Spin-Lattice Relaxation Time of Conduction Electrons in Sodium Metal*

FREDERICK VESCIAL, † N. S. VANDERVEN, AND R. T. SCHUMACHER‡

Department of Physics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

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We have measured the temperature dependence of the spin-lattice relaxation time T_1 in sodium metal from 14 to 77°K. Our results agree with those of Feher and Kip, and Levy, in the range 20 to 40°K, but disagree with Feher and Kip above 40°K. As a consequence, we find marked deviation from the relation T_1T = constant even at the highest temperatures of our measurements. The temperature dependence we observe lends strong support to the recent calculation of Yafet in the temperature range 35 to 77° K.

I. INTRODUCTION

HE question of the temperature dependence of the conduction-electron relaxation time in metals has recently been re-examined by Yafet.¹ He finds that in the very low-temperature limit, $T \ll \theta_D$, where θ_D is an appropriate Debye temperature for the lattice, the spin-lattice relaxation time T_1 should vary as T^{-5} , contrary to the previous expectations that $T_1T = \text{constant}$ over the entire high- and low-temperature range. The only metal in which a temperature-dependent T_1 has been observed over an appreciable range of temperatures is sodium. In that metal Feher and Kip² measured T_1 from 300 to 4°K and concluded that their data supported the relation $T_1T \cong 3.0 \times 10^{-6}$ sec-°K over the entire range of their measurements. In fact, their published data do not support this conclusion below 55°K, nor do the data of Levy.³ All these investigators show longer T_1 's in the range 20 to 40°K than predicted by $T_1T \cong 3.0 \times 10^{-6}$ sec-°K. Narrower lines than expected at 20°K were also observed in this laboratory during a recent remeasurement of the sodium conduction-electron susceptibility.4

We report here a remeasurement of $T_1(T)$ which supports the conclusion of Yafet¹ that $T_1(T)$ deviates from the 1/T dependence as T becomes less than an appropriate Debye temperature for the sodium lattice. We describe those aspects of the apparatus relevant to this particular measurement, some precautions taken in sample preparation and experimental measuring technique, and we compare our results to the conclusions of Yafet.

II. EXPERIMENTAL DETAILS

A. Microwave Apparatus

The measurements were made entirely at X band with a single klystron superheterodyne spectrometer

described previously.⁵ The microwave cavity was cylindrical, and was operated in the TE_{011} mode, which requires that the sample be inserted into the geometric center of the cavity. In this configuration the microwave field H_1 is vertical in the laboratory and the dc field, H_0 , is in the horizontal plane. The cavity was matched by a variable coupler of the type described by Gordon.⁶

The samples, which will be described in detail below, were contained in the innermost of a series of concentric Pyrex tubes. The sample tube was 3 mm o.d., a few centimeters long and was completely sealed. The next tube, 5 mm o.d., was approximately one meter long. It was inserted into a tube 8 mm o.d., which is permanently attached to the microwave system. The 8 mm o.d. tube extends halfway into the cavity, is coaxial with it and sealed at the lower end, and in the other direction extends to the top of the Dewar system, where it forms part of an "air-lock" system similar to one described by Estle⁷ Samples were changed while cryogenic liquid was still in the Dewar system by removing the 5 mm o.d. tube.

B. Cryogenic Apparatus and **Temperature Measurements**

The relative bulkiness of the cylindrical cavity necessitated the use of a Dewar system whose outer diameter (that of the nitrogen Dewar) is 5 in. The inner diameter of the inner Dewar is greater than $2\frac{1}{2}$ in. The cryogenic liquid used in our measurements was in all cases liquid hydrogen. However, the hydrogen is entirely excluded from the interior of the microwave cavity and the inside of the waveguide. The outermost pyrex tube is also not in direct contact with the hydrogen, but is separated from it by a cupronickel alloy sleeve which fits snugly around the Pyrex and is soldered to the top of the cavity. The sample is thus removed from direct contact with the bath by a metal sleeve and three Pyrex tubes, all of which nest together rather snugly. All the tubes except the sample tube were filled with a fraction of an atmosphere of He gas to improve the thermal contact between the sample and the bath.

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<sup>n.D. degree.
† Present address: Autonetics, Inc., Anaheim, California.
‡ Alfred P. Sloan Foundation Fellow, 1959–1963.
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Temperature measurements were made with a nominally 390- Ω carbon resistance thermometer. This thermometer was calibrated from 4.2 to 77°K by a platinum resistance thermometer which had been calibrated by the National Bureau of Standards. The carbon thermometer became rather insensitive above 50°K, but was still adequate for our measurements. The thermometer could not be placed in direct contact with the sample, which was in any event sealed in the 3-mm-o.d. tube. The top of the sample tube projected just above the top of the cavity, and the carbon thermometer was pressed into direct physical contact with the tube at that point. We relied on the physical contact plus the helium exchange gas to keep the thermometer at the same temperature as the sample. In the region from 14 to 20°K there was always adequate agreement between the temperature of the bath as deduced by vapor pressure measurements and the temperature indicated by the thermometer. Since the thermometer was not in any poorer contact with the bath than was the sample, we have no reason to believe that the sample temperature differed in any significant way from that registered by the thermometer.

Above the boiling point of liquid hydrogen data were taken by allowing the system to warm gradually after the liquid hydrogen level dropped below the bottom of the microwave cavity. During this time the field was swept back and forth through the resonance while the derivative of the resonance line was continuously recorded as was the temperature of the carbon resistance thermometer. This procedure gave data at about every 2°K, except for a few intervals during which the microwave system was being retuned. The warmup procedure from 20 to 70°K took about 60 min. Our best estimate of the type of error introduced by this procedure is that the sample was warming faster than the thermometer, and that the error became worse as the temperature became higher. Errors in temperature measurement are probably responsible for the increased scatter in the data above 50°K.

C. Sample Preparation

Our sodium samples were prepared by the technique introduced by Levy.³ Briefly, the technique is to prepare dilute sodium-ammonia solutions, and then freeze them. Metallic sodium precipitates out upon freezing in the form of dispersed small particles. We used sodium, kindly given to us by Dr. Raymond Bowers of Cornell University, which had a resistivity ratio of more than 7000. We found it advisable to dissolve this sodium in ammonia which had first been cleaned by dissolving some normal purity sodium in it. This procedure removes any impurities in the ammonia which might react with sodium. The samples were confined to a length in the 3-mm-o.d. tube of about 2 mm in order to confine the sample to the smallest feasible volume to minimize effects of magnetic field

inhomogeneity. After the required amount of ammonia had been introduced, the sample was frozen in liquid nitrogen and sealed off under vacuum a few centimeters above the sample. The 3-mm-o.d. tube was inserted in a long 5-mm-o.d. tube and stored under liquid nitrogen.

D. Some Experimental Precautions

The relaxation times which we measured were in the range from 5×10^{-8} to 5×10^{-7} sec. Such relaxation times are awkward to measure directly, so we took advantage of the equality of the transverse and longitudinal relaxation times⁸ and measured the linewidth. Such a procedure is line shape-dependent, so it will be given extended attention below. Here we want to point out that at low temperatures, even for relatively short relaxation times, a serious danger to accurate measurement lies in partial saturation of the resonance line. The danger arises not from ordinary saturation broadening, but from the Overhauser effect.^{8,9} We have observed at temperatures as high as 20°K effects predicted by Kaplan¹⁰ and observed by Gueron and Ryter.¹¹ If the external field is swept slowly from above resonance while the rf field is strong enough to saturate the resonance even partially, the sodium nuclei will become partially polarized through the Overhauser effect. They will in turn contribute to the total field seen by the electrons an amount H^* which depends on the microwave power and the size of the sodium particles. Thus, the electrons still satisfy the resonance condition with the applied field an amount H^* below the resonance field, and absorption is still observed.

If large, the effect is readily identifiable, and it is simply required, in order to observe the natural linewidth, that the microwave power be sufficiently small. Our klystron operated at approximately 50 mW. We were able to observe Overhauser polarization at 20°K and below in this manner with powers incident on the cavity which were 20 dB down from the klystron power. Our linewidth measurements were made with powers 40 dB down from 50 mW, and we required power-independent linewidths over a 10-dB range of powers before the data was considered acceptable. Such low power levels required the full sensitivity of the superheterodyne system. This system⁵ stabilizes the klystron to the sample cavity, so the single klystron superheterodyne system cannot be instantaneously retuned as the cavity and sample warm continuously above 20°K towards 77°K. Fortunately the relaxation time is short enough above 30°K to eliminate the saturation problem, and a simpler homodyne detection at higher power could be used. In this system the signal at the modulation frequency is taken directly from the

 ⁸ T. R. Carver and C. P. Slichter, Phys. Rev. 102, 975 (1956).
 ⁹ A. W. Overhauser, Phys. Rev. 89, 689 (1953).
 ¹⁰ J. I. Kaplan, Phys. Rev. 99, 1322 (1955).

¹¹ M. Gueron and C. Ryter, Phys. Rev. Letters 3, 338 (1959).



FIG. 1. (a) Derivative of ideal Dyson absorption line in the region of the anomalous skin effect. (b) Typical absorption derivative observed in our samples. Horizontal scale is not the same as in (a).

microwave crystal detector. Biasing power is provided by a small amount of microwave power reflected from the cavity, which is deliberately mismatched. The klystron is still locked to the microwave cavity, and retuning the system as the cavity frequency drifts takes only a few seconds.

We might remark parenthetically that we have made intensive measurements of the Overhauser shift in the hydrogen range, where the shift H^* becomes as large as 5 G. The sodium heat capacity in this region is large enough to prevent the metal particle temperature from rising above the bath temperature because of the microwave power absorbed by the spin system. Difficulties of this type have plagued Overhauser shift measurements on sodium in the helium region for years.¹² Unfortunately, direct measurements of the shift sufficiently precise to be of interest in themselves proved impossible, and our data was only good enough to be in qualitative agreement with the magnitude of H^* as expected from spin susceptibility⁴ and Knight shift¹⁸ measurements.

III. RESULTS AND DISCUSSION

In most of the temperature region over which our measurements were made, the conductivity of the sample is in the anomalous region; i.e., the electronic mean free path Λ is larger than the classical skin

depth δ . In addition most of the sodium particles were large compared to Λ . The resonance absorption line shape for this case has been calculated by Kittel² based on the calculation by Dyson.¹⁴ The derivative of the power absorbed versus $\gamma(H-H_0)T_1$ in Kittel's theory is plotted in Fig. 1. The line shape is characterized by extreme asymmetry, the ratio of the low-field peak to the high-field peak being given by A/B=5. The full width at half-maximum of the low-field peak is given by

$$\Delta H = 1.36 / \gamma_e T_1, \tag{1}$$

where γ_e is the electron gyromagnetic ratio.

The line shape given by our samples is shown in the lower half of Fig. 1. The asymmetry is markedly less than 5:1, and was in fact always about 2.5:1. We believe our lines did not have the Dyson-Kittel shape because our samples in fact contained a mixture of particle sizes, with a substantial contribution to the signal coming from particles whose dimensions are comparable to or smaller than Λ . For these particles the line shape would be Lorentz, with A:B=1. This rationalization of our line shape is supported by the large amount of data taken on the Overhauser shift in the hydrogen temperature region, where we observed in detail the diminution of the intensity of the shifted line as the shift increased. This effect and its relation to particle size is discussed by Ryter.¹²

For a symmetrical Lorentz line, the relation between T_1 and ΔH is given by

$$\Delta H = 1.22 / \gamma_e T_1. \tag{2}$$

For simplicity we have used Eq. (1) in converting from ΔH to T_1 . A comparison of the observed and theoretical line shapes, along with the relations (1) and (2), leads us to believe that use of (1) does not result in T_1 's more than 5% high. Since the temperature dependence of T_1 rather than its absolute value is our main interest, the uncertainty is of no importance.

The results of our measurements on all samples that showed a temperature-dependent ΔH to 14°K are



FIG. 2. ΔH versus T. O, from Kip and Feher (Ref. 2); +, from Levy; •, our data. Solid line and error flags explained in text. Dashed line is from the relation $T_1T=3\times10^{-6}$ sec $-^{\circ}$ K, converted to ΔH by Eq. (1) of text.

¹⁴ F. J. Dyson, Phys. Rev. 98, 349 (1955).

¹² Private communications from many investigators. See also C. Ryter, Phys. Rev. Letters 5, 10 (1960). ¹³ B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. 21,

^{2114 (1953).}



FIG. 3. The theoretical and experimental T_1 's of Table I on a log-log plot. (), Yafet; +, \bullet , experiment as in Fig. 2. The solid line is T_1T = constant drawn through theory and experiment at 200°K. The constant, 2.6×10^{-6} sec -°K, is not the same as in Fig. 2.

shown in Fig. 2, along with the data of Feher and Kip² and of Levy.³ Approximately 25 data points below 20°K and 25 points between 30 and 50°K are represented by the smooth curve drawn through them and error flags giving the limits within which the data fall at several temperatures. The somewhat more scattered data above 50°K (twenty points) are shown as heavy dots. The straight line above 30°K is a least-squares fit to the data between 35 and 50°K; the equation of this line is

$$\Delta H = 0.0277T - (0.577 \pm 0.010). \tag{3}$$

The data above 50°K is omitted from this fit not because of its scatter but because of line shape changes associated with the change between classical and anomalous skin effect regions.

The data, converted to T_1 , is replotted in log-log form, in Fig. 3. The solid line is one drawn by Feher and Kip,² the dots, crosses, and circles are experiment and theory as explained below. We note several features of the results from Fig. 3. (1) Our data extrapolates at high temperatures towards the $T_1T = 3.0 \times 10^{-6} \text{ sec-}^{\circ}\text{K}$ relation found by Feher and Kip. (2) If the theory of Yafet is fit to our data at 40°K it deviates significantly from T_1T = constant as high as 150°K. (3) Our data fit Yafet's theory from 77°K, our highest temperature, to 30°K, where our T_1 's begin to fall well below the theory; and Yafet's theory, fit to our data at 40°K, agrees with Kip and Feher's data at high temperatures.

Feature (3) deserves discussion. The spin-lattice relaxation mechanism discussed by Yafet is an electronphonon scattering accompanied by a spin flip. The mechanism which couples the two spin states is the spin-orbit interaction. Yafet's theory¹ has three parameters. The Debye phonon spectrum is assumed, but two

Debye θ 's are used, θ_N and θ_U . θ_N is the Debye temperature for longitudinal phonons; the N stands for "normal," since electron-longitudinal-phonon scattering is the normal resistivity scattering mechanism. umklapp processes are important because there is a term in the spin-flip matrix element involving only transverse phonons which vanishes for small electron scattering angle, but which contributes if the electron wave vector changes by the phonon wave vector plus a reciprocal lattice vector. Use of a different Debye θ for processes to which transverse phonons contribute corresponds to a modification of the strict Debye model which is realistic if θ_U is chosen less than θ_N . At least one transverse mode corresponding to a low θ has been observed in neutron diffraction by Woods et al.¹⁵

Dr. Yafet was kind enough to furnish us the details of his calculation, the results of which for $\theta_N = 250^{\circ}$ K, $\theta_U = 200^{\circ}$ K, are shown in Fig. 9 of his paper.¹ We were able to use his work to calculate the points shown in Fig. 3. The third adjustable parameter, the strength of the spin-flip matrix element, was chosen to fit the data at 40°K, and several values of θ_N and θ_U were tried. The results are quite sensitive to θ_U , with values of the pair (θ_N, θ_U) of $(250^{\circ}\text{K}, 80^{\circ}\text{K})$ and $(250^{\circ}\text{K}, 200^{\circ}\text{K})$, respectively, lying distinctly below and above the data. The points shown on Fig. 3 correspond to $\theta_N = 250^{\circ}$ K and $\theta_U = 150^{\circ}$ K. For $\theta_U = 150^{\circ}$ K, longitudinal phonons contribute only from 7% to 15% to the total relaxation rate. It is worth pointing out that the Debye θ deduced from heat-capacity measurements is $(156\pm 2)^{\circ}$ K.¹⁶ Table I presents the calculated and measured T_1 's at several temperatures.

Finally, we note that below 30°K the experimental T_1 's deviate from theory; the data give $(T_1)_{\text{meas}}$ $\cong_{\overline{5}}^{3}(T_{1})_{\text{Yafet}}$ at 25°K, and the theoretical T_{1} is beginning to rise very sharply just as the data are beginning to approach a temperature-independent value. Our line-

TABLE I. Calculated and measured relaxation times.

	T in °K	Calculated ^a $T_1 \times 10^{-7}$ sec	Measured $T_1 \times 10^{-7}$ sec
	20	8.85	
	30	3.00	•••
	35	2.13	2.00 ^b
	40	1.47	1.47 ^b
	45	1.22	1.12 ^b
	50	1.00	0.97ь
	75	0.52	0.52ь
	100	0.357	0.28°
	150	0.223	0.22°
	200	0.128	0.13°

* From Yafet (Ref. 1); fit to data at $T = 40^{\circ}$ K, with parameters $\theta_{T} = 150^{\circ}$ K, $\theta_{N} = 250^{\circ}$ K. b Calculated from Eq. (1), where ΔH was obtained from a least-squares fit of data between 35 and 50°K, as explained in text. Point at 75°K was also calculated from (1) and the least-squares ΔH . • From Kip and Feher (Ref. 2), their Fig. 13.

¹⁵ A. D. B. Woods, B. N. Brockhouse, R. H. March, and R. Bowers, Proc. Phys. Soc. (London) 79, 440 (1962). ¹⁶ Douglas L. Martin, Phys. Rev. 124, 438 (1961).

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width in fact becomes temperature-independent at $\Delta H = 0.1$ G. A simple linewidth measurement of the proton resonance in a water sample of the same dimensions as the sodium sample showed the field inhomogeniety over the sample to be about 0.1 G. The field was so inhomogeneous over the small sample because the ratio of the magnet gap to the pole cap diameter was 5:12; the large gap was required in order to fit in the rather bulky microwave cavity and the glass Dewars. Thus our data may not be compared to Yafet's calculations below about 35°K, where the measured linewidths is 0.4 G. We can say in defense of our poor homogeneity that even if Yafet's calculations are correct only down to 20°K the linewidth would be on

the order of $\frac{1}{10}$ our present limit. Thus a substantial improvement in homogeneity would not extend our range of valid data very significantly. The calculated relaxation times in the hydrogen temperature region are long enough to allow a direct measurement of T_1 by transient techniques.

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Absence of Pronounced Quadrupole Effects in the Nuclear Resonance of In¹¹⁵ in a Noncubic Environment*

LAWRENCE H. BENNETT AND REX J. SNODGRASS[†]

Metallurgy Division, National Bureau of Standards, Washington, D. C.

Department of Physics and Astronomy, University of Maryland, College Park, Maryland (Received 23 December 1963)

The nuclear magnetic resonance of In^{115} has been observed throughout the cubic phase of Pb-In alloys, at 77 and 300°K. The Knight shift is 0.86% and is essentially unchanged with composition. The linewidths increase rapidly with In concentration, probably mostly due to pseudodipolar interaction. The average electric field gradient at a In^{115} nucleus for any configuration of Pb neighbors is about $q\sim 3\times 10^{22}$ cm⁻³, about 20 times smaller than for Cu having a Zn second neighbor in the fcc Cu lattice. The small value of the field gradient is discussed in terms of the behavior of the charge oscillations, and is related to the small change in Knight shift for Pb²⁰⁷ in these same alloys.

I. INTRODUCTION

THE nuclear electric-quadrupole moment interacts with the electric field gradient at the site of the nucleus. In a position of cubic symmetry, the electric field gradient vanishes and there is no quadrupole interaction. In the liquid phase of a metal, atomic motion is usually sufficiently rapid to average out the field gradients. Knight¹ pointed out that, in some cases, strong quadrupole interactions may obliterate the nuclear magnetic resonance (NMR) signal of a quadrupolar nucleus in the noncubic lattice of the pure metal, but that the nucleus may still exhibit a strong NMR signal when substituted in the cubic environment of another metal. For example, in pure orthorhombic Ga, the nuclear magnetic resonance has been observed in the liquid phase only. However, when Ga is substituted in the facecentered cubic lattice of Cu, the cubic environment substantially reduces the quadrupole coupling for many of the Ga atoms and the nuclear magnetic resonance is observable. Knight suggested that it might be possible to make suitable alloys of other metals for which the resonances are unobservable in the pure state.

Following this suggestion, one of the present authors² observed a strong NMR signal of In^{115} substituted in the cubic lattice of a 95% Pb-5% In alloy. If the indium is randomly distributed throughout the lattice, about one-half of the indium atoms have only lead for first, second, and third nearest neighbors. The intensity of the In^{115} resonance compared to the Pb²⁰⁷ in this alloy led to the conclusion that *these* atoms were observed, together with some of the satellite intensity. An alternative possibility is that all In^{115} nuclei participate in the resonance but that some of the satellite intensity is smeared out.

In order to distinguish between these possibilities the

and

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[†] Guest worker (1963-64), University of Paris, Faculté des Sciences, Orsay (Group II), Service de Physique des Solides, Orsay (Seine et Oise), France. ¹ W. D. Knight, in *Solid State Physics*, edited by F. Seitz and

¹ W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2. For further information on nuclear quadrupole effects in solids, see M. H. Cohen and F. Reif, *ibid.*, Vol. 5 (1957).

² L. H. Bennett, Bull. Am. Phys. Soc. 4, 251 (1959).