Nuclear Magnetic Resonance and Relaxation in Liquid Tellurium

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Data are presented for the Te^{125} Knight shift ($\mathcal{K}^{125}$) and spin-lattice relaxation rate ($1/T_1$) over the temperature ranges 675–1250 K and 680–900 K, respectively, in liquid tellurium. The temperature dependence of $\mathcal{K}^{125}$ is compared with that of the total magnetic susceptibility and is shown to result mainly from a temperature-dependent density of states at the Fermi level. The Knight shifts and magnetic relaxation rates are also correlated with the temperature-dependent electrical conductivity and Hall coefficient. These results indicate that electronic transport in Te below about 900 K can be described by a strong-scattering or diffusive model. However, the observed dependence of the Hall coefficient on the inverse square of $\mathcal{K}^{125}$ is in disagreement with theoretical predictions for this situation.

I. INTRODUCTION

Liquid tellurium occupies a pivotal position among electronically conducting liquids. On the one hand, it exhibits a relatively large weakly temperature-dependent electrical conductivity[1–5] (σ) and a "metallic" Knight-shift value[6] ($\mathcal{K}^{125}$), both of which suggest that it is essentially a poor liquid metal. On the other hand, the conductivity and Knight shift are found to *increase* with increasing temperature, the Hall coefficient[2,4,7] (R_H) exceeds the free-electron value by about a factor of 2 and decreases with increasing temperature, and the thermoelectric power is positive.[1–3,5,8] These latter properties are qualitatively similar to those of so-called "liquid semiconductors" in which both electron concentrations and mobilities are found to be strongly dependent on temperature. Tellurium thus appears to be a borderline case exhibiting some features of both metallic and semiconducting behavior.

The transitional character of liquid Te is consistent with the work of Mott.[9] He argues that a conductivity value of about 3000 $(\Omega\,\mathrm{cm})^{-1}$ represents a lower bound for the conductivity of a normal liquid metal whose properties are describable by a nearly-free-electron (NFE) model. This minimum conductivity for NFE behavior occurs when the electron mean free path (λ) becomes comparable with the average interatomic spacing (a) and the predicted value coincides quite closely with the observed conductivity of liquid Te [$\sigma \sim 2000\ (\Omega\,\mathrm{cm})^{-1}$].

The atomic arrangement in liquid Te and the interrelation of its electronic properties and liquid structure have been discussed in a recent paper by Cabane and Friedel.[10] They have interpreted various elastic[10–12] and quasielastic[13] neutron scattering experiments and have proposed a simple and credible model for the temperature-dependent structure of liquid Te. Briefly, they suggest a continuous random network of Te atoms which are either twofold or threefold coordinated. The twofold (binary) coordination is a remnant of the helical chain structure of solid Te and is dominant near the melting point. At higher temperatures, there is increasing incidence of threefold (ternary) coordination with covalent bonding similar to that of the arsenic ($A7$) crystal structure. The binary bonding is responsible for a minimum or pseudogap in the density of states which would explain the apparently low number of electrons per atom (~ 2.5 from Hall coefficient measurements). As the concentration of ternary sites increases at higher temperatures, free electrons are generated, according to this model, and these additional carriers are responsible for the increasingly metallic character of the liquid at higher temperatures.

Nuclear-magnetic-resonance (NMR) measurements have been found to offer a powerful technique for the investigation of microscopic electronic transport phenomena in liquids.[14] The Knight shift, through its dependence on the conduction-electron susceptibility, provides a measure of the density of states at the Fermi level, $N(E_F)$, for a degenerate system. Moreover, the enhancement of the magnetic spin-lattice relaxation rate relative to the Korringa rate[15] provides a direct indication of the breakdown of metallic (i.e., NFE) conditions. This enhancement is a reflection of the fact that once the scattering of the electrons becomes so strong that $\lambda \sim a$, further strengthening of the electron-ion interaction causes the electrons to remain longer near a given atom and conduction proceeds by a kind of diffusion or Brownian motion.[16] It can be shown[14] that in the strong-scattering or "Brownian-motion" regime of conduction by nearest-neighbor diffusion, the conductivity and magnetic relaxation-rate enhancement (η) are connected by the approximate relation

$$\sigma\eta \simeq \sigma_0 \simeq 2000\ (\Omega\ \mathrm{cm})^{-1}\ . \qquad (1)$$

Thus, the onset of enhancement ($\eta > 1$) should occur when $\sigma \lesssim 2000\ (\Omega\,\mathrm{cm})^{-1}$, in rough agreement with Mott's value for the minimum NFE conductivity.

In the first reported NMR study of liquid Te, Cabane and Froidevaux[6] described measurements of the Te^{125} Knight shift ($\mathcal{K}^{125}$) from 750 to 925 K and a single measurement of the spin-lattice relaxation time (T_1) near the melting point ($T_m = 725$ K). Within a relatively large experimental error (± 25%) they found $1/T_1$ to be in agreement with the Korringa value. On the basis of this observation and the rather large values of $\mathcal{K}^{125}$ they measured, they concluded that there is an essentially metallic density of conduction electrons in liquid Te and these behave like free electrons.

As part of a systematic investigation of the NMR properties of liquid metals and semiconductors, the work of Cabane and Froidevaux has been extended in the following ways: (i) $\mathcal{K}^{125}$ has been measured from 675 K in the supercooled liquid to 1250 K and (ii) more precise measurements (± 5 to 10%) of T_1 have been made over a range of temperatures (680–900 K). These experiments were motivated by several factors. First, it was desired to look closely at the relaxation-rate enhancement as a function of temperature in order to determine the conductivity mechanism (NFE or diffusion) in liquid Te. Second, in addition to the σ-η correlation described by Eq. (1), recent theoretical arguments have been advanced which predict simple correlations between σ and $\mathcal{K}$, and between R_H and $\mathcal{K}$ in the diffusion regime. Te is a favorable choice for testing these correlations since there already exists a large amount of data on the macroscopic transport properties over a wide temperature range. Finally, in conjunction with a series of experiments on liquid-Te alloys[17] it was necessary to obtain $\mathcal{K}^{125}$ data on pure Te over a much wider temperature range than was covered in the Cabane and Froidevaux work.

II. EXPERIMENTAL DETAILS

The NMR samples used in these experiments were prepared from single crystal Te of 99.9999% purity.[18] The crystalline material was crushed to obtain particles with diameters of roughly 100 μm and mixed with powdered quartz in approximately equal proportions. The mixtures were then sealed *in vacuo* in quartz ampoules. This dispersion procedure provided adequate particle isolation to ensure rf penetration of the molten Te droplets.

NMR measurements were made with a coherent pulsed spectrometer operating at 16.3 MHz. With the frequency stabilized to 1 part in 10^7 by the master rf source (General Radio model No. 1164-A frequency synthesizer), $\mathcal{K}^{125}$ could be determined directly by sweeping through the resonance position while recording the integral of the free-induction decay (FID) obtained with a boxcar integrator. The Varian Fieldial was calibrated using the resonance positions for Te^{125} in pure Te and dilute TeO_2 in HCl at room temperature. Values of $\mathcal{K}^{125}$ measured relative to TeO_2:HCl were then corrected for chemical shift using the value of the isotropic chemical shift σ_{iso} of solid Te measured by Bensoussan[19]:

$$\mathcal{K}^{125} = \mathcal{K}^{125}(TeO_2:HCl) + \sigma_{iso}\ , \qquad (2)$$

where $\sigma_{iso} = (6.2 \pm 0.5) \times 10^{-4}$.

Spin-lattice relaxation times (T_1) were measured with standard π-$\frac{1}{2}\pi$ rf pulse sequences. In order to overcome low signal-to-noise ratios for the Te^{125} resonance, the free-induction decays (FID) were averaged with a Nicolet model No. 1072 signal-averaging computer. Primary data acquisition was accomplished by a Biomation model No. 610B transient recorder interfaced to the signal averager with a Nicolet model No. SD-78 plug-in. Signals were typically collected at a repetition rate of 100 Hz for 1 min or a total of 6000 FID sweeps per point. The averaged FID was digitally smoothed and plotted on an x-y recorder for each value of the π-$\frac{1}{2}\pi$ pulse separation. From these plots, the FID amplitudes were easily read off and plotted to obtain the value of T_1.

III. EXPERIMENTAL RESULTS

A. Knight Shifts

The observed values of $\mathcal{K}^{125}$ are plotted as a function of temperature in Fig. 1. The shift exhibits appreciable temperature dependence, increasing from a value of (0.342 ± 0.003)% at 675 K to a value of (0.553 ± 0.007)% at 1250 K. The rate of increase of $\mathcal{K}^{125}$ with temperature is greatest in the supercooled state and decreases progressively at higher temperatures. The data are in good agreement with those of Cabane and Froidevaux[6] when the latter are adjusted to the same reference field as used in the present work.

B. Spin-Lattice Relaxation

The spin-lattice relaxation rates $1/T_1$ are plotted in Fig. 2 and compared with the Korringa rate[15] calculated from the observed Knight shifts. The Korringa rate was calculated on the assumption that s electrons make the dominant contribution to $\mathcal{K}^{125}$ and $1/T_1$, and no correction for electron-electron effects was applied. The validity of these assumptions will be discussed in more detail in Sec. IV. It can be seen from Fig. 2 that

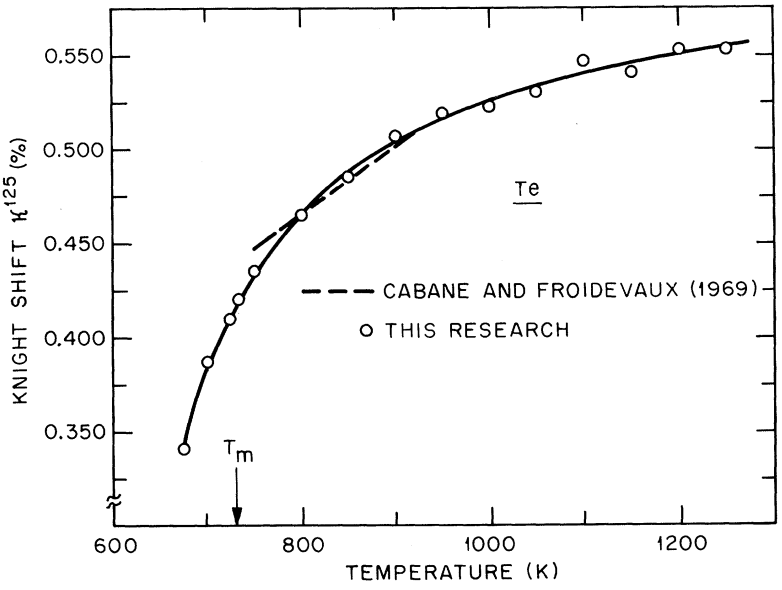

FIG. 1. Knight shift ($\mathcal{K}^{125}$) as a function of temperature for liquid Te. For comparison, the data of Cabane and Froidevaux shown by the dashed line (Ref. 6) have been adjusted to account for the different Knight-shift reference employed. In Ref. 6, Knight shifts were referred to the powder average of the anisotropic chemical shift of solid Te, whereas in the present study the reported (Ref. 19) isotropic chemical shift of the solid was used. Data shown below T_m were taken in the supercooled state.

the observed relaxation rate exceeds the Korringa rate at low temperatures but becomes equal to it or slightly less at the highest temperatures. This trend may be seen more clearly in the upper portion of Fig. 2 where we have plotted the ratio

$$\eta = \frac{1/T_1}{(1/T_1)_{\text{Korr}}} \quad . \tag{3}$$

This quantity, the enhancement factor, decreases with increasing temperature. It should be noted that because Te^{125} has spin $\frac{1}{2}$, there are no contributions to $1/T_1$ from quadrupolar relaxation processes and, hence, the observed behavior of η results entirely from changes in the magnetic relaxation rate.

The spin-phase memory time T_2^* was measured from the FID at several temperatures and found to agree within experimental accuracy ($\pm 15\%$) with the measured values of T_1. This is consistent with expectations for a liquid in a sufficiently homogeneous magnetic field.[20]

IV. DISCUSSION

A. Knight Shift: Temperature Dependence of $N(E_F)$

The valence electrons of Te have a high degree of p character. As a result, there are several potential contributions to the Knight shift in liquid Te: (i) the direct contact contribution from elec-

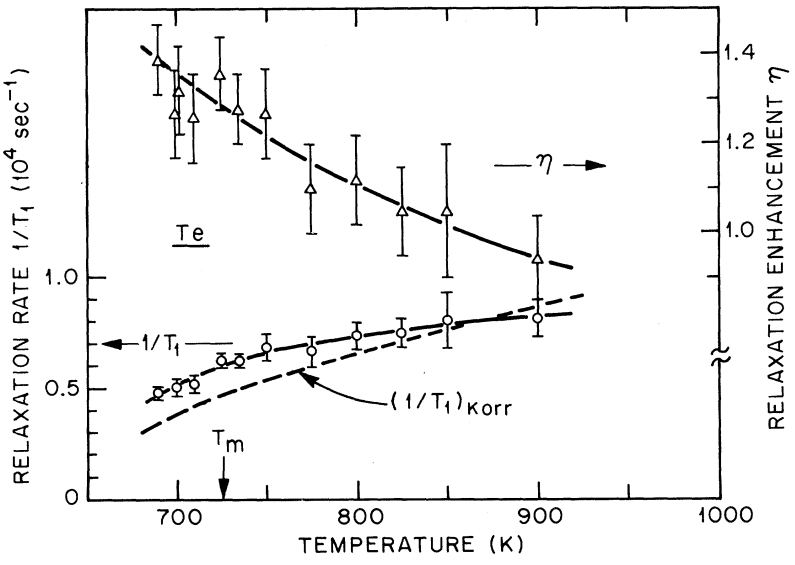

FIG. 2. Spin-lattice relaxation rate ($1/T_1$) and relaxation enhancement (η) as functions of temperature. The dashed line represents the Korringa rate calculated from the measured values of $\mathcal{K}^{125}$. Data shown below T_m were taken in the supercooled state.

trons having s character at the Te nuclei, (ii) core-polarization contributions[21] from both s and p electrons, and (iii) orbital contributions[22] from p electrons. Now the hyperfine fields from the core-polarization and orbital interactions are typically from one to two orders of magnitude smaller than the direct contact field. Thus, even though the fractional s character at the Fermi level in Te has been estimated[10] at only about 15%, the contact interaction should make the dominant contribution to $\mathcal{K}^{125}$ owing to the large s-electron hyperfine coupling. For purposes of the following analysis, we shall assume that the observed value of $\mathcal{K}^{125}$ is due *entirely* to the contact term, but we shall return to this point later to consider the effects of this simplifying assumption on the conclusions.

The s-electron contribution to $\mathcal{K}^{125}$ may be written

$$\mathcal{K}^{125} = \tfrac{8}{3}\pi \langle |\psi(0)|^2 \rangle_F \chi_{\text{spin}} \ , \tag{4}$$

where $\langle |\psi(0)|^2 \rangle_F$ is the probability amplitude for electrons at the nucleus averaged over all electrons at the Fermi level and χ_{spin} is the paramagnetic spin susceptibility per atom. Now, the susceptibility can be expressed in terms of the density of states at the Fermi level of a degenerate system so that

$$\mathcal{K}^{125} = \tfrac{4}{3}\pi (\gamma_e \hbar)^2 \langle |\psi(0)|^2 \rangle_F N(E_F) \varphi \ , \tag{5}$$

where γ_e is the electronic gyromagnetic ratio and φ is a correction factor depending on the enhancement of χ_s due to electron-electron effects, $(1-\alpha)^{-1}$, and the enhancement β of χ_s due to spin-orbit effects[10]:

$$\varphi = \beta/(1-\alpha) \ . \tag{6}$$

I believe that the dominant role in the temperature dependence of $\mathcal{K}^{125}$ is played by a temperature-dependent value of $N(E_F)$. To see this, consider the relation of $\mathcal{K}^{125}$ to the total magnetic susceptibility χ. The various contributions to χ which may be expected to be important in liquid Te may be written

$$\chi = \chi_{\text{ion}} + \chi_{\text{spin}} + \chi_{\text{orb}} \ , \tag{7}$$

where the first term is the diamagnetism of the ion cores, the second term is the spin paramagnetism of the electrons at the Fermi level, and the final term is the orbital susceptibility of all the valence electrons. The spin term in Eq. (7) may be written in terms of $N(E_F)$ and φ to give

$$\chi = \chi_{\text{ion}} + \chi_{\text{orb}} + \tfrac{1}{2}(\gamma_e \hbar)^2 \beta (1-\alpha)^{-1} N(E_F) \ . \tag{8}$$

Now χ_{ion} should not be strongly dependent on temperature. Similarly χ_{orb}, arising from all the valence electrons (i.e., not restricted to those near E_F), should be only weakly temperature dependent barring gross modifications at the electronic structure. The total susceptibility has been observed to increase significantly as the temperature is raised.[23-25] Since there is no reason to expect strong temperature dependences for β and $(1-\alpha)^{-1}$, Eq. (8) suggests that the increase in χ results from an increasing value of $N(E_F)$. This is consistent, of course, with the behavior of the Hall coefficient which indicates an increase in carrier density at higher temperatures. Thus, if it is true that $N(E_F)$ also dominates the temperature dependence of $\mathcal{K}^{125}$, Eqs. (5) and (8) imply that $\mathcal{K}^{125}$ should vary linearly with χ where T is an implicit parameter.

Figure 3 shows a plot of $\mathcal{K}^{125}$ vs χ using susceptibility data of Urbain and Übelacker.[25] The data fit a straight line within experimental error although a smooth line drawn through the data points shows a slight upward curvature. The slope of the best linear fit to the data gives

$$\frac{d\mathcal{K}}{d\chi} = \frac{8}{3}\pi \langle |\psi(0)|^2 \rangle_F = (6.7 \pm 0.4) \times 10^{25} \ \text{cm}^{-3} \ ,$$

while the curvature corresponds to variations of slope of no more than $\pm 15\%$ about this mean value. The intercept at zero value of $\mathcal{K}^{125}$ gives

$$\chi_{\text{ion}} + \chi_{\text{orb}} = (-45 \pm 3) \times 10^{-6} \ \text{emu/mole} \ .$$

This value may be compared with the values of χ_{ion} calculated by Hurd and Coodin[26] for Te^{6+} (-14.62×10^{-6} emu/mole) and Te^{+} (-40.70×10^{-6} emu/mole). This analysis is then consistent with χ_{ion} roughly equal to the calculated value for Te^{+} and a relatively small paramagnetic contribution for χ_{orb}. Since most of the six valence electrons are utilized in forming Te–Te bonds, it is not surprising that χ_{ion} appears to be closer to the value predicted for Te^{+} than to that for fully ionized Te^{6+}.

As a further test of the validity of the $\mathcal{K}$-vs-χ analysis, the density of states can be estimated from the observed values of $\mathcal{K}^{125}$, $d\mathcal{K}^{125}/d\chi$, and Eq. (5). Such a procedure, however, requires estimates of the enhancements β and $(1-\alpha)^{-1}$, neither of which are known with precision. Following Cabane and Friedel,[10] let us assume β to lie in the range $1.25 \lesssim \beta \lesssim 1.50$ and for $(1-\alpha)^{-1}$ we choose a typical value $(1-\alpha)^{-1} \simeq 2$. Thus, we have $\beta(1-\alpha)^{-1} \simeq 2.7$ whence, at T_m,

$$N(E_F) \simeq 1.3 \times 10^{11} \ (\text{erg atom})^{-1} \ .$$

Now, for a fully free-electron (FE) situation, in which all six valence electrons form a free-electron gas, the value of $N(E_F)$ may be calculated from elementary theory:

$$N(E_F)_{\text{FE}} = 2.6 \times 10^{11} \ (\text{erg atom})^{-1} \ .$$

Thus, we have the reasonable result that near the

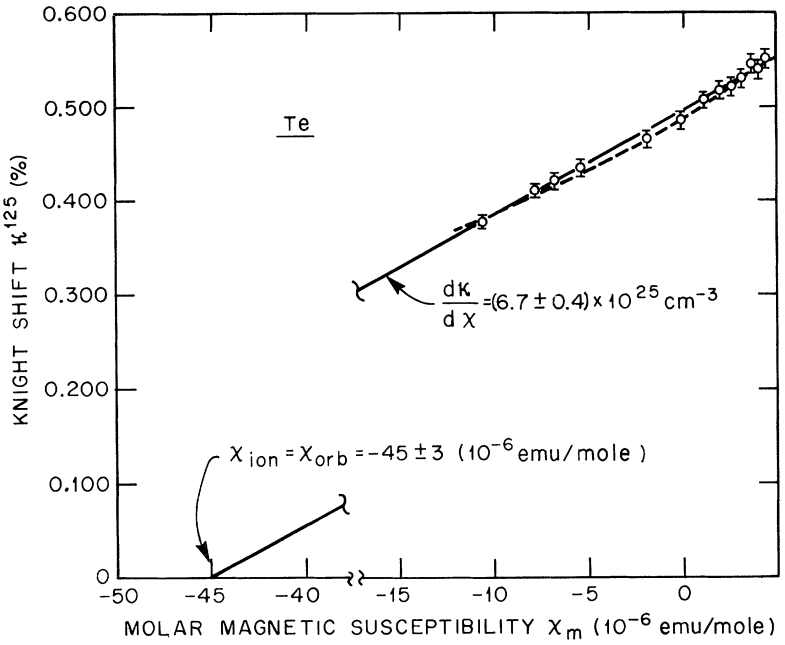

FIG. 3. Knight shift ($\mathcal{K}^{125}$) as a function of total molar susceptibility (χ_m) with temperature being the implicit variable. The susceptibility data were obtained from Ref. 26. The dashed line is a smooth curve drawn through the data points. The solid line is the best linear fit to the data. Note the discontinuity in the abcissa.

melting point the value of $N(E_F)$ is roughly half the free-electron value.

The foregoing discussion demonstrates that a consistent analysis of the magnitudes and temperature dependences of $\mathcal{K}^{125}$ and χ may be obtained under the simple assumptions (i) that the s-electron contact term is the only non-negligible contribution to $\mathcal{K}^{125}$ and (ii) that the temperature dependence of $\mathcal{K}^{125}$ and χ results entirely from the temperature dependence of $N(E_F)$. Before proceeding further we must examine the possible consequences of violations of these assumptions.

The most tenuous assumption is probably neglect of p-electron contributions of $\mathcal{K}^{125}$. In terms of the $\mathcal{K}$-vs-χ analysis, the principal effects of a p-electron contribution would be to alter the values determined for $\chi_{ion}+\chi_{orb}$ and $N(E_F)$. Since $d\mathcal{K}_{orb}/d\chi_{orb}$ may be expected to be much smaller than $d\mathcal{K}_s/d\chi_s$, the presence of a small orbital contribution to $\mathcal{K}^{125}$ could introduce quite large errors in the value of $\chi_{ion}+\chi_{orb}$. On the other hand, the value of $\langle|\psi(0)|^2\rangle_F$ is not affected by a constant orbital contribution so that the value determined for $N(E_F)$ would be in error by a factor $1+\mathcal{K}_{orb}/\mathcal{K}_s$. A similar argument can be made with regard to a p-electron core-polarization contribution.

Experience with d-electron core-polarization and orbital shifts in transition metals[27] suggests that a reasonable upper limit for the p-electron shift contribution in Te (with its much lower density of states) is roughly $\mathcal{K}_p \lesssim 0.100\%$. An uncertainty of this magnitude in $\mathcal{K}_p$ introduces an error of about 30% in the value of $N(E_F)$. I conclude that the ratio of $N(E_F)$ to $N(E_F)_{FE}$ at the melting point is as follows:

$$g \equiv N(E_F)/N(E_F)_{FE} = 0.50 \pm 0.15 .$$

The nearly linear dependence of $\mathcal{K}^{125}$ on χ_m indicates that χ_{ion}, χ_{orb}, $\mathcal{K}_{orb}$ (if present) and $\langle|\psi(0)|^2\rangle_F$ depend only weakly on temperature. Any significant variation in any of these quantities would introduce curvature in the $\mathcal{K}$-vs-χ plot and thus lead to erroneous values of $\langle|\psi(0)|^2\rangle_F$ determined from the slope. In fact, a slight curvature is observed and this probably reflects one or more of these effects. However, the fact that the observed average slope gives a reasonable value for $N(E_F)$ suggests that most of the temperature dependence arises from $N(E_F)$.

B. Correlation of NMR Data with Transport Properties

One of the unique and interesting features of liquid semiconductors is that Knight shifts and magnetic relaxation rates may be related in simple ways to the bulk transport properties.[14] That NMR parameters which depend on the local static and dynamic susceptibilities should be connected to such macroscopic properties as the electrical conductivity is at first sight somewhat surprising and, in fact, this does not occur for ordinary solid or liquid metals. In "good" metals, for example,[3] the conductivity is determined mainly by the mean free path. Since λ is equivalent to several interatomic spacings, the local susceptibility at a site is not strongly influenced by scattering processes. In liquid semiconductors, however, the mean free path is not longer than a single interatomic spacing and electronic transport is

more easily described in terms of a diffusive or hopping mechanism. In such low-mobility liquids the transport mechanism becomes, in effect, a local property and as such is related more or less directly to the local susceptibilities and NMR parameters.

More specifically, previous experiments and theory have identified three distinct types of electronic transport in liquids[9,14,28]: (i) NFE, (ii) strong scattering (diffusion or Brownian motion), and (iii) localized states. The NFE description is embodied in Ziman's theory of the conductivity of liquid metals[29] and applies when the mean free path (λ) exceeds the interatomic spacing (a). The minimum value for the conductivity in this regime is predicted[9] to be roughly 3000 $(\Omega\,\mathrm{cm})^{-1}$. In the diffusive region of strong scattering (ii), the wave functions are believed to be extended as in the NFE regime, but the phase of a typical wave function fluctuates randomly from site to site.[16] In this regime, transport proceeds by a kind of diffusion with the jump distance being equal to one interatomic spacing. The conductivity in this region spans roughly the range from about 300 to 3000 $(\Omega\,\mathrm{cm})^{-1}$. In the range of localization (iii), the conductivity is less than about 300 $(\Omega\,\mathrm{cm})^{-1}$ and the eigenfunctions are no longer extended but become localized about specific sites. In this regime, the electrons are supposed to move from site to site by thermally activated hopping.

The electrical conductivity of liquid Te increases from a value of about 1300 $(\Omega\,\mathrm{cm})^{-1}$ at 675 K to about 2750 $(\Omega\,\mathrm{cm})^{-1}$ at 1100 K.[1-5] Thus, as pointed out in Sec. I, Te lies very close to the predicted transition region between NFE behavior and diffusive conductivity. In this section we consider the expected correlations of NMR and transport parameters and examine the validity of these for liquid Te.

1. *Electrical Conductivity versus Knight Shift*

In the NFE regime, the conductivity may be written[9]

$$\sigma = e^2 S \lambda_{\mathrm{NFE}} / 12\pi^3\hbar \ , \tag{9}$$

where S is the surface area of the free-electron Fermi sphere and λ_{NFE} is the mean free path for NFE's. The value of λ_{NFE} is determined by the liquid structure and pseudopotential and does not depend in a simple way on the density of states.[29] For strong scattering, on the other hand, Mott argues that Eq. (9) takes the form

$$\sigma = e^2 S a g^2 / 12\pi^3\hbar \ . \tag{10}$$

In this regime the temperature dependence of σ should result mainly from the temperature dependence of g since S and a depend only weakly on the temperature. Now if, as has been argued in Sec. IV A, the temperature dependence of $\mathcal{K}$ results mainly from the density of states, we should expect $\mathcal{K}$ to be proportional to g. Thus, we should find in the diffusive regime

$$\sigma \propto \mathcal{K}^2 \ , \tag{11}$$

while in the NFE regime, these properties are not directly related.

A log-log plot of σ vs $\mathcal{K}$ is given in Fig. 4 and the data are compared with the correlation predicted by Eq. (11). The expected dependence for the diffusive regime is observed for conductivity values up to about 2500 $(\Omega\,\mathrm{cm})^{-1}$. Above this value, the conductivity tends to become less strongly dependent on $\mathcal{K}$. This result then suggests that the diffusive strong-scattering description is appropriate for liquid Te up to about 900 K while above this temperature, presumably, the NFE model becomes applicable.

2. *Hall Coefficient versus Knight Shift*

Several theoretical predictions have been made regarding the dependence of the Hall coefficient (R_H) on the density-of-states reduction factor g in the NFE and diffusive regimes. Ziman[30] argued that if the Lorentz force depends on the electron *current* in the NFE regime, then one should find

$$R_H / R_H^0 = 1/g \ , \tag{12}$$

where R_H^0 is the free-electron Hall coefficient. On the other hand, according to Ziman, if the force is determined by the *group velocity* of a wave packet at the Fermi energy, then one should observe

$$R_H / R_H^0 = 1/g^2 \ . \tag{13}$$

The dependence predicted by Eq. (13) was also obtained from a more detailed calculation of Fukuyama, Ebisawa, and Wada[31] for the NFE regime. Friedman[32] calculated R_H/R_H^0 for the strong-scattering diffusive regime and found that R_H/R_H^0 should be proportional to $1/g$ as in Eq. (12). An identical result was obtained by Straub *et al.*[33] for the case of impurity conduction in semiconductors.

I have plotted $\ln R_H$ vs $\ln \mathcal{K}$ in Fig. 4 using the Hall coefficient data summarized in the review by Tieche and Zareba.[34] Within experimental error the data fit a line corresponding to $R_H \propto \mathcal{K}^{-2}$ although there may be some deviation from this dependence above 900 K. It is quite clear that R_H does not vary as $\mathcal{K}^{-1}$ between T_m and 900 K where the $\sigma \propto \mathcal{K}^2$ behavior indicates that the diffusive strong-scattering description should be appropriate. This result shows that the calculations of Straub *et al.* and Friedman cannot account for the temperature dependence of R_H in liquid Te. This conclusion is contrary to one which may be

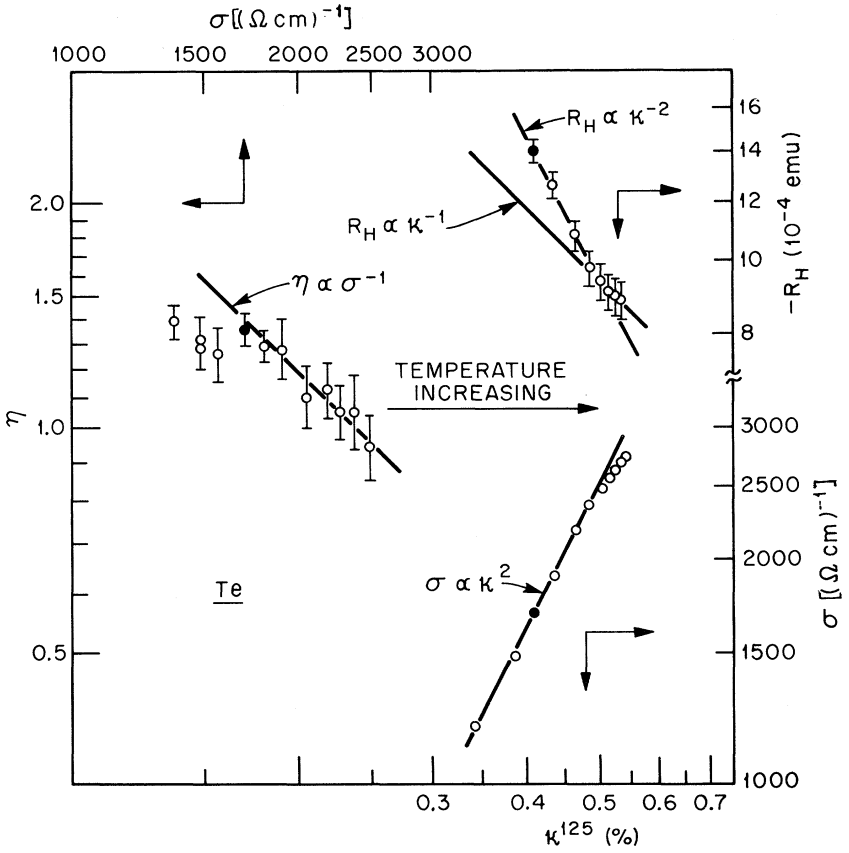

FIG. 4. Log-log correlations of NMR and transport parameters with temperature being the implicit variable: center left, relaxation enhancement (η) vs electrical conductivity (σ); upper right, Hall coefficient (R_H) vs Knight shift ($\mathcal{K}^{125}$); lower right, electrical conductivity vs Knight shift. The closed points correspond to data obtained at the melting point.

drawn from recent measurements of R_H and σ in liquid Hg reported by Even and Jortner.[28] Those authors found that as the density of liquid Hg is reduced by raising the temperature under moderate applied pressure, the value of R_H increases proportional to $\sigma^{-1/2}$ as would be expected from Eqs. (10) and (12). In the case of Te, it is clear that R_H increases approximately proportional to σ^{-1} implying a nearly constant Hall mobility as discussed by Tieche and Zareba.[34]

3. *Relaxation Enhancement versus Electrical Conductivity*

In semiconducting liquid compounds and alloys with conductivities less than 1000–2000 $(\Omega\,\mathrm{cm})^{-1}$, the nuclear magnetic relaxation rates are observed to be enhanced with respect to the Korringa rate calculated from the Knight shift.[14,17] The enhancement increases with decreasing conductivity, and enhancements of more than two orders of magnitude have been observed[14] in liquids with conductivities on the order of 10 $(\Omega\,\mathrm{cm})^{-1}$. The enhancement occurs because in the diffusive or localized regimes individual electrons remain longer on particular sites. This tends to slow down the fluctuation of the local hyperfine field and introduces greater spectral intensity at the (very low) nuclear Larmor frequency. It can be shown from simple arguments[14] that the enhancement parameter η defined by Eq. (3) is, approximately, the ratio of the time spent on a site by an electron to the time a NFE would spend near a given site. The latter is roughly the average interatomic spacing divided by the Fermi velocity.

It is clear that the enhancement is related to the microscopic mobility since both depend on the average time an electron spends on a site. In the diffusive regime, this relation leads to the simple dependence $\eta \propto \sigma^{-1}$ given in Eq. (1). In the NFE regime, we should expect η to be close to the value 1 and independent of the conductivity. This is, of course, normally observed for liquid metals.[35]

The observed values of η are plotted against σ on the log-log plot of Fig. 4. Between T_m and 900 K, η varies as σ^{-1} within experimental error. Below T_m, however, η is somewhat smaller than implied by extrapolation of the higher-temperature data. This result might be viewed as reduction of the constant σ_0 from a value of about 2500 $(\Omega\ \mathrm{cm})^{-1}$ above T_m to about 1900 $(\Omega\ \mathrm{cm})^{-1}$ in the supercooled state. Since σ_0 depends only on the diffusion jump distances and atomic volumes,[14] this change would necessarily reflect some structural modification below T_m. Without detailed structural information about the supercooled liquid,

however, it is difficult to support this conjecture. Another possible explanation for deviations from Eq. (1) is the presence of temperature-dependent electron-electron effects. However, if the exchange enhancement in Te behaves in a manner similar to simple metals,[36] one would expect η to *increase* relative to Eq. (1) when the density of states becomes small. This effect then would cause deviations of the opposite sign to those observed. Finally, it should be noted that it is possible to describe the data over the entire temperature range by $\eta \propto \sigma^{-0.7}$, although this gives a much poorer fit than $\eta \propto \sigma^{-1}$ above T_m. Now the maximum enhancement observed is only about 1.4 so that liquid Te is never very far from the NFE situation even at the lowest temperatures. The fact that the dependence of η on σ may be slightly weaker than predicted by Eq. (1) might be an indication that the conductivity of liquid Te is not fully dominated by local phenomena as assumed in the derivation of Eq. (1).

V. SUMMARY AND CONCLUSIONS

Measurements of the Knight shifts and spin-lattice relaxation rates for Te^{125} in liquid Te have been reported and discussed. The results confirm the status of Te as a transitional liquid with incipient "semiconducting" properties at low temperatures and essentially metallic properties well above the melting point. These results are basically in accord with the structural and bonding model proposed by Cabane and Friedel. The temperature dependence of $\mathcal{K}^{125}$, it was argued, is due mainly to variation of $N(E_F)$. The magnitude of the shift suggests a modest pseudogap ($g \simeq 0.5$) near T_m which "fills" to give $g \simeq 0.7$ at 1200 K. Such behavior is fully consistent with the conversion of binary to ternary coordination suggested by Cabane and Friedel.

Correlation of the NMR data and transport properties are in fairly good agreement with expectations for the strong-scattering or diffusive transport regime for temperatures below about 900 K. Agreement is best for the dependence of σ on g^2 and poorest for the predicted behavior $R_H \propto g^{-1}$. The Hall coefficient in Te varies quite accurately as $\mathcal{K}^{-2}$. The magnetic relaxation rates are slightly enhanced relative to the Korringa rate and the enhancement tends to increase with decreasing temperature and conductivity. The data for η vary as σ^{-1} above T_m, as expected for the strong-scattering regime. In the supercooled state, however, η does not rise as rapidly as the reported drop in conductivity would dictate unless there occurs a 20% reduction of σ_0 below T_m. Such a reduction might well result from structural modifications below T_m but I know of no experimental evidence to support this conjecture. It was also pointed out that the dependence of η on σ may be somewhat weaker than σ^{-1} over the entire range reflecting the NFE character of liquid Te.

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Track-Effect Account of Scintillation Efficiency for Random and Channeled Heavy Ions of Intermediate Velocities

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The high-velocity formulation of the track-effect theory of scintillation efficiency is generalized for applicability at intermediate velocities (velocities spanning the peak in dE/dx) and applied to room-temperature data for O^{16} in NaI(Tl) both for random and channel trajectories. A core-correction term is incorporated into the representation of dE/dx. Electron velocities are taken into account in the calculation of track width $R_{max}(v)$. The contribution to dL/dE from the region of high energy-deposit density is included. Quantitative agreement within experimental error is achieved for the O^{16} random-response data over the range $0.9 \leq v \leq 3.6$, where v is in units of 10^9 cm/sec, including the region of intermediate velocities characterized by a reversal of curvature and leveling off of dL/dE. The channel response is treated only so far as to indicate applicability of the theory. Values for the ratio $[dL/dE(\text{channel})]/[dL/dE(\text{random})]$ are accounted for both in approximate magnitude and qualitative dependence on particle velocity.

I. INTRODUCTION

In a recent work,[1,2] a track-effect theory was proposed to account for the general characteristics of the heavy-ion pulse-height data of a wide range of scintillating crystals. The model was applied to the high-velocity ($v \gtrsim 2.2\times10^9$ cm/sec) data of Newman and Steigert[3] for room-temperature bombardment of NaI(Tl) with ions in the range $5 \leq Z \leq 10$. Subsequent data of Altman *et al.*[4,5] for O^{16} bombardment of NaI(Tl) extend the pulse-height characteristics to intermediate velocities, i.e., velocities which span the peak in dE/dx and demonstrate that channeling enhances scintillation efficiency dL/dE in NaI(Tl). The latter is particularly apparent when particle velocities are reduced to the intermediate range. Indeed, this phenomenon was predicted in an earlier work,[6,7] and quantitative estimates of relative pulse heights, $L(\text{channel})/L(\text{random})$, were made.

In the present paper, the track-effect theory[2] is generalized for applicability at intermediate as well as high velocity, and a quantitative account is given for the channeling effect and for the behavior of the new intermediate-velocity data for randomly incident ions. A core-correction term is incorporated into the representation of specific energy loss dE/dx. Electron velocities are taken into account in the calculation of the track width $R_{max}(v)$. The contribution to dL/dE from the region of high energy-deposit density is included. A quantitative account is provided for dL/dE data[3-5] corresponding to room-temperature bombardment of NaI(Tl) by O^{16} ions in the approximate range $0.9 \leq v \leq 3.6$, where v is in units of 10^9 cm/sec. Estimates are made of the ratio of dL/dE (channel) to dL/dE (random) which agree with observation both in magnitude and qualitative behavior. Insights which result from this treatment regarding the track effect and its role in luminescence are discussed.

II. GENERAL FORMULATION OF THEORY

Theoretical analysis of heavy-ion pulse-height characteristics of scintillators demands consideration of a two-step process in which energy is transferred by the particle to the crystal lattice and then transported from the track and subsequently absorbed at luminescence centers. For purposes of analysis, pulse-height data are generally reduced to dL/dE, the so-called "scintillation efficiency," from which the total pulse may be generated through integration over the particle trajectory. Hence, all theoretical considerations refer to processes which occur in a differentially thin section of crystal perpendicular to the particle track. The present treatment concerns velocities $v \gtrsim v_{TF}$, where v_{TF} is the characteristic Thomas-Fermi velocity of the penetrating ion. In this domain, elastic-collision losses constitute a