

Nuclear Magnetic Resonance and Relaxation in Liquid In, Sb, and InSb*

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Measurements of the Knight shift and nuclear spin-lattice relaxation rate of In^{115} , Sb^{121} , and Sb^{123} in liquid In, liquid Sb, and liquid InSb are reported over temperatures ranging from near the respective melting points up to 1200–1450°K. An attempt to relate the observed relaxation rates to existing theories indicates that the latter are not adequate to explain all aspects of the observations. In the case of InSb, where an unusual temperature dependence appears in the quadrupolar contribution to the relaxation rate of the Sb isotopes, it is proposed that important changes occur in the electronic structure of the liquid metal as its temperature is raised above the melting point.

I. INTRODUCTION

MEASUREMENTS of the nuclear spin-lattice relaxation time (T_1) and Knight shift (\mathcal{K}) have been important for the study of internal motions and electronic properties of liquid and solid metals. In this paper, we present such measurements for In^{115} in liquid In, Sb^{121} and Sb^{123} in liquid Sb, and In^{115} , Sb^{121} , and Sb^{123} in liquid InSb. A temperature range extending from near the respective melting points to 1200–1450°K is covered, and several resonance frequencies are employed. In addition to the measurements, an evaluation of the various mechanisms responsible for our observations is presented. Preliminary reports of this work have been given elsewhere.¹

The experimental work has been guided by a need to evaluate the relative importance of the various mechanisms which can contribute to T_1 and \mathcal{K} . For this reason, we have placed a heavy emphasis on covering a wide temperature range, achieving high accuracy, and using all of the naturally abundant isotopes. This approach has been especially fruitful for the Sb^{121} and Sb^{123} isotopes, as it has been possible to resolve the observed values of the relaxation rate (W) into magnetic (W_M) and quadrupolar (W_Q) contributions.

There is some overlap between our measurements and those reported by others. In particular, for In metal, Flynn and Seymour² have reported values of \mathcal{K} between 446 and 636°K. Rossini, Geissler, Dickson, and Knight³ have reported values of T_1 and \mathcal{K} between 403 and 573°K, which were later extended by Rossini⁴ up to 700–775°K. In liquid Sb, Odle and Flynn⁵ have reported

a measurement of \mathcal{K} for Sb^{121} at the melting point. Finally, Allen and Seymour⁶ reported a value of \mathcal{K} at the melting point for In^{115} in InSb.

The interpretation of our results differs somewhat from those presented elsewhere.^{3,4} The most noticeable difference occurs over the origin of the quadrupolar contribution to relaxation in liquid In and liquid Sb. Although we are not able to conclude that a particular mechanism is clearly responsible, we believe our results favor a model based on the scattering of Fermi surface electrons over one based on the diffusion of ion cores.

The measurements in liquid InSb display an unusual temperature dependence for W_M and W_Q . It is proposed that this is caused by the conduction electrons which interact with Sb nuclei changing from p to s character as the temperature is increased.

The organization of this paper is as follows: A discussion of the experimental apparatus, techniques, and samples is given in Sec. II. Section III contains a presentation of the data, which are interpreted in Sec. IV. Conclusions and acknowledgments follow in Secs. V and VI, respectively. A compilation of the relevant physical properties of In, Sb, and InSb near the melting points appears in Table I.

II. EXPERIMENTAL DETAILS

A. Samples and Apparatus

The InSb samples used in these experiments were prepared from grade 35S single-crystal n -type material supplied by Cominco America Inc.⁷ It was crushed and sieved to obtain particle sizes in the range 100–150 μ . The crushed InSb was then mixed with an equal amount of quartz powder of comparable particle dimensions⁸ to ensure that in the liquid state the sample would approximate a dispersion of particles small enough to permit nearly complete penetration of the rf magnetic field.

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¹ W. W. Warren and W. G. Clark, *Bull. Am. Phys. Soc.* **11**, 916 (1966); **12**, 57 (1967).

² C. P. Flynn and E. F. W. Seymour, *Proc. Phys. Soc. (London)* **76**, 301 (1960).

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

⁴ F. A. Rossini, thesis, University of California, Berkeley, 1968 (unpublished).

⁵ R. L. Odle and C. P. Flynn, *J. Phys. Chem. Solids* **26**, 1685 (1965); also see L. H. Bennett, R. M. Cotts, and R. J. Snodgrass, in *Nuclear Magnetic Resonance and Relaxation in Solids*, edited by L. Van Gerven (North-Holland Publishing Co., Amsterdam, 1965), pp. 171–180.

⁶ P. S. Allen and E. F. W. Seymour, *Proc. Phys. Soc. (London)* **85**, 509 (1965).

⁷ Cominco America Inc., West 818 Riverside Avenue, Spokane, Wash.

⁸ W. D. Knight, A. G. Berger, and V. Heine, *Ann. Phys. (N.Y.)* **8**, 173 (1959).

Indium and antimony metals were obtained in powdered form from Electronic Space Products, Inc.⁹ The particle sizes ranged from 50–100 μ . The specified purity of the indium powder was 99.9995%, and that of the antimony 99.9999%. These powders were also mixed with equal amounts of quartz powder.

The In^{115} , Sb^{121} , and Sb^{123} nuclear magnetic resonances were observed using a pulsed spectrometer with phase coherent detection similar to one described previously.¹⁰ The system utilized a crossed-coil rf coil configuration with gold or platinum coils in a high-temperature probe.¹¹ The samples were maintained in an inert (argon) atmosphere at approximately 1 atm pressure. The rotating component of the pulsed rf magnetic field was typically 20 G.

B. Measurement Techniques and Accuracies

Values of \mathcal{K} were obtained by comparing the resonance frequency (ν_x) of the appropriate nucleus in the liquid metal and in an aqueous solution (reference sample) with the frequency (ν_D) of the deuteron resonance (D_2O doped with GdCl_3) in the same magnetic field. The center of the NMR line for the liquid-metal nucleus was located by recording the integral of most of the free-induction decay with a boxcar integrator¹² as the magnetic field was swept through resonance.¹⁰ In the case of In^{115} , the reference sample was a dilute $\text{In}_2(\text{SO}_4)_3$ solution; for Sb, it was dilute HSbF_6 .¹³ The accuracy of the shift measurements was limited mainly by the error in setting the relative phase between the NMR and master oscillator reference signals to 0° (see last section of Ref. 10). This experimental error was $\pm 0.004\%$ of the resonance frequency for In^{115} and $\pm 0.007\%$ for Sb^{121} and Sb^{123} .

Spin-lattice relaxation times were measured with approximately 180° – 90° pulse sequences spaced many times T_1 apart. 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. Typical T_1 measurements were accurate to $\pm 3\%$ over most of the temperature range studied. At the highest temperatures, the accuracy of Sb^{121} and Sb^{123} T_1 measurements deteriorated to $\pm 6\%$ due to reduced signal-to-noise ratio.

Spin-phase memory times (T_2) were measured by analyzing the free-induction decay shape with the magnetic field carefully set to the center of the resonance line and the reference phase shift set to 0° . The decay shapes were recorded either by photographing the os-

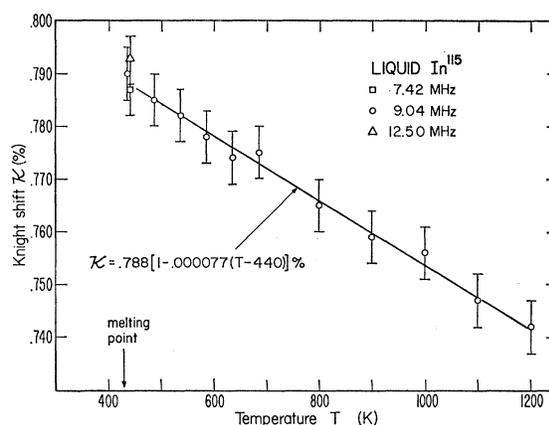


FIG. 1. The experimental Knight shift $\mathcal{K}(\text{In}^{115})$ for In^{115} in liquid indium as a function of temperature. Note the discontinuity in the vertical scale.

cilloscope trace, or by recording the output of the boxcar integrator as a narrow sampling gate was swept along the decay. The accuracy of T_2 measurements ranged from 5–15% for In^{115} and from 10–30% for Sb^{121} and Sb^{123} . No spin echoes could be observed in any of the three liquid metals investigated.

Sample temperatures were measured with chromel versus alumel or platinum versus platinum—10% rhodium thermocouples using standard calibration tables.¹⁴ In the presence of rf pulsing, sample temperatures were regulated with a feedback system to within $\pm 0.2\%$ over most of the temperature range. The maximum temperature variation over the sample volume was usually less than 0.5%. The over-all accuracy of the temperature determinations was at least $\pm 0.6\%$, with somewhat higher accuracy at the lower end of the temperature range.

III. EXPERIMENTAL RESULTS

A. Indium

The noncubic (tetragonal) structure of solid In metal and corresponding large electric quadrupole interaction (Table I) rendered the In^{115} resonance unobservable in our powdered samples between room temperature and the melting point. In the liquid, however, rapid thermal motion averages the static quadrupole interaction to zero, yielding a single strong nuclear resonance line. The resonance is slightly asymmetric due to the presence of In^{113} (4.2% abundance), which has a slightly smaller gyromagnetic ratio. Measurements of the In^{115} Knight shift [$\mathcal{K}(\text{In}^{115})$] in liquid In were made from the melting point (430°K) to 1200°K at 9.04 MHz. These data are shown in Fig. 1. The observed values of $\mathcal{K}(\text{In}^{115})$ decrease with increasing temperature according to the relationship (solid line in Fig. 1)

$$\mathcal{K}(\text{In}^{115}) = (0.788 \pm 0.005) [1 - 0.000077(T - 440^\circ\text{K})] \%$$

¹⁴ Leeds and Northrup, Philadelphia, Pa.

⁹ Electronic Space Products, Inc., 854 S. Robertson Blvd., Los Angeles, Calif. 90035.

¹⁰ W. G. Clark, Rev. Sci. Instr. **35**, 316 (1964).

¹¹ W. W. Warren, Jr., and W. G. Clark, J. Phys. **E1**, 1019 (1968).

¹² W. G. Clark and A. L. Kerlin, Rev. Sci. Instr. **38**, 1593 (1967).

¹³ Our observed ratios ν_x/ν_D were 1.427442 ± 0.000014 for a dilute aqueous solution of $\text{In}_2^{115}(\text{SO}_4)_3$ and 1.55905 ± 0.00002 and 0.844279 ± 0.000008 for Sb^{121} and Sb^{123} , respectively, in dilute HSbF_6 .

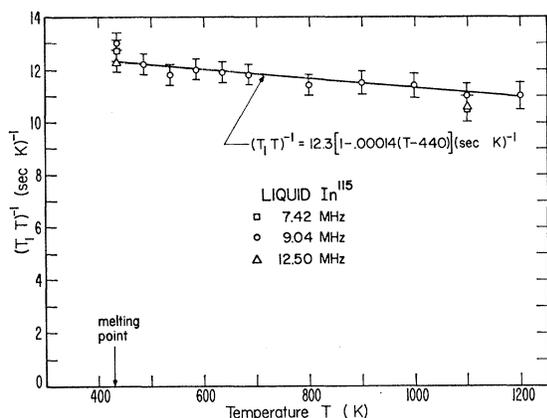


FIG. 2. The experimental values of $(T_1T)^{-1}$ for In^{115} in liquid indium as a function of temperature.

where T is the temperature in $^{\circ}\text{K}$. Measurements near the melting point at frequencies of 7.42 and 12.50 MHz indicate that \mathcal{K} is independent of frequency in this range.

Our measurements may be compared with the earlier measurements of Flynn and Seymour,² who measured $\mathcal{K}(\text{In}^{115})$ for liquid In over the temperature range 446–636 $^{\circ}\text{K}$. Both measurements agree near the melting point. Our value of $d\mathcal{K}/dT$ is, however, 2.3 times smaller than theirs. Since our measurement applies over a much wider temperature range, we believe ours to be the correct value. More recently, this has been verified by Rossini.⁴

The In^{115} nuclear relaxation rate in liquid In is plotted in the form $(T_1T)_{115}^{-1}$ versus T in Fig. 2. The data, which show that $(T_1T)_{115}^{-1}$ decreases slowly with temperature, have been fitted to the empirical relationship (solid line)

$$(T_1T)_{115}^{-1} = (12.3 \pm 0.3)[1 - 0.00014(T - 440^{\circ}\text{K})] (\text{sec } ^{\circ}\text{K})^{-1}.$$

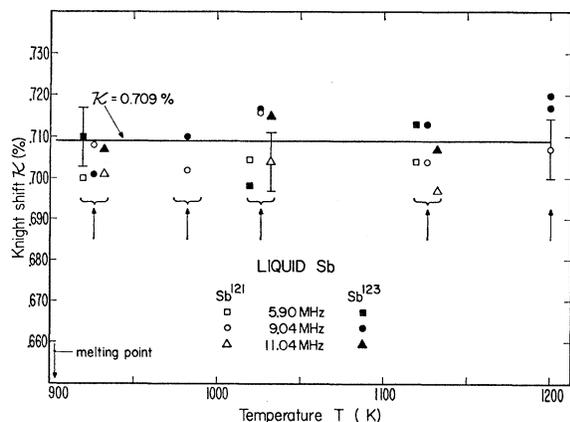


FIG. 3. The experimental Knight shifts $\mathcal{K}(\text{Sb}^{121})$ and $\mathcal{K}(\text{Sb}^{123})$ for Sb^{121} and Sb^{123} in liquid antimony as a function of temperature. Representative errors are indicated by the flags. Data points within a given grouping were all taken at the temperature indicated by the corresponding arrow. Note the discontinuity in the vertical scale.

These results agree within experimental error with T_1 measurements reported by Rossini *et al.*^{3,4} over the more limited temperature range 403–775 $^{\circ}\text{K}$. No frequency dependence was observed in measurements at 7.42, 9.04, and 12.50 MHz.

The In^{115} free-induction decay shapes were exponential. Their value of T_2 was equal to T_1 with the experimental error in T_2 . This error was $\pm 5\%$ at 435 $^{\circ}\text{K}$ and increased to $\pm 15\%$ at 1200 $^{\circ}\text{K}$.

B. Antimony

The Sb^{121} and Sb^{123} resonances were not observed in the powdered Sb samples below the melting point (903 $^{\circ}\text{K}$) because of quadrupolar splitting in the non-cubic (rhombohedral) crystalline structure of the solid. In the liquid, measurements of \mathcal{K} and T_1 were made from 925 to 1200 $^{\circ}\text{K}$. The \mathcal{K} data, obtained at resonance frequencies (ν_{Sb}) of 5.90, 9.04, and 11.04 MHz, are

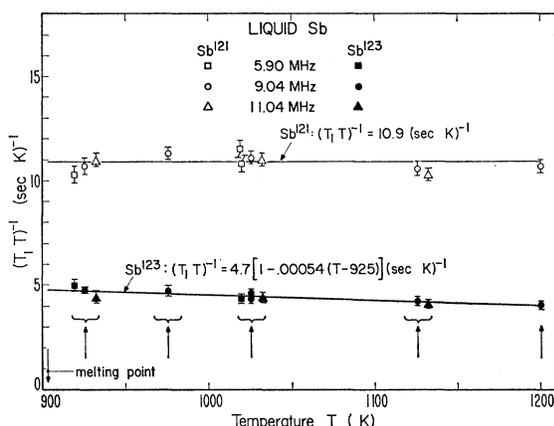


FIG. 4. The experimental values of $(T_1T)^{-1}$ for Sb^{121} and Sb^{123} in liquid antimony as a function of temperature. Data points within a given grouping were all taken at the temperature indicated by the corresponding arrow.

shown in Fig. 3. The observed values of \mathcal{K} were the same for both Sb^{121} and Sb^{123} , and independent of ν_{Sb} and T over the ranges investigated. The measured shift was found to be

$$\mathcal{K}(\text{Sb}^{121}) = \mathcal{K}(\text{Sb}^{123}) = (0.709 \pm 0.010) \%,$$

which agrees with the previous value obtained by Odle and Flynn⁵ in the vicinity of the melting point.

The relaxation rate data for Sb^{121} and Sb^{123} in liquid antimony are plotted in Fig. 4. The results are independent of ν_{Sb} for frequencies of 5.90, 9.04, and 11.04 MHz. For Sb^{121} , $(T_1T)_{121}^{-1}$ is given by

$$(T_1T)_{121}^{-1} = (10.9 \pm 0.5) (\text{sec } ^{\circ}\text{K})^{-1},$$

independent of T . In the case of Sb^{123} , $(T_1T)_{123}^{-1}$ decreases slowly with temperature according to the relaxation

$$(T_1T)_{123}^{-1} = (4.7 \pm 0.3)[1 - 0.00054(T - 925^{\circ}\text{K})] (\text{sec } ^{\circ}\text{K})^{-1}.$$

The Sb^{121} and Sb^{123} free-induction decays in liquid antimony are exponential. Measurements of T_2 from the decays were accurate to $\pm 10\%$ at 925°K and $\pm 30\%$ at 1200°K . Within this accuracy, T_1 and T_2 are the same for each isotope.

C. Indium Antimonide

Our Knight-shift data for liquid InSb are shown in Fig. 5 together with measurements of the resonance shift in the solid just below the melting point. Liquid measurements below the melting point were possible due to supercooling. An obvious feature of these data is the appearance of a large positive \mathcal{K} for both In and Sb nuclei accompanying the transition from the semi-conducting to metallic phase at the melting point. The Knight shift appears abruptly at the transition temperature with no evidence of an intermediate value of the shift in partially melted samples. The shift of the resonance frequency from its value in the solid to its value in the liquid occurs within a temperature range of 5°K , which is equal to the temperature variation over the sample volume. The value of the In^{115} shift at the melting point is

$$\mathcal{K}(\text{In}^{115}\text{Sb}) = (0.932 \pm 0.004) \% \quad (803^\circ\text{K}),$$

in agreement with the earlier data of Allen and Seymour.⁶ A second important feature is the equality of the observed shifts for InSb^{121} and InSb^{123} . At the melting point, the shifts for the Sb isotopes are

$$\begin{aligned} \mathcal{K}(\text{InSb}^{121}) &= \mathcal{K}(\text{InSb}^{123}) \\ &= (0.643 \pm 0.006) \% \quad (803^\circ\text{K}). \end{aligned}$$

The experimental resolution is insufficient to resolve the hyperfine anomaly¹⁵ for liquid InSb^{121} and InSb^{123} . A third characteristic of the data is the weak temperature dependence exhibited by shifts for In^{115}Sb and $\text{InSb}^{121,123}$. The In^{115}Sb shift decreases slowly with in-

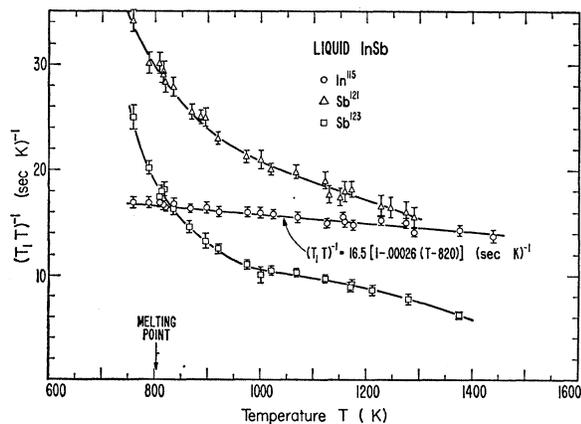


FIG. 5. The experimental Knight shifts $\mathcal{K}(\text{In}^{115}\text{Sb})$, $\mathcal{K}(\text{InSb}^{121})$, and $\mathcal{K}(\text{InSb}^{123})$ for In^{115} , Sb^{121} , and Sb^{123} in liquid indium antimonide as a function of temperature. Note the discontinuities in the vertical scale. The small, negative shift at 780°K was measured in solid indium antimonide.

¹⁵ J. Eisinger and G. Feher, Phys. Rev. **109**, 1172 (1958).

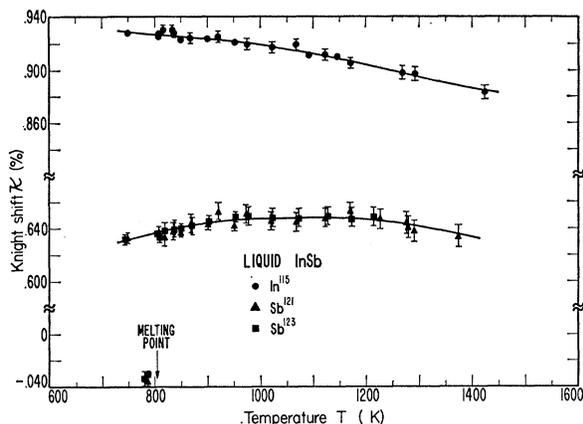


FIG. 6. The experimental values of $(T_1T)^{-1}$ for In^{115} , Sb^{121} , and Sb^{123} in liquid indium antimonide as a function of temperature.

creasing temperature such that

$$\mathcal{K}(\text{In}^{115}\text{Sb})_{803^\circ\text{K}} - \mathcal{K}(\text{In}^{115}\text{Sb})_{1425^\circ\text{K}} = (0.050 \pm 0.005) \%.$$

The shifts for $\text{InSb}^{121,123}$ are almost independent of temperature, passing through a broad maximum at about 1000°K . Most of the data shown in Fig. 5 were obtained at an NMR frequency of 9.0 MHz. Measurements at 835°K made at 4.0 and 13.0 MHz agree within experimental error with those at 9.0 MHz.

The transition from a solid semiconductor to a liquid metal is reflected in the observed values of T_1 as well as \mathcal{K} . For example, $(T_1)_{115}^{-1}$ increases by the factor 76 ± 2 upon increasing T through the melting point, and $(T_1)_{121}^{-1}$ and $(T_1)_{123}^{-1}$ both increase by the factor 83 ± 4 . The T_1 data for liquid InSb are plotted as $(T_1T)^{-1}$ versus temperature in Fig. 6. Considering first the In^{115} data, we note that $(T_1T)_{115}^{-1}$ decreases slowly with increasing temperature. The temperature dependence is described by the term linear in temperature in the following empirical representation of the In^{115} T_1 data:

$$\begin{aligned} (T_1T)_{115}^{-1} \\ = (16.5 \pm 0.3) [1 - 0.00026(T - 820^\circ\text{K})] (\text{sec } ^\circ\text{K})^{-1}. \end{aligned}$$

This linear representation is valid within experimental error from 760°K (supercooled liquid) to 1425°K .

In striking contrast to the slow variation of $(T_1T)_{115}^{-1}$, the Sb^{121} and Sb^{123} data exhibit a rapid decrease of $(T_1T)^{-1}$ with increasing temperature between the supercooled region and 1100°K , and a somewhat slower decrease at higher temperatures. Throughout the temperature range investigated, $(T_1T)^{-1}$ for the Sb isotopes shows a more rapid variation with temperature than for In^{115} . The observed relaxation rates are independent of resonance frequency over the range 4.0–13.0 MHz for all three nuclear species and fully reversible with respect to the direction of temperature variation.

Nuclear free-induction decay shapes were observed to be exponential in the case of all three isotopes. Analysis of the free-induction decays indicates that within the

experimental error (± 10 to $\pm 20\%$), T_1 equals T_2 for In^{115} , Sb^{121} , and Sb^{123} in liquid InSb .

IV. INTERPRETATION

A. Introduction: Knight Shifts and Spin-Lattice Relaxation in Liquid Metals

In this section we include a brief survey of those mechanisms which appear to be important for interpreting \mathcal{K} and T_1 in liquid In , Sb , and InSb . In the following sections, an interpretation of our experimental results in terms of these mechanisms is presented.

1. Knight Shift

The principal contribution to \mathcal{K} in simple (nontransition) metals is due to the hyperfine field of the spin-polarized conduction electrons interacting with the nucleus via the Fermi contact interaction. This "direct" contact interaction is nonzero only for those conduction electrons having a finite probability amplitude at the nucleus, i.e., whose wave functions are s -like. This contribution to \mathcal{K} is given by¹⁶

$$\mathcal{K}_s = \frac{8}{3}\pi\chi_s\Omega\langle |u_F(0)|^2 \rangle, \quad (1)$$

where χ_s is the spin susceptibility per unit volume for the s electrons, Ω the atomic volume, and $\langle |u_F(0)|^2 \rangle$ the average density at the nucleus of s -like, Fermi surface electrons.

The noncontact dipolar interaction with the electron spin vanishes in spherical symmetry and is therefore excluded for s electrons. Moreover, even for non- s electrons in a liquid metal, rapid thermal motion leads to *time-averaged* spherical symmetry and thus to a vanishing dipolar contribution to the Knight shift.

The interaction between the nucleus and the orbital moment of non- s conduction electrons introduces a contribution \mathcal{K}_0 to the Knight shift given by¹⁷

$$\mathcal{K}_0 = 2\beta^2\Omega \sum_{n,n'}' \int \frac{d^3k}{(2\pi)^3} \left[\frac{f(E_{nk}) - f(E_{n'k})}{E_{nk} - E_{n'k}} \right] \times \langle n\mathbf{k} | L | n'\mathbf{k} \rangle \langle n'\mathbf{k} | (L/r^3) | n\mathbf{k} \rangle, \quad (2)$$

where β is the Bohr magneton, $f(E_{nk})$ is the Fermi function of the electron energy E_{nk} , \mathbf{k} is the wave vector, n and n' are band indices, L is the orbital angular momentum operator, and r is the electron coordinate. The summation is carried out over all pairs of filled and unfilled states in the conduction band, except those for which $n=n'$. The evaluation of Eq. (2) is difficult for a liquid metal since it requires knowledge of the energy bands E_{nk} and eigenstates $|n\mathbf{k}\rangle$ for the entire conduction band.

Another contribution to \mathcal{K} is from polarization of

the ionic core states by the conduction electrons, which leads to different radial distributions for spin-up and spin-down electrons. The resulting net hyperfine field leads to the core-polarization contribution \mathcal{K}_{cp} given by¹⁸

$$\mathcal{K}_{\text{cp}} = \beta^{-1} \sum_{l=s,p,\dots} H_{\text{cp}}(l)\chi_l, \quad (3)$$

where $H_{\text{cp}}(l)$ and χ_l are the core-polarization hyperfine field and susceptibility, respectively, of the corresponding conduction electrons.

In addition to \mathcal{K}_s , \mathcal{K}_0 , and \mathcal{K}_{cp} , there are additional contributions to \mathcal{K} from the Landau diamagnetism of the conduction electrons and the diamagnetism of the core states (chemical shift). Since these contributions are expected to be small compared to the values of \mathcal{K} observed in these experiments,^{2,19} they are neglected in the interpretation which follows.

2. Spin-Lattice Relaxation

The important nuclear spin-lattice relaxation processes may be classified into two types. The first type, which will be referred to as "magnetic" relaxation, includes all processes in which transitions between nuclear Zeeman levels are induced by coupling between the nuclear magnetic dipole moment and time-dependent magnetic fields. The second, which we denote by "quadrupolar" relaxation, includes mechanisms involving coupling between the nuclear electric quadrupole moment and time-dependent electric field gradients.

It is often very useful to separate an observed relaxation rate into its magnetic and quadrupolar components.^{20,21} This can usually be done under the conditions which prevail in a liquid metal if T_1 can be measured for two isotopes of the same atom. The essential steps of the analysis are as follows.

First, it can be shown by time-dependent perturbation theory²² that if the nuclear Zeeman levels are equally spaced and if relaxation due to interactions between spins of the same species can be ignored, the magnetic spin-lattice relaxation rate (W_M) is proportional to the square of the nuclear gyromagnetic ratio (γ_n):

$$W_M \propto \gamma_n^2. \quad (4)$$

These conditions are satisfied in a liquid metal, as the short correlation time for atomic motion averages the *static* quadrupolar interaction to zero and the observed relaxation rates are much faster than those expected of nuclear spin-spin interactions. Similarly, in the short correlation time limit, the dependence of the rate W_Q

¹⁸ A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

¹⁹ T. P. Das and E. P. Sondheimer, Phil. Mag. **5**, 529 (1960).

²⁰ D. A. Cornell, Phys. Rev. **153**, 208 (1967).

²¹ A. Narath and D. W. Alderman, Phys. Rev. **143**, 328 (1966).

²² C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 141.

¹⁶ C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

¹⁷ R. J. Noer and W. D. Knight, Rev. Mod. Phys. **36**, 177 (1964).

for electric quadrupolar coupling is given by²³

$$W_Q \propto [(2I+3)/I^2(2I-1)]Q^2 \equiv f(I)Q^2, \quad (5)$$

where I is the nuclear spin and Q is the nuclear quadrupole moment.

Next, the total relaxation rate W for each isotope (A and B) is written as the sum of its magnetic and quadrupolar parts:

$$W_A = 1/T_1^A = W_M^A + W_Q^A, \quad (6)$$

$$W_B = 1/T_1^B = W_M^B + W_Q^B.$$

Equations (4)–(6) can be solved for W_M^A , W_M^B , W_Q^A , and W_Q^B in terms of the observed values of W , $f(I)$, and the ratios γ_A/γ_B and Q_A/Q_B :

$$W_M^A = (W_A - R_Q W_D) / (1 - R_Q/R_M),$$

$$W_M^B = W_M^A / R_M, \quad (7)$$

$$W_Q^A = (W_A - R_M W_B) / (1 - R_M R_Q),$$

$$W_Q^B = W_Q^A / R_Q,$$

where $R_M = (\gamma_A/\gamma_B)^2$ and $R_Q = [f(I_A)/f(I_B)](Q_A/Q_B)^2$. Hence, if I_A , I_B , γ_A/γ_B , and Q_A/Q_B are known, it is then possible to decompose the observed relaxation rates W_A and W_B into their magnetic and quadrupolar components.

a. Magnetic relaxation processes. The direct magnetic contact hyperfine interaction provides a strong dynamic coupling between the nuclei and conduction electrons having s -like wave functions at the Fermi surface. The relaxation rate for degenerate conduction electrons in Bloch states is given by²⁴

$$W_M = (64/9)\pi^3 \hbar^3 \gamma_e^2 \gamma_n^2 \langle |u_F(0)|^2 \rangle^2 N^2(E_F) \kappa T, \quad (8)$$

where $N(E_F)$ is the density of states for s electrons at the Fermi surface, \hbar is Planck's constant, γ_e is the electronic gyromagnetic ratio, and κ is Boltzmann's constant. The linear temperature dependence in Eq. (8) is a consequence of the degeneracy of the conduction-electron system and reflects the fact that only those electrons whose energies lie within κT of the Fermi surface are available for nuclear relaxation. Equation (8) is expected to remain valid in liquid metals provided that (i) the system remains degenerate ($T \ll T_F$), and (ii) the effects of motion and collisions in the liquid metal are included in $N(E_F)$ and $\langle |u_F(0)|^2 \rangle$. The first condition is easily satisfied in polyvalent liquid metals at $T \approx 10^3$ °K since, in that case, $T/T_F \approx 10^{-2}$. Although detailed treatment of $\langle |u_F(0)|^2 \rangle$ and $N(E_F)$ is very difficult, Eq. (8) should correctly describe the temperature dependence of W_M as long as the Fermi surface remains sharp (of width κT) in energy space. Faber²⁵ has pointed out that although the Fermi surface is blurred in k space as a result of the short mean free path for conduction electrons, the Fermi energy remains well defined. We shall assume, therefore, that

²³ A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), p. 314.

²⁴ J. Korringa, *Physica* **16**, 601 (1950).

²⁵ T. E. Faber, *Advan. Phys.* **15**, 547 (1966).

the direct contact relaxation rate is given correctly by Eq. (8).

The relaxation rate is related to the corresponding Knight-shift contribution (\mathcal{K}_s) of Eq. (1) by the modified Korringa relation²⁶

$$T_1 T \mathcal{K}_s^2 = (\hbar/4\pi\kappa) (\gamma_e/\gamma_n)^2 [K(\alpha, r_0)]^{-1}. \quad (9)$$

The correction factor $K(\alpha, r_0)$ accounts for the effects of electron correlation and exchange on the Knight shift²⁷ and relaxation rate.²⁸ It is a function of the parameter α describing the enhancement of the susceptibility χ_s relative to the value χ_s^0 for independent free electrons, i.e.,

$$\alpha = 1 - \chi_s^0/\chi_s, \quad 0 \leq \alpha \leq 1 \quad (10)$$

and a parameter r_0 which describes the range of the electron-electron interaction.²⁹

It is necessary to consider the interaction of the nuclear spin with both the orbital and dipolar fields of the electron, even though the latter does not contribute to the Knight shift. The reason is that the instantaneous local configuration in the liquid may exhibit noncubic symmetry such that the nucleus experiences time-dependent magnetic fields from both the electron spin and orbital moment. The orbital and dipolar contributions have been discussed by Obata³⁰ for electrons in the tight-binding approximation, and by Mitchell³¹ for electrons in Bloch states. Since conduction electrons in nontransition liquid metals are expected to resemble nearly free electrons in broad energy bands, the Mitchell treatment is the more appropriate for these systems. Mitchell's expression for the relaxation rate due to p electrons, which includes both orbital and dipolar contributions, is

$$W_M = (65/9) (\pi Z^2 m^{*2} B^2 / \hbar) \gamma_e^2 \gamma_n^2 \kappa T, \quad (11)$$

$$B = \int [\langle |v(r)|^2 \rangle / r] dr, \quad (12)$$

where Z is the number of conduction p electrons per atom, $\langle |v(r)|^2 \rangle$ is the radial part of the p -wave component of the Bloch function averaged over the Fermi surface, and m^* is the electron effective mass. Since the conduction-electron states in solid In and Sb and the valence states in solid InSb are composed mainly of s - and p -like components,³² it seems justified to neglect higher angular momentum components in the liquid state. If the relative fraction of p character of the wave functions at the Fermi surface is independent of temperature, then except for small changes in B due to thermal expansion, W_M/T is independent of temperature for this process.

The core-polarization hyperfine interaction also con-

²⁶ A. Narath, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).

²⁷ D. Pines, *Phys. Rev.* **92**, 626 (1954).

²⁸ T. Moriya, *J. Phys. Soc. Japan* **18**, 516 (1963).

²⁹ A. Narath and H. T. Weaver, *Phys. Rev.* **175**, 373 (1968).

³⁰ Y. Obata, *J. Phys. Soc. Japan* **18**, 1020 (1963).

³¹ A. H. Mitchell, *J. Chem. Phys.* **26**, 1714 (1957).

³² M. Gueron, *Phys. Rev.* **135**, A200 (1964).

tributes to the magnetic relaxation rate. The relation between the transition probability and the corresponding contribution to \mathcal{K} has been calculated for p electrons by Yafet and Jaccarino.³³ Their result is

$$W_M = (4\pi/3\hbar) (\gamma_n/\gamma_e)^2 \mathcal{K}_{\text{ep}}^2 \kappa T. \quad (13)$$

Thus, except for changes in \mathcal{K}_{ep} , the quantity W_M/T is temperature-independent for this process also.

b. Quadrupolar relaxation processes. There are at least two possible sources of time-dependent electric field gradients responsible for spin-lattice relaxation in liquid metals: thermal modulation of the charge distribution around a nucleus by vibrational, rotational, and diffusional motion³; and direct nuclear interaction with the conduction-electron charge³¹ in a scattering process analogous to the magnetic relaxation described by Eq. (8). The two quadrupolar mechanisms are distinct in that the first is a high-temperature phenomenon involving large amplitude nuclear motions. The second process utilizes the kinetic energy of conduction electrons at the Fermi surface, and may be present in solids at very low temperatures, when nuclear motion is small.

The contribution of thermal motion to the quadrupolar relaxation rate may be calculated using standard perturbation theory for a quadrupole interaction which is a random function of time. The quadrupole interaction Hamiltonian \mathcal{H}_Q is often written in the form³⁴

$$\mathcal{H}_Q(t) = \sum_{m=-2}^2 Q^m V^{-m}(t), \quad (14)$$

where

$$\begin{aligned} Q^0 &= A(3I_x^2 - I^2), & V^0 &= V_{zz} - \frac{1}{3}\nabla^2 V, \\ Q^{\pm 1} &= A(I_{\pm}I_x + I_zI_{\pm}), & V^{\pm 1} &= V_{xz} \pm iV_{yz}, \\ Q^{\pm 2} &= AI_{\pm}^2, & V^{\pm 2} &= \frac{1}{2}(V_{xx} - V_{yy}) \pm iV_{xy}, \end{aligned} \quad (15)$$

in which $A = eQ/4I(2I-1)$, $I_{\pm} = I_x \pm iI_y$, V is the electric potential at the nucleus due to external charges, and coordinate subscripts on V indicate partial differentiation with respect to the coordinate. In the "extreme narrowing" limit the transition probability is given by²³

$$W_Q = (3/80) (eQ/\hbar)^2 f(I) J(0), \quad (16)$$

where the spectral density $[J(\omega)]$ and correlation functions $[g_m(t)]$ are, respectively,

$$J(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} g_m(t) dt, \quad (17)$$

$$g_m(t) = \langle V^m(t) V^{-m}(0) \rangle. \quad (18)$$

The angle brackets denote an ensemble average for $g_m(t)$. The behavior of $g_m(t)$ is such that there is a cor-

relation time τ for which $g_m(t)$ becomes negligibly small for $t > \tau$. It is easily shown that the short correlation time limit should apply for nuclear relaxation in liquid metals. The extreme narrowing condition for the validity of Eq. (16) is $\omega_0 \tau \ll 1$, where ω_0 is the nuclear Larmor frequency. But the correlation time for thermal motion in a liquid metal is typically $\tau \lesssim 10^{-11}$ sec, so that at a Larmor frequency $\omega_0 \sim 10^8$ we have $\omega_0 \tau \gtrsim 10^{-3}$. In cases where the short correlation time limit does not apply, the relaxation rate depends on ω_0 . It is therefore possible to make an independent experimental check of the applicability of the short correlation time limit by measuring W_Q as a function of ω_0 .

Now let us discuss the contributions to W_Q from diffusion motion. Borsa and Rigamonti³⁵ have evaluated the contribution of diffusing ions to $J(0)$ using screened ionic potentials of the form

$$V(r) = (Ze/r) \exp(-\alpha_s/r) (1 - \gamma_{\infty}), \quad (19)$$

where α_s is the screening constant and γ_{∞} is the Sternheimer antishielding factor.³⁶ The correlation function is assumed to be of the form

$$g_m(t) = \langle |V^m|^2 \rangle e^{-t/\tau}. \quad (20)$$

The ensemble average is obtained by assuming a uniform density of ions in the liquid (ρ) and integrating the ionic electric field gradient between the distance of closest approach (d) and infinity. The resulting expression for the relaxation rate is³⁵

$$\begin{aligned} W_Q &= \frac{\pi e^4 Z^2 (1 - \gamma_{\infty})^2 \rho f(I) Q^2}{90 \hbar^2 D d} \\ &\times \exp(-2\alpha_s d) [9 + (37/4)\alpha_s d + \frac{7}{2}(\alpha_s d)^2 + \frac{1}{2}(\alpha_s d)^3], \end{aligned} \quad (21)$$

where D is the coefficient of self-diffusion. The distance of closest approach should not be strongly temperature-dependent. Hence, if we assume an activation energy model for D , the principal contribution to the temperature dependence of Eq. (21) is given by

$$W_Q \propto \rho/D \propto \rho \exp(Q_D/RT), \quad (22)$$

where Q_D is the activation energy for self-diffusion. It has been pointed out by Nachtrieb³⁷ that D for liquid metals can as well be expressed by $D \propto T^{-1}$. In this case we have

$$W_Q \propto \rho/T. \quad (23)$$

Since ρ usually decreases slowly at higher temperatures, W_Q should decrease slightly faster than T^{-1} as the temperature increases.

The ionic contribution to quadrupolar relaxation has also been calculated by Sholl,³⁸ who included the long-range screening effects of the conduction electrons

³³ Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).

³⁴ M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

³⁵ F. Borsa and A. Rigamonti, Nuovo Cimento **488**, 144 (1967).

³⁶ R. M. Sternheimer, Phys. Rev. **84**, 244 (1951). See also Ref. 34, Appendix C.

³⁷ N. H. Nachtrieb, Advan. Phys. **16**, 309 (1967).

³⁸ C. A. Sholl, Proc. Phys. Soc. (London) **91**, 130 (1967).

by using a potential of the form

$$V(r) = C[\cos(2k_F r)/(2k_F r)^3](1 - \gamma_\infty), \quad (24)$$

where k_F is the Fermi momentum. The product $C(1 - \gamma_\infty)$ was determined from experimental measurements of the static quadrupolar interaction in the corresponding solid metal. The correlation functions $g_m(t)$ were evaluated using the radial distribution functions and three-particle correlation functions, rather than the exponential assumption of Eq. (20). The resulting expression for the relaxation rate is

$$W_Q = [\pi e^2 C^2 (1 - \gamma_\infty)^2 \rho / 75 \hbar^2 D] f(I) Q^2 (I_1 + 2\pi \rho I_2), \quad (25)$$

where I_1 and I_2 are appropriate integrals over the radial distribution function for two- and three-particle correlations, respectively. These integrals may be evaluated numerically if the radial distribution functions are known. The temperature dependence of Eq. (25) is described by

$$W_Q \propto (\rho/D) (I_1 + 2\pi \rho I_2). \quad (26)$$

Sholl has pointed out that since the peaks in the radial distribution functions become smaller and broader at higher temperatures, I_1 and I_2 should decrease with increasing temperatures. Thus, according to this model, W_Q decreases somewhat more rapidly than ρ/D as the temperature increases, i.e., somewhat more rapidly than T^{-1} [see Eq. (23)].

Although only ionic diffusion has been considered here, other types of thermal motion such as diffusion or rotation of molecular clusters will lead to qualitatively similar temperature dependence, as long as the correlation time is sufficiently short.

The appearance of the antishielding factor $(1 - \gamma_\infty)$ in Eq. (21) and Eq. (25) is not strictly correct. The usual ionic antishielding factor $(1 - \gamma_\infty)$ is appropriate only if the sources of the electric field gradient are external to the ion of interest. However, the conduction electrons involved in screening probably have appreciable overlap with the ionic cores. Since $\gamma(r)$ decreases with r , the use of $(1 - \gamma_\infty)$ leads to an overestimate of the relaxation rate. This point has been recognized by Rossini *et al.*,³ who calculated separately the contributions to the field gradient from the neighboring ionic charges and the p -like conduction electrons treated as covalent bonds. These authors used $(1 - \gamma_\infty)$ for the ionic field gradient and assumed no antishielding effects for the conduction-electron contribution in liquid indium.

Now we turn to quadrupole relaxation due to scattering of conduction electrons at the Fermi surface, which has been considered by Obata³⁹ in the tight-binding limit, and by Mitchell³¹ for Bloch electrons. The transition probability for Bloch electrons is

$$W_Q = (1/50) (\pi e^4 Z^2 m^{*2} / \hbar^5) B^2 f(I) Q^2 \kappa T. \quad (27)$$

It can be seen from the form of Eq. (27) that this process may be distinguished from the motional relaxa-

tion process by the temperature dependence. The relaxation rate associated with ionic diffusion decreases at higher temperatures, whereas the quadrupolar rate for scattering of conduction electrons increases linearly with T . If the degree of p character at the Fermi surface is independent of temperature, W_Q/T should be constant for this process.

c. Impurity relaxation. In some previous studies of relaxation in liquid metals, measured T_1 values have been found to depend on sample history and on the choice of medium for dispersal of the small liquid-metal particles. Also, in these cases T_2 was generally shorter than T_1 . Hanabusa and Bloembergen⁴⁰ attribute these effects to the presence of solid impurities and consequent relaxation at the solid-liquid interface. On the other hand, Cornell²⁰ blames the inequality of T_1 and T_2 in liquid gallium on magnetic field inhomogeneity due to the bulk susceptibility of the dispersing medium. We believe such effects are not important in the present experiments for the following reasons: (i) Within experimental error $T_1 = T_2$; (ii) we observe no dependence of T_1 values on sample history, i.e., no change after temperature cycling, annealing, and no change from run to run; (iii) the dispersing medium in these experiments was solid quartz, which was probably in less intimate contact with the liquid metals than the liquid hydrocarbons and Epoxy resins used in the earlier work. Impurity relaxation effects will therefore not be considered further in this paper.

B. Indium

First, we consider the effects of fusion on \mathcal{K} and T_1 in metallic In. This is possible because these quantities have also been measured in the solid. The value of \mathcal{K} in the liquid at the melting point is equal within experimental error to the isotropic Knight shift measured at 4.2°K by Adams, Berry, and Hewitt⁴¹ and at 300°K by Torgeson and Barnes⁴²:

$$\begin{aligned} \mathcal{K}(\text{In}^{115})_{\text{solid}} &= (0.80 \pm 0.02) \% & (4.2^\circ\text{K}) \\ \mathcal{K}(\text{In}^{115})_{\text{solid}} &= (0.82 \pm 0.04) \% & (300^\circ\text{K}) \\ \mathcal{K}(\text{In}^{115})_{\text{liquid}} &= (0.788 \pm 0.005) \% & (440^\circ\text{K}). \end{aligned}$$

The observation⁴¹ that $\mathcal{K}(\text{In}^{115})_{\text{solid}}$ is in close agreement with the value of the direct contact hyperfine contribution ($\mathcal{K}_{\text{iso}} = 0.82\%$) calculated for the solid by Gaspari and Das⁴³ suggests that core polarization and orbital contributions to $\mathcal{K}(\text{In}^{115})$ are small. The constancy of $\mathcal{K}(\text{In}^{115})$ through the melting transition suggests further that these additional contributions are unimportant in liquid In. We shall therefore assume that the dominant contributions to $\mathcal{K}(\text{In}^{115})$ in liquid In is provided by the direct contact hyperfine interaction.

⁴⁰ M. Hanabusa and N. Bloembergen, *J. Phys. Chem. Solids* **27**, 363 (1966).

⁴¹ J. E. Adams, L. Berry, and R. R. Hewitt, *Phys. Rev.* **143**, 164 (1966).

⁴² D. R. Torgeson and R. G. Barnes, *Phys. Rev. Letters* **9**, 255 (1962).

⁴³ G. D. Gaspari and T. P. Das, *Phys. Rev.* **167**, 660 (1968).

³⁹ Y. Obata, *J. Phys. Soc. Japan* **19**, 2348 (1964).

The value of T_1 in solid In has been measured by pure quadrupole resonance at 4.2 and 77°K by McLaughlin and Butterworth.⁴⁴ These results suggest that $(T_1T)^{-1}$ also changes only slightly at the melting transition:

$$(T_1T)_{\text{solid}}^{-1} = 11.6 \pm 0.2 \text{ (sec } ^\circ\text{K)}^{-1}, \quad (4.2^\circ\text{K})$$

$$(T_1T)_{\text{solid}}^{-1} = 12.7 \pm 0.3 \text{ (sec } ^\circ\text{K)}^{-1}, \quad (77^\circ\text{K})$$

$$(T_1T)_{\text{liquid}}^{-1} = 12.3 \pm 0.3 \text{ (sec } ^\circ\text{K)}^{-1} \quad (440^\circ\text{K}).$$

The observation that \mathcal{K} and T_1 in many metals exhibit small changes at the melting point has often been considered paradoxical. The difficulty has arisen from the belief that the density of states $N(E_F)$ in a liquid metal should be close to that of a free-electron gas, whereas $N(E_F)$ in the corresponding solid should differ from the free-electron value as a consequence of Brillouin-zone effects, i.e., long-range order. The model implies that \mathcal{K} should change as a result of the change in $N(E_F)$ at the melting point. Ziman,⁴⁵ however, has recently argued that $N(E_F)$ in the solid may be very close to the free-electron value and has attempted to explain the small changes in \mathcal{K} on that basis.

Alternatively, one can argue⁴⁶ that the electron states on the Fermi surface depend primarily on the local configuration of atoms and are rather insensitive to long-range order effects. Thus, if a metal melts without appreciably changing its short-range order, one expects to see only small changes in \mathcal{K} and T_1 . Solid indium has a distorted fcc structure in the solid state and a quasi-close-packed structure in the liquid (Table I). The local order is therefore similar in both phases, and it is not surprising that \mathcal{K} , T_1 , and other electronic properties (Table I) are only slightly affected by fusion.

Now we turn to the temperature dependence of T_1 and \mathcal{K} in liquid In. It is customary to consider \mathcal{K} as a function $\mathcal{K}(T, V)$ of temperature and volume (V) at constant pressure (P) and interpret its temperature dependence with the expression

$$\left(\frac{\partial \ln \mathcal{K}}{\partial T}\right)_P = \left(\frac{\partial \ln \mathcal{K}}{\partial T}\right)_V + \left(\frac{\partial \ln \mathcal{K}}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_P. \quad (28)$$

The first term on the right describes the intrinsic temperature dependence at constant volume and the second term the effect of thermal expansion. The contributions of intrinsic temperature dependence and thermal expansion can be separated experimentally by measuring \mathcal{K} as a function of pressure and determining $(\partial \ln \mathcal{K} / \partial \ln V)_T$. This has been done for the solid alkali metals and copper by Benedek and Kushida⁴⁷ and for liquid gallium by Cornell.²⁰ The experiments show that the volume dependence $(\partial \ln \mathcal{K} / \partial \ln V)_T$ in these metals is significantly more positive than the value

$$(\partial \ln \mathcal{K} / \partial \ln V)_T = -\frac{1}{3}$$

⁴⁴ D. E. McLaughlin and J. Butterworth, *Phys. Letters* **23**, 291 (1966).

⁴⁵ J. M. Ziman, *Advan. Phys.* **16**, 421 (1967).

⁴⁶ J. M. Ziman, *Proc. Phys. Soc. (London)* **91**, 701 (1967).

⁴⁷ G. B. Benedek and T. Kushida, *J. Phys. Chem. Solids* **5**, 241 (1958).

predicted by free-electron theory for uniform thermal expansion. The temperature-dependent term $(\partial \ln \mathcal{K} / \partial T)_V$ was found to be positive for the solid metals, but negative for liquid gallium.

Since $(\partial \ln \mathcal{K} / \partial \ln V)_T$ has not been measured in liquid In, it is not possible to obtain $(\partial \ln \mathcal{K} / \partial T)_V$ from our data. It appears likely, however, that the sign of $(\partial \ln \mathcal{K} / \partial T)_V$ is negative. This can be seen by treating T as the implicit parameter. Then

$$\left(\frac{\partial \ln \mathcal{K}}{\partial \ln V}\right)_P = \left(\frac{\partial \ln \mathcal{K}}{\partial T}\right)_V \left(\frac{\partial T}{\partial \ln V}\right)_P + \left(\frac{\partial \ln \mathcal{K}}{\partial \ln V}\right)_T. \quad (29)$$

Now by using measured values⁴⁸ of the density as a function of T to evaluate $(\partial T / \partial \ln V)_P$, we find that the observed temperature dependence of $\mathcal{K}(\text{In}^{115})$ corresponds to

$$\left(\frac{\partial \ln \mathcal{K}}{\partial \ln V}\right)_P = \left(\frac{\partial \ln \mathcal{K}}{\partial T}\right)_V \left(\frac{\partial T}{\partial \ln V}\right)_P = -0.8 \pm 0.2.$$

The data suggest $(\partial \ln \mathcal{K} / \partial \ln V)_P < (\partial \ln \mathcal{K} / \partial \ln V)_T$, since the observed value of the former is significantly more negative than $(\partial \ln \mathcal{K} / \partial \ln V)_T$, as determined experimentally in other metals^{20,47} or calculated from free-electron theory. It then follows from Eq. (29) that the intrinsic temperature dependence $(\partial \ln \mathcal{K} / \partial T)_V$ is negative in liquid indium.

The reduction of $\chi_s \Omega$ and $|u_F(0)|^2$ responsible for the observed decrease of the Knight shift at higher temperatures should have a corresponding effect on the contribution of the magnetic contact interaction to the spin-lattice relaxation rate. The relationship is given by Eq. (9), which predicts that the product $T_1 T \mathcal{K}^2$ is a constant. We find that $T_1 T \mathcal{K}^2$ is a constant within experimental error over the entire range 430–1200°K and is equal to

$$T_1 T \mathcal{K}^2 = 5.1 \pm 0.3 \times 10^{-6} \text{ sec } ^\circ\text{K}.$$

It is probably fortuitous that $T_1 T \mathcal{K}^2$ is close to the theoretical value of $5.45 \times 10^{-6} \text{ sec } ^\circ\text{K}$ for independent free electrons. The correction factor $K(\alpha, r_0)$ for electron interactions has been estimated to be about 0.72 in liquid indium.³ This increases the theoretical value of $T_1 T \mathcal{K}^2$ to $7.6 \times 10^{-6} \text{ sec } ^\circ\text{K}$.

A likely explanation of the discrepancy between the observed relaxation rate and that predicted by the modified Korringa relation is the presence of an additional relaxation mechanism. Let us consider this additional relaxation (with rate W_x) on the assumption that $K(\alpha, r_0) = 0.72$.³ It then follows that (i) near the melting point (433°K) $W_x = (1.9 \pm 0.2) \times 10^3 \text{ sec}^{-1}$, and (ii) the temperature dependence is given by $W_x \propto T \mathcal{K}^2$, which is almost directly proportional to T . These properties are now to be compared with possible sources of the relaxation.

It has already been proposed^{3,35,38,49} that the addi-

⁴⁸ R. N. Lyon, *Liquid Metals Handbook* (U.S. Government Printing Office, Washington, D.C., 1952), 2nd ed.

⁴⁹ E. F. W. Seymour and G. A. Styles, *Proc. Phys. Soc. (London)* **87**, 473 (1966).

TABLE I. Melting-point changes of structural, electronic, and NMR parameters for indium, antimony, and indium antimonide.

Type of conductor Structure	Indium		Antimony		Indium antimonide	
	Solid	Liquid	Solid	Liquid	Solid	Liquid
Density (g/cm^3)	metal tetragonally distorted fcc ^a 7.202 °	metal close-packing ^b 7.026 °	semimetal rhombohedral ^a with two atoms per unit cell 6.43 °	metal approx. simple cubic ^c 6.49 °	semiconductor cubic ^a (zinc-blende) 5.75 °	metal approx. NaCl ^d 6.48 °
Electrical conductivity ($\Omega \text{ cm}$) ⁻¹	6.58 × 10 ⁴ °	3.02 × 10 ⁴ °	1.11 × 10 ⁸ °	5.46 × 10 ⁸ °	2.0 × 10 ⁸ °	9.4 × 10 ⁸ °
Hall coefficient (emu)	-2.6 × 10 ⁻⁴ °	-5.5 × 10 ⁻⁴ °	+98 × 10 ⁻⁴ °	-4.5 × 10 ⁻⁴ °	-37 ⁱ	-5.0 × 10 ⁻⁴ °
Magnetic susceptibility (emu/g)	-0.060 × 10 ⁻⁶ k	-0.066 × 10 ⁻⁶ k	-0.40 × 10 ⁻⁶ k	-0.008 × 10 ⁻⁶ k	-0.30 × 10 ⁻⁶ k	0.06 × 10 ⁻⁶ k
Static quadrupole interaction e^2qQ/h (MHz)	45.24 ± 0.02 ^l	0	Sb ¹²¹ : 76.867 ± 0.001 ^m Sb ¹²³ : 97.999 ± 0.001	0	0	0
$\mathcal{K}(\text{In})$ (%)	0.80 ± 0.02 ⁿ (4.2°K)	0.788 ± 0.005 °	0.07 (theory) ^q	0.709 ± 0.010 °	-0.030 ± 0.005 °	0.932 ± 0.004 °
$\mathcal{K}(\text{Sb})$ (%)	-0.025 ± 0.007 °	0.643 ± 0.006 °
$(T_1 T)_{115}^{-1}$ (sec °K) ⁻¹	12.7 ± 0.3 ° (77°K)	12.3 ± 0.3 °	...	10.9 ± 0.5 °	0.203 ± 0.006 °	16.5 ± 0.3 °
$(T_1 T)_{121}^{-1}$ (sec °K) ⁻¹	4.7 ± 0.3 °	0.349 ± 0.025 °	29.8 ± 1.0 °
$(T_1 T)_{123}^{-1}$ (sec °K) ⁻¹	0.224 ± 0.019 °	18.8 ± 0.6 °

^a R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), 2nd ed.,

Vol. 1, pp. 18, 32, and 110.

^b Reference 60.

^c Reference 61.

^d Reference 63.

^e Reference 48.

^f N. P. Mokroski and A. R. Regel, *Zh. Tekhn. Fiz.* 22, 1281 (1952), quoted in G. Busch and S.

Yuan, *Physik Kondensierten Materie* 1, 37 (1963).

^g N. E. Cusack, *Rept. Progr. Phys.* 26, 361 (1963).

^h D. R. Hamilton and R. G. Seidensticker, *J. Appl. Phys.* 34, 2697 (1963).

ⁱ G. Busch, A. Menih, and B. Natterer, *Z. Naturforsch.* 19a, 542 (1964).

^j G. Busch, H.-J. Gündherodt, and Y. Tische, *Phys. Verh.* 16, 33 (1965).

^k G. Busch and S. Yuan, *Physik Kondensierten Materie* 1, 37 (1963).

^l R. R. Hewitt and W. D. Knight, *Phys. Rev. Letters* 3, 18 (1959).

^m R. R. Hewitt and B. V. Williams, *Phys. Rev.* 129, 1188 (1963).

ⁿ Reference 41.

^o This work.

^p W. G. Clark and W. Warren, Jr. (to be published).

^q Reference 51.

^r Reference 44.

tional relaxation is via quadrupolar coupling due to diffusion motion of the particles in the liquid. The value of W_x near the melting point is predicted to be $1.9 \times 10^3 \text{ sec}^{-1}$ by Rossini *et al.*³ and Sholl,³⁸ and $0.2 \times 10^3 \text{ sec}^{-1}$ by Borsa and Rigamonti.³⁵ Hence, the magnitude of W_x at the melting point is given quite well by the former and to within an order of magnitude for the latter. On the other hand, both calculations predict W_x varies approximately as T^{-1} , whereas the indication is that it varies approximately as $W \propto T$. We believe the failure of the diffusion model to give the indicated temperature dependence casts serious doubt on its importance.

The nearly linear temperature dependence of W_x suggests that the additional process involves scattering of conduction electrons on the Fermi surface. Two possible processes are noncontact (orbital and dipolar) magnetic hyperfine processes [Eq. (11)] and the quadrupolar interaction with the electronic charge [Eq. (27)]. Two difficulties emerge to hamper this interpretation.⁵⁰ First, experimental results are available on but one isotope, In¹¹⁵. It is therefore not possible to decompose the observed rates into magnetic and quadrupolar contributions and determine experimentally the relative importance of the processes. The second point is that estimates³¹ of W_x based on Eqs. (11) and (27) are at least one order of magnitude smaller than W_x . One is thus faced with a choice between a mechanism which gives the correct order of magnitude of W_x but the wrong temperature dependence (ionic diffusion) and others which give the right temperature dependence but rates which are much too small. Since it has often happened that the temperature dependence of a relaxation process was predicted more reliably than its rate, especially when quadrupolar coupling was involved, we are inclined to prefer the mechanisms involving electron scattering at the Fermi surface and expect that a way will be found to increase the relaxation rates attributed to them by theory.

C. Antimony

The transition of antimony from semimetal to metal at the melting point is characterized by an increase in electrical conductivity, magnetic susceptibility, and Hall coefficient (Table I). It is reasonable to expect that the changes of band structure associated with fusion will lead to a large change in the magnitude (and perhaps a change in sign) of \mathcal{K} and a change in T_1 . Unfortunately, measurements of \mathcal{K} and T_1 have not yet been reported for solid antimony, so a direct comparison of the solid and liquid states is not possible.

⁵⁰ A further difficulty arises from the possibility that many-body effects described by the correction factor $K(\alpha, \nu_0)$ in Eq. (9) may be temperature-dependent (see Ref. 56) and lead to an incorrect determination of the magnitude and temperature dependence of W_x . We believe that this is probably not the case as $T_1 T \mathcal{K}^2$ is constant over a change of a factor of 3 in temperature. It is also possible, though unlikely, that magnetic and quadrupolar processes could combine in such a way that $T_1 T \mathcal{K}^2$ is fortuitously constant.

However, the isotropic Knight shift in the solid has been calculated by Hygh and Das,⁵¹ who obtained $\mathcal{K}_{\text{iso}} = 0.07\%$. This value is an order of magnitude smaller than the experimental value in the liquid and indicates that \mathcal{K} probably increases appreciably on passing through the semimetal to metal transition at the melting point.

Next we consider the relative importance of the various potential contributions to \mathcal{K} in liquid Sb. Although the contribution of direct contact and dipolar interactions have been calculated for solid Sb,⁵¹ the large changes in electronic properties at the melting point suggest that these calculations are not valid for the liquid. Since calculations of \mathcal{K} in liquid Sb have not yet appeared, it is not possible to make precise quantitative statements concerning the magnitudes of the various contributions. On the other hand, we can utilize the information which is available for solid Sb and other metals in order to estimate the approximate importance of the various mechanisms. For example, the fact that the atomic valence states of Sb include three occupied p states ($5s^2 5p^3$ configuration) indicates that the conduction-electron states in the metal contain an appreciable amount of p character. This, combined with the fact that Sb is a relatively heavy metal, suggests that orbital interactions may make an appreciable contribution to \mathcal{K} . Hygh and Das⁵¹ speculate that \mathcal{K}_0 in solid Sb is comparable to \mathcal{K}_s and it is plausible that the *relative* magnitudes of \mathcal{K}_0 and \mathcal{K}_s are similar in both phases. The core-polarization contribution \mathcal{K}_{cp} has been calculated for several light nontransition metals including all the alkali metals.⁵²⁻⁵⁴ In these metals $|\mathcal{K}_{\text{cp}}|$ lies in the range 10-20% of \mathcal{K}_s , and \mathcal{K}_{cp} may be either positive or negative. In the absence of specific information for Sb we shall assume that \mathcal{K}_{cp} lies in this range, making a moderate but not a dominant contribution to $\mathcal{K}(\text{Sb}^{121,123})$.

Within experimental error, $\mathcal{K}(\text{Sb}^{121,123})$ is independent of temperature over the range 903-1200°K. Because of the relatively small temperature range available, we are unable to draw any conclusions about the intrinsic temperature and volume dependence of $\mathcal{K}(\text{Sb}^{121,123})$.

We turn now to interpretation of the spin-lattice relaxation times in liquid Sb. Since measurements have been made for both isotopes in this case, we can obtain additional information about the relaxation processes by decomposing the observed rates into magnetic and quadrupolar rates. The results of this decomposition are shown in Fig. 7.⁵⁵ There it is seen that magnetic and

⁵¹ E. H. Hygh and T. P. Das, Phys. Rev. **143**, 452 (1966).

⁵² G. D. Gaspari, Wei-Mei Shyu, and T. P. Das, Phys. Rev. **134**, A852 (1964); **141**, 603 (1965); **152**, 270 (1966).

⁵³ P. Jena, S. D. Mahanti, and T. P. Das, Phys. Rev. Letters **20**, 544 (1968).

⁵⁴ L. Tterlikkis, S. D. Mahanti, and T. P. Das, Phys. Rev. (to be published).

⁵⁵ The values used here, $R_M(121/123) = 3.40$ and $R_Q(121/123) = 1.47$, were derived from values of γ , I , and the Q ratio given in *Nuclear Data Sheets*, compiled by K. Way *et al.* (U.S. Government Printing Office, National Academy of Sciences—National Research Council, Washington, D.C. 20025, 1962), Appendix 1.

quadrupolar interactions make comparable contributions to the total relaxation rate. Furthermore, there is the somewhat surprising result that W/T is not constant for any of the separate rates and that the near constancy of $(T_1T)^{-1}$ results from a fortuitous cancellation of the temperature dependence of W_M and W_Q .

There are four potential contributions to the magnetic relaxation rate W_M . These are the direct contact, the core-polarization, the dipolar, and the orbital contributions. As in the case of the Knight shift, there are no direct calculations of the relative magnitudes of these contributions for liquid Sb. However, except for the dipolar, each of the magnetic relaxation mechanisms has a corresponding contribution to \mathcal{K} and we can make use of our estimates of \mathcal{K}_s , \mathcal{K}_{cp} , and \mathcal{K}_0 to estimate the importance of the relaxation processes.

In the case of the orbital interaction, we expect an orbital contribution to relaxation if \mathcal{K}_0 and \mathcal{K}_s are comparable. However, for $\mathcal{K}_s \simeq \mathcal{K}_0$, the direct contact relaxation rate should be larger than the orbital rate. This is a consequence of the fact that all the conduction electrons in the band contribute to \mathcal{K}_0 while only those at the Fermi surface can contribute to relaxation. This reduces W_M^0/\mathcal{K}_0^2 for orbital interactions relative to W_M^s/\mathcal{K}_s^2 for the direct contact interaction.

The dipolar rate W_M^D is expected to be even smaller than the orbital rate W_M^0 ($W_M^D \sim \frac{1}{3}W_M^0$ for tight-binding electrons⁵⁰) and is probably unimportant. Similarly, if $|\mathcal{K}_{cp}| \simeq 10\text{--}20\%$ of \mathcal{K}_s , then according to Eq. (13), the core-polarization contribution to W_M is less than 1–2% of the direct contact contribution, and can therefore be neglected.

The contribution of the direct contact interaction to the magnetic relaxation rate should be related to the corresponding Knight-shift contribution by Eq. (9). Using the observed values of \mathcal{K} and W_M (total magnetic relaxation rate), we obtain a value of the correction factor at the melting point:

$$K(\alpha, r_0) = 0.64 \pm 0.13 \quad (903^\circ\text{K}).$$

As the temperature is raised above the melting point, W_M/T increases relative to $\mathcal{K}(\text{Sb}^{121,123})$, leading to an increase in $K(\alpha, r_0)$:

$$K(\alpha, r_0) = 0.81 \pm 0.13 \quad (1200^\circ\text{K}).$$

This increase in $K(\alpha, r_0)$ could result from a temperature-dependent electron-electron correction due to mean-free-path effects,⁵⁶ a change in the orbital contribution of \mathcal{K} and W_M at the higher temperatures, or both. At the present time, it is not clear how one can unravel the various effects without reliable theoretical calculations of at least some of the contributions to \mathcal{K} and W_M .

Quadrupolar spin-lattice relaxation in metals has been previously detected directly by comparing re-

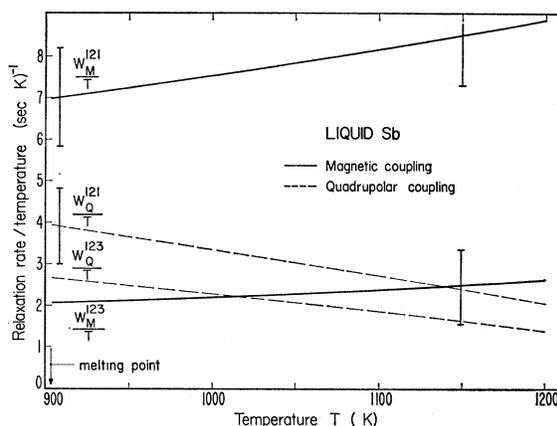


FIG. 7. The experimental relaxation rate/temperature as a function of temperature for magnetic and quadrupolar relaxation of Sb^{121} and Sb^{123} in liquid antimony. The rates were calculated from Eq. (7) using experimental T_1 values represented by the "best-fit" solid lines in Fig. 4.

laxation rates of two isotopes in liquid mercury,²⁰ liquid gallium,²⁰ and solid molybdenum.²¹ It has also been inferred indirectly through the use of Eq. (9) for liquid In,^{3,4} liquid Bi,⁴⁹ and liquid bismuth alloys.⁴⁹ As was discussed in the previous section, the most important quadrupole relaxation process in liquid metals has been assumed in previous work to be the one involving modulation of the electronic charge distributions and ionic charges by thermal motion. Theoretical calculations of the magnitude of the motional relaxation rate W_Q in liquid Sb have been made by Rossini⁴ using the theory of Sholl³⁸ [Eq. (25)]. The theoretical values for the relaxation rates agree with the observed values of W_Q^{121} and W_Q^{123} . However, we have pointed out that the temperature dependence of W_Q may be a more sensitive test of the validity of the model than the magnitude of the relaxation rate, and it is therefore important to compare the observed temperature dependence of W_Q with the prediction of Eq. (26). This could be accomplished easily if the self-diffusion coefficient were known at various temperatures since, in that case, one could calculate the expected temperature dependence using $W_Q \propto \rho D^{-1}$ and compare it directly with experiment. Unfortunately, self-diffusion measurements have not yet been reported for liquid antimony. However, the activation energy has been calculated from experimental values of the viscosity by Saxton and Sherby,⁵⁷ who obtained $Q_D = 5400$ cal/mole. On the other hand, if it is assumed that the experimental values of W_Q obey the temperature dependence described by Eq. (22), it is found that $Q_D = 2700\text{--}2700\text{--}3300$ cal/mole, suggesting a weaker temperature dependence than predicted by Eq. (22). A similar difference occurs in the case of liquid gallium,²⁰ for which W_Q does not decrease as rapidly with increasing temperature as implied by the measured value

⁵⁶ W. W. Warren, Jr., W. G. Clark, and P. Pincus, *Solid State Commun.* **6**, 371 (1968).

⁵⁷ H. S. Saxton and O. D. Sherby, *Am. Soc. Metals, Trans. Quart.* **55**, 826 (1966).

of Q_D .⁵⁸ An additional example of this type of discrepancy occurs for the quadrupolar relaxation in liquid xenon.⁵⁹ In that case, the value of Q_D extracted from T_1 measurements is about half that obtained from self-diffusion measurements.

It has been proposed^{3,20} that the quadrupole coupling increases at higher temperatures in liquid metals. This leads to a weaker temperature dependence than described by Eq. (22). Some evidence to support this is found in x-ray diffraction studies of liquid indium, which show that the nearest-neighbor distance tends to decrease at higher temperatures due to the formation of void spaces.⁶⁰ In liquid antimony, x-ray measurements indicate an approximately simple cubic structure near the melting point.⁶¹ This implies nonrandom local order, which can be expected to become more disordered at higher temperatures with a larger coordination number and possibly smaller nearest-neighbor distance. This point should be clarified when neutron or x-ray diffraction data are available for a wide range of temperatures in liquid antimony.

As an alternative explanation of the origin of W_Q , there remains the possibility that scattering of conduction electrons at the Fermi surface provides an important contribution to the quadrupolar relaxation. This requires that the transition probability be enhanced over the value estimated from Eq. (26). Although W_Q/T should be constant for this process, it would decrease at higher temperatures if there is a reduction in the amount of p character at the Fermi surface. Such a decrease in p character implies a corresponding increase in s character and an increase in the magnetic relaxation rate. The fact that this is observed in liquid antimony lends support to speculation that Fermi surface p -like electrons make an important contribution to the quadrupole relaxation rate.

D. Indium Antimonide

Since the direct contact contribution to \mathcal{K} depends on the electronic susceptibility and the density of s -like conduction electrons at the nucleus, it is of interest to compare the shifts observed in liquid indium antimonide with the values obtained in the pure liquid metals indium and antimony. The Knight shift of In^{115} in InSb [$\mathcal{K}(\text{In}^{115}\text{Sb})$] is 18% larger than $\mathcal{K}(\text{In}^{115})$ in liquid In , whereas the shift $\mathcal{K}(\text{InSb}^{121})$ in InSb is 9% smaller than $\mathcal{K}(\text{Sb}^{121,123})$ in liquid Sb . The qualitative features of these changes are reasonable since the average number of electrons per atom in indium antimonide is intermediate between the valence of indium ($Z=3$) and that of antimony ($Z=5$). However, it is difficult to explain the changes quantitatively, since it

⁵⁸ N. H. Nachtrieb and J. Petit, *J. Chem. Phys.* **24**, 746 (1956); J. Petit and N. H. Nachtrieb, *ibid.* **24**, 1027 (1956).

⁵⁹ W. W. Warren, Jr., and R. E. Norberg, *Phys. Rev.* **148**, 402 (1966).

⁶⁰ H. Ocken and C. N. J. Wagner, *Phys. Rev.* **149**, 122 (1966).

⁶¹ H. K. F. Möller and H. Hendus, *Z. Naturforsch.* **12a**, 102 (1957); Ya. I. Dutchak, *Fiz. Metalov i Metallovedenie* **9**, 314 (1960) [English transl.: *Physics of Metals and Metallography* **9**, 139 (1960)].

is necessary to take into account changes in electron-electron effects and in the electronic s and p character of the wave functions at the Fermi surface. Such effects appear to be important in liquid Sb and it is reasonable that they should also be present in liquid InSb . Moreover, by the same arguments given for liquid Sb , it is probable that there are appreciable orbital contributions to $\mathcal{K}(\text{InSb}^{121,123})$ and possibly to $\mathcal{K}(\text{In}^{115}\text{Sb})$. It therefore becomes important to consider the additional information available from the T_1 data.

First we consider the simpler case, In^{115}Sb . The temperature dependences of T_1 and $\mathcal{K}(\text{In}^{115}\text{Sb})$ for liquid In^{115} are qualitatively similar to those of the corresponding quantities in liquid In^{115} . The values of $(T_1T)^{-1}$ and $\mathcal{K}(\text{In}^{115}\text{Sb})$ decrease slowly with increasing temperature in such a way that the product $T_1T\mathcal{K}^2$ is nearly constant from the supercooled state to 1400°K:

$$T_1T\mathcal{K}^2 = (5.17 \pm 0.25) \times 10^{-6} \text{ sec } ^\circ\text{K}, \quad (800^\circ\text{K})$$

$$T_1T\mathcal{K}^2 = (5.57 \pm 0.30) \times 10^{-6} \text{ sec } ^\circ\text{K}, \quad (1400^\circ\text{K}).$$

These values can be compared to the one calculated from independent free-electron theory using $K(\alpha, r_0) = 1$ in Eq. (9):

$$T_1T\mathcal{K}^2 = 5.45 \times 10^{-6} \text{ sec } ^\circ\text{K}.$$

As was pointed out for the case of liquid In , the close agreement of the observed values of $T_1T\mathcal{K}^2$ with the theoretical value for independent electrons may be fortuitous and it is necessary to consider the effects of electron-electron interactions and additional relaxation mechanisms.

Since the electron-electron correction factor has not been calculated for In^{115}Sb , we use the value $\mathcal{K}(\alpha, r_0) = 0.72$ for liquid indium³ in Eq. (9) to estimate the strength of any additional relaxation mechanism. It is found that there is an additional relaxation process whose rate near the melting points is

$$W_x = (4.1 \pm 0.3) \times 10^3 \text{ sec}^{-1}.$$

Since data are available for only one isotope, it is impossible to determine directly whether W_x is of magnetic or quadrupolar origin.

The temperature dependence of W_x for liquid In^{115}Sb is in better agreement with the linear temperature dependence predicted for relaxation (quadrupolar or magnetic) via scattering of Fermi surface electrons than with the T^{-1} dependence predicted for the quadrupolar ionic diffusion mechanism. Thus, although a precise statement cannot be formulated, our results are consistent with a picture in which the direct contact interaction with s -like conduction electrons makes the principal contribution to \mathcal{K} and T_1 . Also, there is indirect evidence for the presence of a smaller quadrupolar relaxation process involving scattering of electrons on the Fermi surface. If W_x is of magnetic origin, the experimental value of \mathcal{K} would require large, cancelling contributions from \mathcal{K}_0 and \mathcal{K}_{cp} ; therefore, it is likely that W_x is primarily of quadrupolar origin.

Now let us consider the data for the Sb isotopes. One of the most surprising results of these experiments is the observation of extremely rapid relaxation rates for Sb^{121} and Sb^{123} near the melting point in liquid InSb, and the very different character of the temperature dependence of the relaxation rates of the antimony isotopes relative to the In^{115}Sb rate. By using Eqs. (7), it is possible to decompose the observed rates into separate rates for magnetic and quadrupolar processes, as shown in Fig. 8. In the vicinity of the melting point, there exist very strong quadrupolar relaxation processes and relatively small magnetic rates. The effect is even more pronounced in the supercooled state, and at about 40°K below the melting point the relaxation is, within experimental error, due entirely to quadrupolar processes. The temperature dependences of the relaxation rates indicate two distinct regions of interest. Below about 1000°K , the quadrupolar relaxation rates fall sharply with increasing temperature, while the magnetic rates increase rapidly. Above 1000°K , W/T for both magnetic and quadrupolar processes decreases slowly with increasing temperature. The antimony relaxation rates in the upper temperature region exhibit nearly the same temperature dependence as the In^{115} rate. The relative strengths of magnetic and quadrupolar relaxation processes are essentially independent of temperature above 1000°K .

It is helpful at this point to indicate what we believe to be the key to the complicated behavior of the Sb relaxation rates, namely, that the s and p character of the electronic wave functions are temperature-dependent. This proposal will be assumed in the discussion which follows. Additional comments on it are given at the end of this section.

The observed values of W_M^{121}/T and W_M^{123}/T correspond to a value for the correction factor of Eq. (9) which lies in the range $0.25 \leq K(\alpha, r_0) \leq 0.60$ at 775°K in the supercooled liquid. On the other hand, above 1000°K , $K(\alpha, r_0) = 1.06 \pm 0.25$, which agrees with the value for independent free electrons. The apparent increase in $K(\alpha, r_0)$ could result from either (i) temperature-dependent electron-electron effects,⁵⁶ or (ii) an orbital contribution which decreases at higher temperatures due to changes in electronic structure. We have already presented arguments for the presence of an orbital contribution in liquid Sb and it is reasonable that a similar situation should obtain for liquid $\text{InSb}^{121,123}$. The temperature dependence of the data suggests that the degree of p character in the vicinity of the Sb nuclei decreases with increasing temperature in the range 760 – 1000°K and that these changes are complete above 1000°K .

Now consider the origin of W_Q for the Sb isotopes. The first point to be made is that conduction electrons play a crucial role in the quadrupolar coupling. If this were not so, i.e., if the origin of fluctuating electric field gradients was simply the motion of In and Sb ions, W_Q for In should have the same temperature dependence and magnitude as for Sb. Although a direct experi-

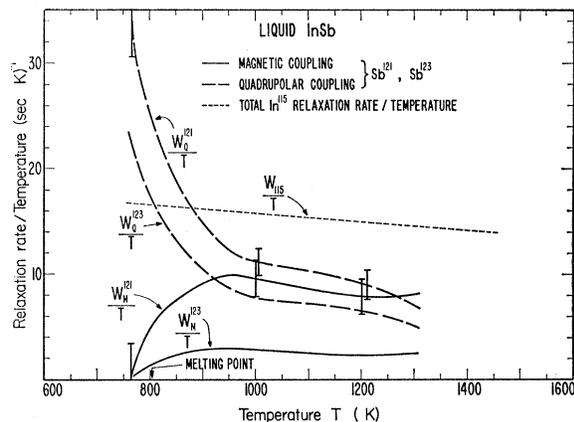


Fig. 8. The experimental relaxation rate/temperature as a function of temperature for magnetic and quadrupolar relaxation of Sb^{121} and Sb^{123} in liquid indium antimonide. The rates were calculated from Eq. (7) using experimental T_1 values represented by the "best-fit" solid lines in Fig. 6. The total relaxation rate/temperature for In^{115} in liquid indium antimonide is also shown.

mental measurement of W_Q for In^{115}Sb is not possible, the fact that $T_1 T \mathcal{K}^2$ is almost constant for this isotope suggests there is no important quadrupolar process with a temperature dependence similar to that of the Sb isotopes. Since the quadrupole moments and anti-shielding factors⁶² of In and Sb ions are nearly equal, the contribution of diffusing ions should have comparable magnitudes for both species. These characteristics not observed; hence the evidence indicates that W_Q is strongly affected by conduction electrons, and that the differences between the In and Sb behavior are a result of importance differences in the spatial distribution of the p -like conduction electrons in the vicinity of the two constituent ions.

Once it is granted that the p -like conduction electrons do make an important contribution to quadrupole relaxation in indium antimonide, the question arises whether this contribution is provided by scattering of p -like electrons at the Fermi surface or by modulation of the p -electron density by thermal motion (or possibly both). The rapid decrease of W_Q/T between the supercooled state and 1000°K is not consistent with the temperature dependence of the rates for motional relaxation given by Eqs. (22) and (26) for reasonable values of D . Furthermore, the increasing magnetic relaxation rate relative to $\mathcal{K}(\text{InSb}^{121,123})$ between 760 and 1000°K indicates an increase in s character for the wave functions in the vicinity of the antimony nuclei and a corresponding reduction of p character over the same temperature region. Also, the similarity of the temperature dependences of W_M and W_Q above 1000°K strongly suggests that both the magnetic and quadrupolar processes involve scattering of conduction electrons at the Fermi surface.

The foregoing considerations of the Knight shifts and relaxation rates lead us to propose a simple phenomenological model of liquid indium antimonide. The

⁶² F. Bridges and W. G. Clark, Phys. Rev. **164**, 288 (1967).

very existence of InSb as a liquid compound implies the presence of some kind of molecular structure. This is confirmed by x-ray measurements near the melting point, which show that liquid indium antimonide exhibits a NaCl-like structure.⁶³ The liquid therefore resembles a short-range ordered binary solid alloy in which it is highly probable that an atom has six neighbors of the other species. The present NMR experiments indicate that the electronic states in this structure are predominantly *s*-like, while the electrons around an antimony nucleus are mainly *p*-like. This property of the conduction-electron wave functions is plausible for two reasons. First, the 5*p* valence shell of atomic Sb contains 3 *p* electrons, while that of indium contains only 1. Thus, from the point of view of tight binding, one would expect a greater *p* character for the conduction electrons in the vicinity of the antimony ion in the compound. Second, the larger valence of Sb leads to a stronger potential at the Sb site and thus to a higher density of conduction electrons in the vicinity of the Sb ions. This phenomenon, known in the literature as "charging,"⁶⁴ should increase the relative amount of *p* character at the Sb site since the *p* electrons are most easily attracted away from the neighboring In ions.

It is reasonable to expect the degree of order in the NaCl structure to decrease at higher temperatures with an increase in the number of nearest neighbors and a loss of atomic order. The local environment of the Sb ion would thus become more spherical, causing a decrease in the *p* character of the wave functions near the Sb ions. This would explain the decreasing quadrupolar rate and rapidly increasing magnetic rate observed for InSb¹²¹ and InSb¹²³ between the melting point and 1000°K. The change in the temperature dependences of the relaxation rates and the constancy of the relative strengths of the magnetic and quadrupolar rates above 1000°K suggest that the important changes in electronic structure are complete above this temperature. This would occur if the liquid is essentially a close-packed, disordered liquid alloy above 1000°K.

As a consequence of the model, we observe that the degree of local order ought to increase as the temperature is lowered into the supercooled state. The sharp increase observed in the InSb¹²¹ and InSb¹²³ quadrupolar relaxation rates as the temperature is lowered below the melting point and the corresponding drop in the magnetic relaxation rate suggest that this is true.

V. CONCLUSIONS

Measurements of the Knight shift and nuclear spin-lattice relaxation rate of In¹¹⁵, Sb¹²¹, and Sb¹²³ in liquid In, Sb, and InSb are reported over temperatures ranging from near the respective melting points up to 1200–1450°K.

⁶³ H. Krebs, M. Hauke, and M. Weyand, in *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds* (Chemical Publishing Co., New York, 1960).

⁶⁴ E. A. Stern, *Phys. Rev.* **144**, 545 (1966).

In liquid In, it is found that $T_1 T \mathcal{K}^2$ is constant over the entire temperature range. In addition to the contact hyperfine contribution to the relaxation rate, there is some indirect evidence of a contribution (quadrupolar or magnetic) to the relaxation rate which varies approximately as $W \propto T$. Although there is no clear-cut choice between a quadrupolar coupling based on diffusive motion of ions^{3,4,35,38} or scattering of conduction electrons at the Fermi surface,^{31,39} our interpretation favors the latter.

In liquid Sb, the observed relaxation rate is separated into its magnetic and quadrupolar components. The values of W_M and \mathcal{K} indicate W_M is caused primarily by the contact hyperfine interaction, although there may also be an appreciable orbital contribution to \mathcal{K} . The temperature dependences of W_M and \mathcal{K} indicate that $K(\alpha, r_0)$ is temperature-dependent, perhaps via a change in the many-body enhancement of the electronic susceptibility³⁶ or a reduction of the orbital contribution due to changes in electronic structure. As with liquid In, there is no clear choice between ionic diffusion and conduction-electron scattering as mechanisms to explain W_Q .

In liquid InSb, the temperature dependence of the spin-lattice relaxation rates is quite complicated, with especially important quadrupolar contributions for the Sb isotopes. The unusual temperature dependences of W_M and W_Q are attributed to important changes in the *s* and *p* character of the electronic wave functions as the temperature is varied.

Although it has been possible to present plausibility arguments in favor of and in opposition to various models for the coupling mechanisms responsible for the observed quadrupolar relaxation, in none of the cases has it been possible to make an unequivocal identification of the correct mechanism. There is, therefore, a serious need for further theoretical investigation of this problem in liquid metals. The interpretation of our results would also be helped by the availability of other experimental and theoretical results which would help to elucidate the structure and motions of these liquid metals.

Note added in proof. In a recent work (to be published as part of the proceedings of the Fifteenth Colloque Ampère) Bonera, Borsa, and Rigamonti report values of $1/T_1$ for liquid In between 425 and 560°K and increase the calculated quadrupolar contribution above the value $W_Q = 0.2 \times 10^3 (\text{sec } ^\circ\text{K})^{-1}$ reported in Ref. 35. The more recent value is $W_Q \approx 1.4 \times 10^3 (\text{sec } ^\circ\text{K})^{-1}$ at the melting point.

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