eq. (12) can be approximated as

$$N(E_F) \sim \frac{1}{(2\pi)^3} \left. \frac{1}{(dE/dK)} \right|_{K_F} S , \tag{13}$$

where S is the face area of the Fermi surface. It equals approximately the surface of a sphere, the radius of which is the average radius of the actual

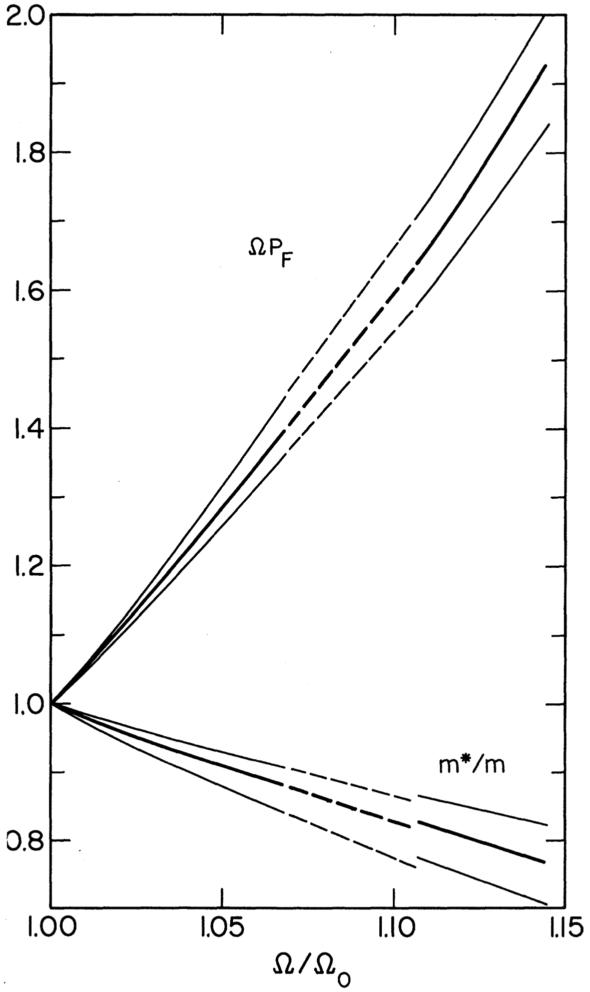

FIG. 7. m^*/m and ΩP_F as against volume, derived from the experimental data of K and T_1 (see text). Both quantities are presented as relative to their room-temperature values. The dashed lines are an analytic extrapolation from the solid.

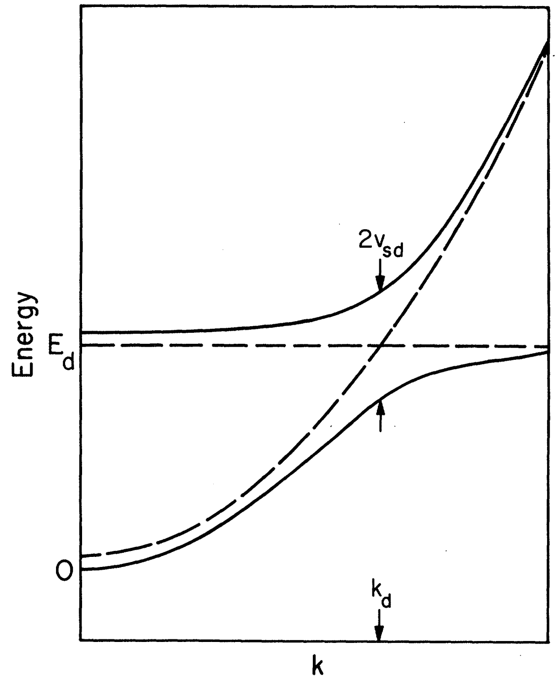

FIG. 8. Hybridization between a free-electron band and a a d level (the dashed lines), for the case $V_{sd} = \frac{1}{4}E_d$.

Fermi surface, minus the total cross section of the eight necks.

In this way the band-structure effective-mass ratio, defined as $N(E_F)/N_f(E_F)$, will be obtained from Eqs. (11) and (13):

$$\frac{m^*}{m} = \frac{S}{S_f} \frac{1}{1 - [V_{sd}/(E_F - E_d)]^2} , \qquad (14)$$

where S_f is the face area of the equivalent free-electron Fermi sphere. We estimated S from de Haas–van Alphen measurements[33,34] as $S \sim 0.88 S_f$ (the total cross section of the necks is about 7% of S_f). The value of $(E_F - E_d)$ was taken from optical measurements,[32] whereas the value of $V_{sd} \sim 2.1$ eV was evaluated from band-structure calculation of copper.[37]

In this way we obtained a value of $m^*/m = 1.28$. This value is in very good agreement with the value obtained for the density of states by direct band-structure calculations.[26,38] It is also in good agreement with values obtained from specific-heat[39] and cyclotron-resonance[40] experiments, after excluding electron-phonon effects. It is interesting to note that this agreement is good in spite of the simplifications used in this model; we did not take into consideration, for instance, the width and structure of the d band.

In order to obtain the volume dependence of m^*/m, we had to know S, $E_F - E_d$, and V_{sd} as a function of volume. This information for both S and $E_F - E_d$ was derived from experimental data: in the former case from de Haas–van Alphen measurements under pressure,[33,34] and in the latter from optical measurements as a function of temperature[32] and pressure.[31] The volume dependence of V_{sd}, on the other hand, was taken from band-structure calculations made by Jacobs.[41] The volume dependence obtained in this way was confirmed by an independent estimate based on the measurement of the $L_1^u L_2^1$ direct optical transition as function of temperature.[42]

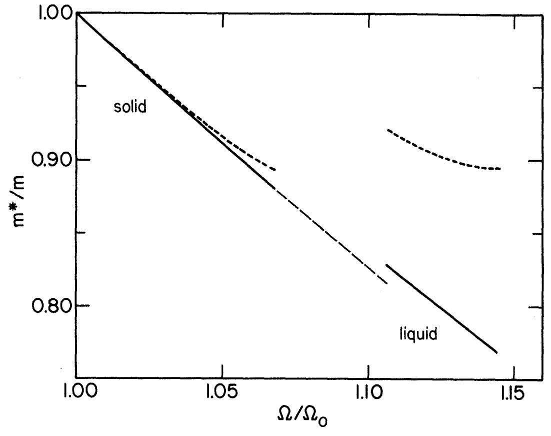

FIG. 9. m^*/m as against volume (relative to room-temperature value). The solid line is the experimentally derived value whereas the dashed line is theoretical (see text).

In Fig. 9 the dashed line represents the volume dependence of m^*/m in the solid and liquid states, derived using the described procedure. We assumed that in the liquid state the necks disappear, thus causing an increase in m^*/m. The necks disappear because order is not preserved upon melting and the Fermi surface, which in the solid touches the face of the Brillouin zone, becomes a sphere (see Sec. IV).

The solid line in Fig. 9 presents m^*/m as de-

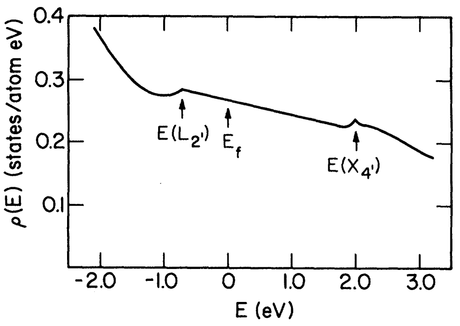

FIG. 10. Density of states in copper in the vicinity of E_F (Ref. 38).

rived from our measurements. One can see that in the solid the agreement between the experimental and calculated m^*/m is very good. In the liquid, there is a considerable difference; m^*/m in the liquid is almost an extrapolation from the solid, in contrast to the positive jump on melting predicted by the model.

The reason for this discrepancy seems to be the following one. While calculating m^*/m in the *solid* we neglected those contributions to the density of states which are due to singularities in the energy. These singularities arise from actual contact of the Fermi surface with the Brillouin-zone boundaries. The contributions are positive and equal to a few percent of the total density of states, as shown in Fig. 10 [which gives a detailed calculation of $N(E)$ near E_F, by Faulkner, Davis, and Joy[38]]. Upon melting, as order is destroyed, these singularities disappear together with the Brillouin zone and the necks. Thus, the melting brings about a decrease in m^*/m which seems to cancel the increase caused by the disappearance of necks.

The change in m^*/m presented in Fig. 9 is chiefly due to expansion of the lattice. The explicit temperature dependence of the band structure of copper is negligible. This can be evaluated following a procedure similar to that used by Kasowski and Falicov[43] in calculating the temperature-dependent band structure of cadmium. In that case the parameter characterizing the change in the band structure is the Debye-Waller factor $e^{-2W(\vec{q},T)}$. However, in copper near the melting point this parameter is not significantly different from unity—about 0.90 even for $q=2K_F$. Thus, the rise in temperature has only a small direct influence on quantities which are order dependent, such as the necks and the singularities in the density of states. The hybridization presented by the parameter V_{sd} is not dependent on order and structure. Therefore it is a function of volume only and not of temperature.

Let us see now what is the volume dependence of P_F predicted by the described model. The simplest approximation of P_F is made assuming a single orthogonalized-plane-wave (OPW) behavior of the Fermi electrons:

$$\psi_K = |k\rangle - \textstyle\sum_\alpha |\alpha\rangle\langle\alpha|k\rangle \,, \tag{15}$$

where the summation α is made over all the populated core states $|\alpha\rangle = |nlm\rangle$. Thus, P_F is approximately[44,45]

$$P_F = \left[1-\sum_n\left(\int_0^\infty j_0(k_F r)\,R_{n0}(r)\,4\pi r^2\,dr\right)R_{n0}(0)\right]^2 \Bigg/ \left[1-\left(\frac{1}{\Omega}\right)\sum_{n,l}(2l+1)\left(\int_0^\infty j_l(k_F r)\,R_{nl}(r)\,4\pi r^2\,dr\right)^2\right] \,. \tag{16}$$

Micah *et al.*,[45] using Herman-Skillman core functions, obtained a value of $P_F = 5.43$ a.u. for copper.[46] This value is much greater than that derived from experimental results, as we shall see later. In addition, their value for P_F is almost independent of volume, in contrast to our results (see Fig. 7).

In Eq. (16) we have disregarded the influence of hybridization. Its influence on the Fermi wave function can be approximated by rewriting Eq. (15) as

$$\psi_k = |K\rangle - \textstyle\sum_\alpha|\alpha\rangle\langle\alpha|K\rangle - \sum_d|d\rangle\,[V_{sd}/(E_F-E_d)] \,, \tag{17}$$

where the last term is mixing of the d function into the OPW function, brought about by hybridization. The addition of this last term modifies P_F of Eq. (16), by adding $+\,V_{sd}^2/(E_F-E_d)^2$ to its denominator.

Using $V_{sd}=2.1$ eV and $E_F-E_d=3.7$ eV, as before, this denominator will be 1.18, instead of 0.86 calculated without hybridization.[45] Thus, the new value of P_F would be 3.95 a.u. instead of 5.43 a.u., with no hybridization.

The volume dependence of P_F, in its new form is brought about via V_{sd} and (E_F-E_d). Employing the values with which we calculated the volume dependence of m^*, we calculated that P_F increases by about 15% when the volume is increased by 15%. This increase is much smaller than that derived from our measurements, which is about five times greater (see Fig. 7).

The OPW model not only predicts too small a volume dependence of P_F, but also too high an absolute value. The value of P_F is derived from the room-temperature Knight shift $K=0.237\%$, using Eqs. (1), (4), and (8). We assumed $m^*/m=1.3$, $\alpha=0.5$ [from the experimental value of $\mathcal{K}(\alpha)$] and used the free-electron values of $\chi_f^0=0.97$ and $\Omega=80$ a.u. Thus we obtained an effective value of $(P_F)_{\text{eff}} \sim 1.38$ a.u. However, this value includes the contribution of the s core polarization (see Sec. IV), which is 10–50% of the direct contribution.[26] Therefore, the experimental derived value of the direct spin density is $P_F = 0.92-1.25$ a.u.

This value of P_F is about three to four times smaller than that predicted by the OPW model in

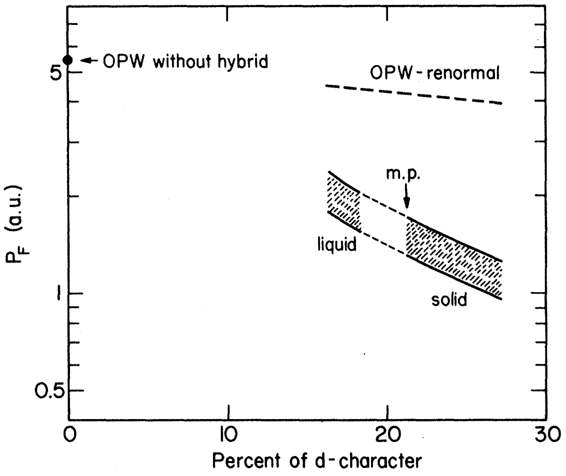

FIG. 11. P_F as against d character of the Fermi electrons (defined in the text). The shaded area is experimentally derived, whereas the dashed line is calculated by the OPW method.

its modified form. The reason for this great difference is apparently the inaccurate way in which we introduced the effect of the hybridization. In Eq. (16) its only effect is due to renormalization caused by mixing of the d core states into the Fermi states. We did not take into consideration, for instance, the influence of hybridization on the core states through correlation.

More realistic values are obtained by direct calculations. Davis,[47] using the Korringa-Kohn-Rostoker (KKR) method of calculation, obtained $P_F \sim 2.0$ a.u. Misetich, Hodges, and Watson,[48] who made a model Hamiltonian fit to a recent augmented-plane-wave (APW) calculation,[49] attained a value of $P_F = 1.7$ a.u. It is interesting to note that in the last calculation, it was found that the Fermi electrons have 28% of d character. This value agrees with the 27% derived from our model {the fraction of d character in our case is $x/(0.8+x)$, where $x \equiv [V_{sd}/(E_F - E_d)]^2$}. There is also a very good agreement between the $m^*/m = 1.32$, which they have calculated and the $m^*/m = 1.27$ deduced from the model.

In Fig. 11 we present P_F as against d character of the Fermi electrons, keeping the volume an implicit parameter. The uncertainty in the experimental value is due to the doubtful value of the core polarization. When one extrapolates P_F to zero hybridization (zero d character), one gets a value near to that calculated by the OPW method. It is reasonable to conclude, therefore, that hybridization not only reduces the value of P_F, but also brings about its strong volume dependence.

The dependence of P_F on volume in the liquid is an extrapolation of that in the solid. The only effect of melting on P_F is that of the accompanying volume change. This picture agrees well with the conclusion that copper band structure is dominated by hybridization, which is a nonstructural effect, and is very weakly influenced by structure and order.

VII. CONCLUSIONS

We have seen how information on the volume and temperature dependence of band structure in metals can be derived from detailed measurements of Knight shift and spin-lattice relaxation.

In copper we have derived the temperature dependence of m^* and P_F, and have shown that it is caused mainly by thermal expansion. This volume dependence of m^* and P_F has been explained semiquantitatively using the known band structure of copper which is governed by hybridization. The effect is nonstructural and thus there is almost no effect brought about by loss of order accompanying melting. Thus, the derived behavior in the liquid is almost an extrapolation of that in the solid.

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