

anisotropy or the nuclear-spin temperature as function of time. However, we have only compared the relaxation times measured by Brewer *et al.* with those calculated from formulas (18) and (20). The agreement appeared to be satisfactory, when we use parameters $T_Z = 7.9 \text{ m}^\circ\text{K}$ and $(\tau_1 T)_\infty = 1.5 \text{ sec } ^\circ\text{K}$.³

³ The value of T_Z is calculated from experimentally measured value of hyperfine field given by D. A. Shirley, in *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and

The present theory suggests that some recent measurements of $\tau_1 T$ for nuclei in ferromagnetic materials should be reexamined in the light of the saturation effects.⁴

D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968), Appendix B. The value of $(\tau_1 T)_\infty$ is an approximate fit to the measurements.

⁴ See, e.g., P. G. E. Reid, M. Scott, and N. J. Stone, in Ref. 3, p. 799. For the nuclei Ir^{192} , Au^{198} , and Sb^{125} , I has the values 4, 2, and $\frac{5}{2}$ and T_Z has the values 17, 14, and 6°mK .

Knight Shift and Nuclear Spin-Lattice Relaxation Rate in Solid and Liquid Copper*

WILLIAM W. WARREN, JR.,† AND W. GILBERT CLARK

Department of Physics, University of California at Los Angeles, Los Angeles, California 90024

(Received 5 November 1968)

Measurements of the Knight shift K of Cu^{63} and the nuclear spin-lattice relaxation rate T_1^{-1} of Cu^{63} and Cu^{65} are reported for solid and liquid copper. The temperature T range covered for the solid is 300°K to the melting point (1356°K). Measurements of K in the liquid extend from 1200°K (supercooled) to 1450°K ; measurements of T_1^{-1} cover the range 1200 – 1370°K . In the solid, the Knight shift shows a slight increase with temperature and, up to about 1000°K , the product $T_1 T K^2$ is constant. Above 1000°K , an additional contribution to T_1^{-1} is observed which is attributed to a quadrupolar interaction with diffusing imperfections. There is a sudden increase of about 3.7% in K and 20% in the inferred magnetic contribution to T_1^{-1} on going from the solid to the liquid state at 1356°K . In the liquid state, both K and $T_1 T$ are independent of T . The values of T_1^{-1} in the liquid are consistent with a lack of quadrupolar contribution to T_1^{-1} .

I. INTRODUCTION

RECENT pulsed nuclear-magnetic-resonance investigations of the polyvalent liquid metals gallium,¹ mercury,¹ indium,^{2,3} antimony,² and indium antimonide² have yielded useful information about the electronic structure and local atomic order of these systems. Some characteristics of the static and dynamic magnetic fields experienced by a nucleus in a liquid metal can be obtained from measurements of the Knight shift K and the contribution of magnetic hyperfine interactions to the nuclear spin-lattice relaxation rate T_1^{-1} . Such measurements permit inference of the changes of electronic structure and changes in electron-electron correlation and exchange effects that accompany fusion. Unfortunately, interpretation of the experiments in the above polyvalent metals is rendered difficult by the fact that most of them exhibit noncubic structures in the solid state. The resulting large static electric quadrupolar interactions complicate measurement of K and T_1 in the solids and make accurate de-

terminations of their melting-point changes difficult. (Although indium antimonide exhibits cubic symmetry in the solid state, it transforms from a liquid metal to a semiconductor on solidification, and is thus not typical of a normal metal.) Investigations of T_1 and K in the solid and liquid states of cubic metals are therefore particularly valuable, since in these metals the melting-point changes may be rather precisely determined.

In addition to the magnetic interactions, some characteristics of the dynamic electric field gradients in the liquid may also be obtained for nuclei which possess electric quadrupole moments, since the quadrupolar interaction may make an observable contribution to spin-lattice relaxation. The experiments cited above show that these effects are quite important in the polyvalent liquid metals. They have not, however, appeared in the monovalent alkali metals.⁴ This is presumably due to the smaller ionic charge and low degree of p character of the conduction-electron wave functions in the alkali metals. However, for reasons given below, a direct experimental determination of the quadrupolar spin-lattice relaxation contribution is possible in only one alkali metal (rubidium). It is thus of interest to

* Work supported in part by the U. S. Atomic Energy Commission.

† Permanent address: Bell Telephone Laboratories, Murray Hill, N. J. 07974.

¹ D. A. Cornell, Phys. Rev. **153**, 208 (1967).

² W. W. Warren, Jr., and W. G. Clark, Phys. Rev. **177**, 600 (1969).

³ F. A. Rossini, E. Geissler, E. M. Dickson, and W. D. Knight, Advan. Phys. **16**, 287 (1967); F. A. Rossini and W. D. Knight, Phys. Rev. **178**, 641 (1969).

⁴ D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955). Rossini (Ref. 3) has decomposed the liquid-Rb relaxation rates of Holcomb and Norberg into magnetic and quadrupolar components. Since the experimental error includes the possibility of *no* quadrupolar relaxation, we shall assume it to be so for the purposes of this paper.

search for quadrupolar relaxation in the monovalent noble metals and compare it with polyvalent liquid metals from the same part of the periodic table.

Of the three noble metals, copper, silver, and gold, copper is by far the most suitable choice for high-temperature NMR studies. Copper possesses two stable isotopes Cu^{63} and Cu^{65} whose abundances are 69.1 and 30.9%, respectively. Both isotopes have relatively strong magnetic dipole moments, and both have spin $\frac{3}{2}$ and electric quadrupole moments. The possibility of making measurements of two isotopes is particularly important for spin-lattice relaxation studies since this permits unambiguous separation of competing magnetic dipole and electric quadrupole relaxation processes.^{1,2,5} Until recently, the only published Cu NMR experiments in the vicinity of the melting point (1356°K) were the measurements of K through the melting point by Odle and Flynn.⁶ However, concurrently and independently of the work described here, El-Hanany and Zamir⁷ have measured T_1 and the spin-spin relaxation rate of Cu through the melting point. In this paper, we describe measurements of the Knight shift for Cu^{63} over the range 300–1450°K and spin-lattice relaxation times for Cu^{63} and Cu^{65} from 300 to 1375°K. Although we are mainly concerned with changes in K and T_1 which occur at the melting point, measurements in the solid were performed over a wide temperature range in order to interpret properly the shift and relaxation mechanism just below the melting point.

II. EXPERIMENTAL DETAILS

The samples used in these experiments were prepared from purified copper powder supplied by the Baker Chemical Co.⁸ The powder was sieved to 325 mesh (44 μm) to ensure penetration of the rf field into the metal particles. It was found necessary to prevent sintering of the powder at elevated temperatures by diluting the copper with 325-mesh quartz powder in the ratio of one part copper to five parts quartz. The quartz powder also maintained the separation of droplets of copper in the liquid state.

The nuclear magnetic resonances of Cu^{63} and Cu^{65} were observed with a coherent pulsed NMR spectrometer similar to one described previously.⁹ Most of the measurements were made at a frequency of 9.1 MHz. Samples were maintained at temperatures up to 1450°K under an argon atmosphere in a high-temperature apparatus described in detail elsewhere.¹⁰ Sample tempera-

tures were measured with platinum versus platinum-10%-rhodium thermocouples, which were calibrated against the copper melting point. Temperatures were stabilized with a temperature-regulation system employing the thermocouple as the sensing element. This system regulated the temperature to $\pm 0.2\%$ over the temperature range investigated. The temperature variation over the sample at the melting point was $\pm 0.3\%$. The over-all accuracy of the temperature determinations was $\pm 0.5\%$.

Knight shifts were measured by comparing the resonance frequency ν_{63} of Cu^{63} with the frequency ν_D of the deuteron resonance in the same applied magnetic field. The deuteron sample was D_2O doped with GdCl_3 . The field at the center of the Cu^{63} NMR line was located by recording the integral of most of the free induction decay with a boxcar integrator¹¹ as the magnetic field was swept through resonance. The D_2O sample was positioned outside the furnace, but as close as possible to the copper sample. The frequency ν_D was corrected for the difference in magnetic field between the locations of the D_2O sample and the copper sample. The corrected ratio ν_{63}/ν_D was compared with the corresponding reference ratio measured by us for Cu^{63} in CuCl powder:

$$(\nu_{63}/\nu_D)_{\text{ref}} = 1.72678 \pm 0.00002.$$

The accuracy of the shift measurements was typically $\pm 0.002\%$ of the resonance frequency.

Spin-lattice relaxation times were measured with approximately 180° – 90° rf pulse sequences. The amplitude of the free induction decay following the 90° pulse was measured with a boxcar integrator as a function of the interval between the 180° and 90° pulses. The accuracy of T_1 measurements varied from ± 2 to $\pm 4\%$, with the larger error obtaining for some of the measurements in the liquid state.

III. EXPERIMENTAL RESULTS

A. Knight Shift

The Cu^{63} Knight shift $K(\text{Cu}^{63})$ was measured in solid copper from room temperature to the melting point and in liquid copper from 1200 (supercooled liquid) to 1450°K. The data are shown in Fig. 1. In the solid, $K(\text{Cu}^{63})$ increases slowly with temperature from its room-temperature value

$$K(\text{Cu}^{63}) = 0.234 \pm 0.002 \quad (300^\circ\text{K})$$

to its value just below the melting point

$$K(\text{Cu}^{63}) = 0.250 \pm 0.002 \quad (1356^\circ\text{K}).$$

At the melting transition, $K(\text{Cu}^{63})$ increases abruptly to

$$K(\text{Cu}^{63}) = 0.259 \pm 0.002 \quad (1356^\circ\text{K})$$

¹¹ W. G. Clark and A. L. Kerlin, *Rev. Sci. Instr.* **38**, 1593 (1967).

⁵ A. Narath and D. W. Alderman, *Phys. Rev.* **143**, 328 (1966).

⁶ R. L. Odle and C. P. Flynn, *J. Phys. Chem. Solids* **26**, 1685 (1965).

⁷ *Magnetic Resonance and Radio Frequency Spectroscopy*, edited by P. Auerbuch (North-Holland Publishing Co., Amsterdam, 1969), pp. 355–8.

⁸ J. T. Baker Chemical Co., Phillipsburg, N. J. 08865.

⁹ W. G. Clark, *Rev. Sci. Instr.* **35**, 316 (1964).

¹⁰ W. W. Warren, Jr., and W. G. Clark, *J. Phys. E* **1**, 1019 (1968).

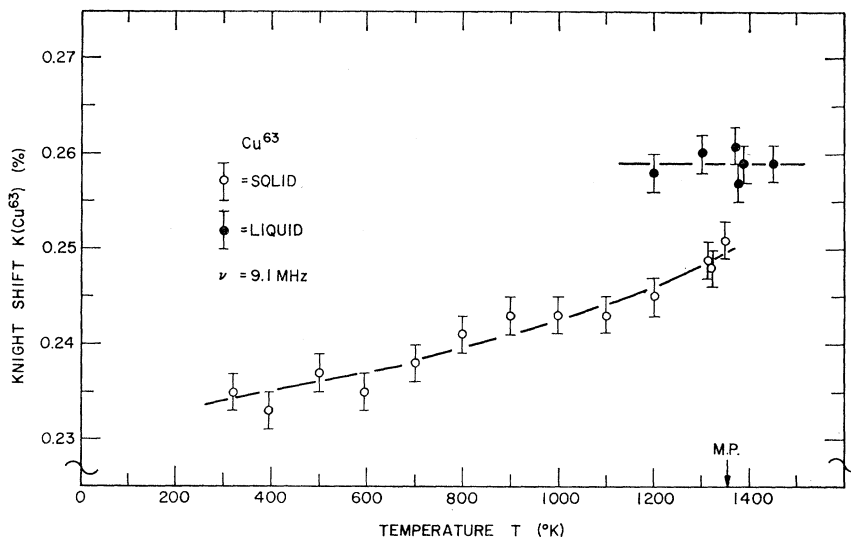


FIG. 1. Knight shift of Cu^{63} in solid and liquid Cu as a function of temperature. Solid circles below the melting point (M.P.) are for liquid in the supercooled state.

in the liquid. These changes in $K(\text{Cu}^{63})$ are in (marginal) agreement with the earlier results obtained by Odle and Flynn.⁶ Within experimental error, $K(\text{Cu}^{63})$ in liquid copper is independent of temperature in the range 1200–1450°K.

B. Spin-Lattice Relaxation

Spin-lattice relaxation times for Cu^{63} and Cu^{65} in solid copper were measured from room temperature to the melting point. In the liquid, T_1 data were obtained for both isotopes at 1300 and 1375°K and for Cu^{63} at 1200°K. The observed values of $(T_1T)^{-1}$ are plotted in Fig. 2.

The values of $(T_1T)^{-1}$ for Cu^{63} and Cu^{65} at 326°K are

$$(T_1T)_{63}^{-1} = 0.81 \pm 0.02 \text{ (sec } ^\circ\text{K)}^{-1}$$

and

$$(T_1T)_{65}^{-1} = 0.92 \pm 0.02 \text{ (sec } ^\circ\text{K)}^{-1}.$$

As the temperature is increased, $(T_1T)^{-1}$ for both isotopes increases slowly up to about 1000°K. Above this temperature, $(T_1T)^{-1}$ increases very rapidly and the relaxation rate T_1^{-1} passes through a maximum near 1300°K. The T_1^{-1} values in the range 1000–1356°K exhibited a strong dependence on the history of the sample. In particular, the value of T_1^{-1} at a given temperature in this range decreased when the sample temperature was maintained above 1000°K for periods of the order of 24–48 h. A further change is mentioned at the end of Sec. IV B 1. The values of T_1^{-1} at 1300°K were frequency-dependent in the range 5.0–9.2 MHz with a broad maximum at about 7.0 MHz.

In liquid copper, the values of $(T_1T)^{-1}$ for both isotopes were independent of sample history and temperature over the range investigated. The results for liquid copper are

$$(T_1T)_{63}^{-1} = 1.12 \pm 0.03 \text{ (sec } ^\circ\text{K)}^{-1},$$

$$(T_1T)_{65}^{-1} = 1.31 \pm 0.03 \text{ (sec } ^\circ\text{K)}^{-1}.$$

The correspondence between our observed values of T_1 and those of El-Hanany and Zamir⁷ is roughly as follows. Up to about 1000°K, they find T_1T to be constant, in mild disagreement with our observation of a slight temperature dependence. They also find a sharp rise in $(T_1T)^{-1}$ as T is increased in the liquid state. This rise is not observed in our experiments, which, however, cover a slightly lower temperature range. The reasons for these discrepancies are not, at present, understood. The large rise in $(T_1T)^{-1}$ which we observe in the solid between 1050°K and the melting point is not present in their measurements. A possible reason for this discrepancy is discussed at the end of Sec. IV B 1.

IV. INTERPRETATION

A. Knight Shift

The principal contribution to K in simple (non-magnetic) metals is usually due to the hyperfine field of the polarized s -like conduction electrons interacting with the nucleus via the Fermi contact interaction. This contribution to K is given by¹²

$$K_s = (8\pi/3)\chi_s\Omega\langle|U_F(0)|^2\rangle, \quad (1)$$

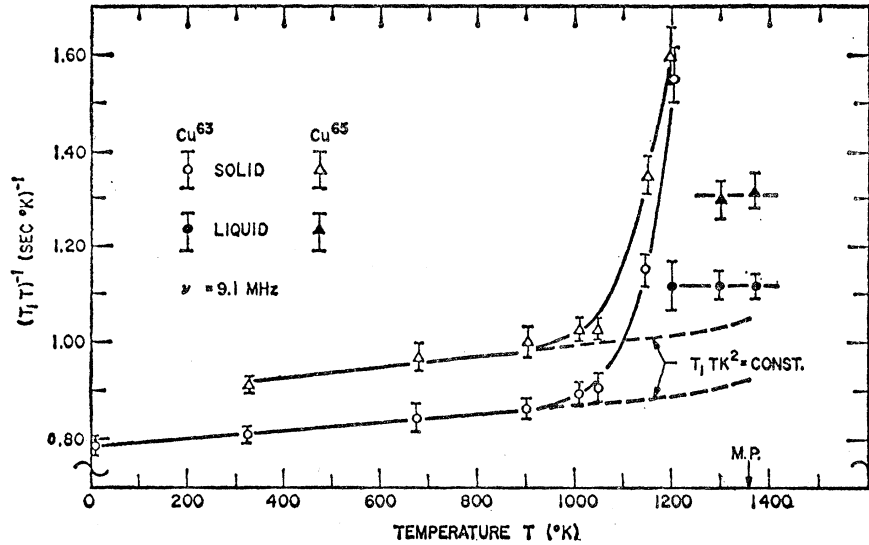
where χ_s is the spin susceptibility per unit volume for the s electrons, Ω is the atomic volume, and $\langle|U_F(0)|^2\rangle$ is the average density at the nucleus of s -like Fermi-surface electrons. Although Eq. (1) contains no explicit temperature dependence, K_s may be expected to be weakly temperature-dependent due to the effects of thermal expansion^{13,14} and thermal motion¹⁴ on K_s , Ω , and $\langle|U_F(0)|^2\rangle$.

¹² C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

¹³ B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **21**, 2114 (1953).

¹⁴ G. B. Benedek and T. Kushida, J. Phys. Chem. Solids **5**, 241 (1958).

FIG. 2. Product $1/T_1T$ for Cu^{63} and Cu^{65} in liquid and solid Cu as a function of temperature. Solid circles below the melting point (M.P.) are for liquid in the supercooled state. The rapid rise in $1/T_1T$ above 1000°K is attributed to motional relaxation which couples to the spins mainly through the quadrupolar interaction. The dashed line indicates our estimate of the correct extrapolation of the magnetic relaxation rate from lower temperatures. The point at 4.2°K is that of B. C. de Torné, Compt. Rend. 250, 512 (1960).



The temperature dependence of $K(\text{Cu}^{63})$ can be interpreted conveniently by treating K as a function of the thermodynamic variables pressure P , volume V , and temperature T . With temperature as an implicit parameter, the variation of the shift with volume at constant pressure is written

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_P = \left(\frac{\partial \ln K}{\partial \ln V}\right)_T + \left(\frac{\partial \ln K}{\partial T}\right)_V \left(\frac{\partial T}{\partial \ln V}\right)_P, \quad (2)$$

where the first term on the right-hand side is the explicit volume dependence and the second term describes the intrinsic temperature dependence.

The explicit volume dependence $(\partial \ln K / \partial \ln V)_T$ has been determined from the pressure dependence of $K(\text{Cu}^{63})$ by Benedek and Kushida.¹⁴ In principle, one can utilize the thermal-expansion data $[(\partial \ln V / \partial T)_P]$ in solid copper¹⁵ and the experimental values of K to determine the contribution from intrinsic temperature dependence. In Fig. 3 the experimental values of $\ln K(\text{Cu}^{63})$ are plotted against $\ln V$ with temperature as an implicit variable. The data in solid copper are represented by

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_P = 0.84 \pm 0.08.$$

This agrees within experimental error with the volume dependence measured by Benedek and Kushida,¹⁴

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_T = 0.7 \pm 0.3,$$

which suggests that $(\partial \ln K / \partial T)_V = 0$, i.e., the observed temperature dependence of $K(\text{Cu}^{63})$ in solid copper may be due solely to the effects of thermal expansion. Un-

fortunately, it is not possible at present to determine $(\partial \ln K / \partial T)_V$ precisely, because of the rather large experimental error in $(\partial \ln K / \partial \ln V)_T$ and because this quantity was measured over a much smaller range of volume than occurs in thermal expansion between 300°K and the melting point.

It can be seen from Fig. 3 that the discontinuity of $K(\text{Cu}^{63})$ at the melting point is consistent with that which would be expected from extrapolation of the volume dependence observed in the solid. This result does not agree with the previous measurements of Odle and Flynn,⁶ who reported that the change of $K(\text{Cu}^{63})$ exceeded the value given by the extrapolated solid volume dependence. The discrepancy is due to the combined effects of the larger value of $K(\text{Cu}^{63})$ measured by us just below the melting point and our use of somewhat different values¹⁶ for the volume changes.

The volume dependence in the liquid is given by

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_P = \begin{matrix} +0.72 \\ 0.00 \\ -0.45 \end{matrix}$$

and is thus smaller or of opposite sign than the volume dependence in solid copper. Since $K(\text{Cu}^{63})$ has not been measured as a function of pressure in liquid copper, it is not possible to decompose the observed constant pressure data into separate volume and temperature dependences. It can be concluded, however, that the value of $(\partial \ln K / \partial \ln V)_P$ in liquid copper is closer to the value $-\frac{1}{3}$ for noninteracting electrons than is the corresponding quantity in the solid.

B. Spin-Lattice Relaxation

Nuclear spin-lattice relaxation processes may be classified as magnetic or quadrupolar according to whether nuclear transitions are induced via coupling to

¹⁵ *Metals Handbook*, edited by T. Lyman (American Society for Metals, Metals Park, Ohio, 1961).

¹⁶ J. A. Cahill and A. D. Kirshenbaum, J. Phys. Chem. **66**, 1080 (1962).

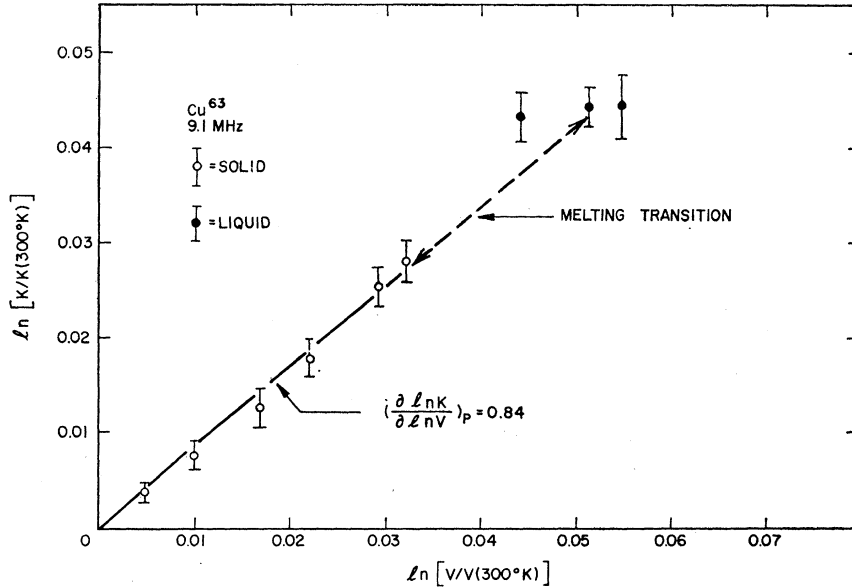


FIG. 3. Logarithm of Knight-shift ratio as a function of logarithm of the volume ratio for Cu^{63} in liquid and solid Cu (temperature is the implicit parameter).

the nuclear magnetic dipole moment or electric quadrupole moment. Under conditions which usually prevail in liquid metals,² the transition probabilities W_M for magnetic processes are proportional to the square of the gyromagnetic ratio γ_n . Thus, for copper,¹⁷

$$\frac{W_M^{63}}{W_M^{65}} = \left(\frac{\gamma_{63}}{\gamma_{65}} \right)^2 = 0.870.$$

Similarly, the transition probabilities W_Q for quadrupolar processes are proportional to a function $f(I)$ of the nuclear spin I and the square of the quadrupole moment Q . Thus, since the spins are the same for Cu^{63} and Cu^{65} , we have¹⁷

$$\frac{W_Q^{63}}{W_Q^{65}} = \left(\frac{Q_{63}}{Q_{65}} \right)^2 = 1.169.$$

Measurement of T_1 for both isotopes at a given temperature permits determination of the type of coupling responsible for relaxation by comparing T_1^{65}/T_1^{63} with the above ratios. The observed values of T_1^{65}/T_1^{63} are consistent with the expected ratio for magnetic relaxation in solid copper below 1000°K and at all temperatures in liquid copper. Between 1000°K and the melting point, the ratio T_1^{65}/T_1^{63} for our samples increased, indicating the presence of a quadrupolar contribution in this temperature range.

1. Solid

The dominant magnetic relaxation process in simple (nonmagnetic) metals is usually due to the magnetic contact hyperfine interaction. The relaxation rate for

this process is given by¹⁸

$$W_M = (64/9)\pi^3 \hbar^3 \gamma_e^2 \gamma_n^2 \langle |U_F(0)|^2 \rangle N^2(E_F) kT, \quad (3)$$

where \hbar is Planck's constant, γ_e is the electron gyromagnetic ratio, k is Boltzmann's constant, and $N(E_F)$ is the density of states at the Fermi surface. The relaxation rate is related to the contribution of the contact interaction to K by the modified Korringa relation¹⁹

$$T_1 T K_s^2 = \frac{\hbar}{4\pi k} \left(\frac{\gamma_e}{\gamma_n} \right)^2 \frac{1}{K(\alpha, r_0)}, \quad (4)$$

where $K(\alpha, r_0)$ is a factor introduced to account for effects of electron correlation and exchange. The parameter α describes the enhancement of the electronic susceptibility χ relative to the value χ_0 for free electrons, i.e.,

$$\alpha = 1 - \chi_0/\chi, \quad 0 \leq \alpha \leq 1 \quad (5)$$

and the parameter r_0 describes the range of the electron-electron interaction.²⁰

Although $T_1 T$ and K usually exhibit small temperature dependences, Eq. (4) predicts that $T_1 T K^2$ should be independent of temperature if the electron-electron effects contained in $K(\alpha, r_0)$ are temperature-independent. In solid copper, we find that

$$T_1 T K^2 = (6.75 \pm 0.26) \times 10^{-6} \text{ sec } ^\circ\text{K}$$

between 300 and 1000°K. This constancy of $T_1 T K^2$ and the agreement of T_1^{65}/T_1^{63} with the theoretical ratio for magnetic relaxation indicate that the magnetic contact interaction is the dominant relaxation mechanism in this temperature range.

¹⁸ J. Korringa, *Physica* **16**, 601 (1950).

¹⁹ A. Narath, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).

²⁰ A. Narath and H. T. Weaver, *Phys. Rev.* **175**, 373 (1968).

¹⁷ *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences-National Research Council, Washington, D. C., 1962), Appendix 1.

The sharp increase of $(T_1T)^{-1}$ above 1000°K (see Fig. 2) suggests the presence of an additional relaxation mechanism for which we denote the transition probability by W_x . We have determined W_x in the range 1150–1300°K by subtracting the inferred magnetic hyperfine contribution W_M from the total relaxation rate $(T_1)^{-1}$. The magnetic rates W_M^{63} and W_M^{65} in this range were determined by extrapolation of the rates measured below 1000°K with the assumption that T_1TK^2 remains constant. The results are shown in Fig. 4. Since the total rates $(T_1)^{-1}$ and hence also W_x decreased slowly with time in this temperature range, the values of W_x plotted in Fig. 4 correspond to a particular time interval in the sample's history. The values of W_x were determined from T_1 measurements made within a period of a few hours.

At 1300°K the ratio of the rates W_x for the two isotopes is

$$W_x^{63}/W_x^{65} = 1.11 \pm 0.08.$$

This agrees within experimental error with the theoretical ratio for quadrupolar relaxation, indicating that the additional relaxation is primarily of quadrupolar origin. The temperature dependences of W_x^{63} and W_x^{65} are the same within experimental error and can be represented by

$$W_x \propto e^{-Q/RT}, \quad (6)$$

where the activation energy Q is

$$Q = 38.0 \pm 3.0 \text{ kcal/mole.}$$

The exponential temperature dependence indicates that the correlation time for the quadrupolar process is related to thermally activated diffusional motion in the solid, although the activation energy is somewhat smaller than the measured activation energy for self-diffusion²¹:

$$Q_D = 47.12 \pm 0.33 \text{ kcal/mole.}$$

This may indicate that the quadrupolar relaxation is due to impurities, since these can be expected to have a different activation energy than for self-diffusion.

Previous steady-state measurements by Flynn and Seymour²² yielded anomalously large linewidths for Cu⁶³ and Cu⁶⁵ in the range 1000–1200°K. The quadrupolar relaxation rates observed in the present experiments are of the correct order of magnitude to explain these steady-state linewidth results. Furthermore, the apparent lack of temperature dependence of the linewidths measured by Flynn and Seymour in this temperature range is explained by the nearly equal motivation energies obtained from dipolar motional narrowing²² (48.1 ± 0.9 kcal/mole) and from quadrupole relaxation (38.0 ± 3.0 kcal/mole). Thus, the temperature

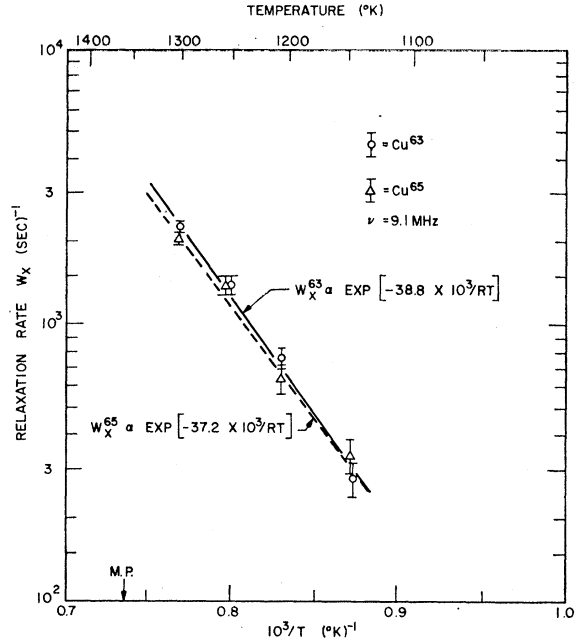


FIG. 4. Additional relaxation rate W_x as a function of $1/T$ (or T) for Cu⁶³ and Cu⁶⁵ in solid Cu. This increment is attributed to diffusion motion of imperfections which couple to the Cu nuclei mainly through the quadrupolar interaction. The characteristics shown here are representative of our samples which have not been taken through the melting point or annealed at high temperatures for long periods of time.

dependence of the dipolar contribution has nearly the same magnitude but the opposite sign as the quadrupolar relaxation broadening, leading to a temperature-independent linewidth in this temperature range. At higher temperatures, one expects the linewidths to increase as the quadrupolar relaxation begins to dominate the dipolar contribution. We have measured the free induction decay lifetimes in the range 1200–1300°K and find that this is the case. It is interesting to note that the work of El-Hanany and Zamir⁷ exhibits only a very small ($\sim 16\%$) increase in $(T_1T)^{-1}$ below the melting point. Hence, their samples show at most a vestige of the motional relaxation observed in our experiments. This difference can be attributed to the different sources and/or histories of the samples. As an example of the effect of sample history, we have noted from measurements of the free induction decay shape in our samples that W_x is greatly reduced or eliminated by cycling a sample into the liquid and then back to the solid state.

2. Liquid

The ratios of the Cu⁶³ and Cu⁶⁵ relaxation rates in liquid copper agree with the theoretical ratio for magnetic relaxation. A reasonable upper limit for a quadrupolar component of the Cu⁶³ relaxation rate is given by

$$W_Q^{63} \lesssim 60 \text{ sec}^{-1},$$

²¹ A. Kuper, H. Letaw, Jr., L. Slifkin, E. Sonder, and C. T. Tomizuka, Phys. Rev. **96**, 1224 (1954); **98**, 1870 (1955).

²² C. P. Flynn and E. F. W. Seymour, Proc. Phys. Soc. (London) **77**, 922 (1961).

which corresponds to only 4% of the total relaxation rate. Moreover, T_1TK^2 is constant over the temperature range investigated indicating that the dominant relaxation process is due to the magnetic contact hyperfine interaction. The weakness of the dynamic electric field gradients responsible for quadrupolar relaxation in noble metals relative to polyvalent metals in the same part of the periodic table is demonstrated by noting that the upper limit for W_Q^{63} is an order of magnitude smaller than W_Q^{69} for Ga⁶⁹ in trivalent liquid gallium,¹ even though their quadrupole moments¹⁷ differ by only about 25%.

C. Effects of Fusion: Korringa Relation

It has been argued²³ that since K is dependent upon χ_s and $\langle |U_F(0)|^2 \rangle$, it should serve as a sensitive indicator of changes of electronic structure that accompany fusion. In fact, K has been found to change only slightly through the melting transition of a number of metals,²³ suggesting that the density of states $N(E_F)$ and wavefunction amplitudes are nearly the same in the liquid and solid. One can understand why this should be so for metals with high coordination numbers in the solid state. The melting transition in close-packed metals probably involves only a slight increase in free volume and loss of long-range order. The local atomic arrangement, which is of primary importance in determining the electronic structure,²⁴ remains practically unchanged. Thus in the bcc alkali metals and fcc metals aluminum and lead, K changes by only a few percent.²³ The observed change $\Delta K(\text{Cu}^{63})$ at the melting point of copper is consistent with the results in other fcc metals:

$$\Delta K(\text{Cu}^{63})/K(\text{Cu}^{63})_{\text{sol}} = (3.7 \pm 1.2)\%.$$

Similar arguments apply to the magnetic relaxation rates for which the following changes were observed at the melting point:

$$\Delta(W_M^{63})/(W_M^{63})_{\text{sol}} = (18.5 \pm 4.5)\%,$$

$$\Delta(W_M^{65})/(W_M^{65})_{\text{sol}} = (20.2 \pm 5.5)\%.$$

According to the above interpretation, one might expect to find larger changes in K or W_M for metals with low coordination numbers in the solid state, since the local arrangement should change appreciably during fusion

in such metals. This has been confirmed in Ga,¹ Sb,² and InSb.^{2,25}

Although the small changes of K and W_M observed in copper are in qualitative agreement with the simple model for close-packed metals, it appears that volume effects alone cannot account quantitatively for the data and that some structure-dependent effects must be considered. According to Eq. (4), T_1TK^2 should be independent of volume and thus not affected by the volume change upon melting. In fact, it is likely that T_1TK^2 does change at the melting point, as shown by the following small but discernable change in the correction factor $K(\alpha, r_0)$ between its value in the solid at 900°K and that in the liquid at 1200°K:

$$K(\alpha, r_0)_{\text{sol}} = 0.555 \pm 0.025 \text{ (900°K)},$$

$$K(\alpha, r_0)_{\text{liq}} = 0.623 \pm 0.025 \text{ (1200°K)}.$$

The value of $K(\alpha, r_0)$ in the liquid is closer to the value for noninteracting free electrons [$K(\alpha, r_0) = 1$] than in the solid, suggesting an apparent reduction of electron-electron effects coinciding with the loss of long-range order.

We have proposed elsewhere²⁶ that rapid spin-flip scattering in metals may reduce the exchange enhancement of the Pauli susceptibility. This effect would cause $K(\alpha, r_0)$ to increase at high temperatures or in the liquid states of medium and heavy metals. Although the observed increase of $K(\alpha, r_0)$ at the melting point of copper does not prove the existence of this reduction of the exchange enhancement, the data are consistent with the expected effect.

Note added in proof. While this article was in press, a more detailed report of the work of El-Hanany and Zamir (Ref. 7) has appeared [U. El-Hanany and D. Zamir, Phys. Rev. **183**, 809 (1969)]. When the uncertainties of the measurements are considered, there appears to be no significant difference between most of our measurements and those of El-Hanany and Zamir. The exception is the irregular behavior reported by them for the copper Knight shift below the temperature for motional narrowing of the resonance line. It was not observed in our experiments.

ACKNOWLEDGMENT

We thank P. Pincus for several helpful discussions.

²³ W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) **8**, 173 (1959); C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. **7**, 865 (1962); N. E. Cusack, Rept. Progr. Phys. **26**, 361 (1963).

²⁴ J. M. Ziman, Proc. Phys. Soc. (London) **91**, 70 (1967).

²⁵ P. S. Allen and E. F. W. Seymour, Proc. Phys. Soc. (London) **85**, 509 (1965).

²⁶ W. W. Warren, Jr., W. G. Clark, and P. Pincus, Solid State Commun. **6**, 371 (1968).