

Here  $\vec{\nabla}V$  is the gradient of the effective screened electron-ion potential. In simple metals the average on the right-hand side of (A12) can be readily computed using a pseudopotential and a single orthogo-

nalized plane-wave band structure. The results are in good agreement with the empirically determined moments for  $l=0$ .

- <sup>1</sup>R. R. Joyce and P. L. Richards, Phys. Rev. Letters **24**, 1007 (1970).  
<sup>2</sup>T. Holstein, Phys. Rev. **96**, 535 (1954).  
<sup>3</sup>W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).  
<sup>4</sup>A. B. Pippard, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited F. Abeles (North-Holland, Amsterdam, 1966).  
<sup>5</sup>T. Holstein, Ann. Phys. (N. Y.) **29**, 410 (1964).  
<sup>6</sup>H. Scher, Bull. Am. Phys. Soc. **12**, 672 (1967); Phys. Rev. Letters **25**, 759 (1970).  
<sup>7</sup>T. Holstein, Phys. Rev. **88**, 1427 (1952).  
<sup>8</sup>G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).  
<sup>9</sup>S. B. Nam, Phys. Rev. **156**, 470 (1967).  
<sup>10</sup>See, for example, K. L. Kliewer and R. Fuchs, Phys. Rev. **181**, 552 (1969).  
<sup>11</sup>A physical derivation has been given by Pippard (Ref. 4) among others.  
<sup>12</sup>This result is explicitly valid for a free-electron Fermi surface with  $\omega_p^2 = 4\pi ne^2/m$ . However, this result (and later results as well) is also valid for light incident along a cube axis of an arbitrary cubic metal if we define  $\omega_p^2$  to be  $\omega_p^2 \int_{FS} dS_{\mathbf{k}} |\vec{\nabla}_{\mathbf{k}}| / 4\pi k_F^2 v_F$ .  
<sup>13</sup>R. B. Dingle, Physica **19**, 311 (1953).  
<sup>14</sup>J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).  
<sup>15</sup>Y. Nambu, Phys. Rev. **117**, 648 (1960); L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [Soviet Phys. JETP **7**, 505 (1958)]; G. M. Eliashberg, *ibid.* **38**, 966 (1960) [*ibid.* **11**, 696 (1960)].  
<sup>16</sup>D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).  
<sup>17</sup>P. B. Miller, Phys. Rev. **118**, 928 (1960).  
<sup>18</sup>D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969); J. P. Carbotte and R. C. Dynes, Phys. Rev. **172**, 476 (1968);

- P. B. Allen and M. L. Cohen, Phys. Rev. B **1**, 1329 (1970).  
<sup>19</sup>P. B. Allen and M. L. Cohen, Phys. Rev. **187**, 525 (1969).  
<sup>20</sup>A. E. O. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).  
<sup>21</sup>P. B. Allen and M. L. Cohen (unpublished).  
<sup>22</sup>J. C. Swihart and W. Shaw, Proceedings of the Stanford Superconductivity Conference, August, 1969 (unpublished).  
<sup>23</sup>S. B. Nam, Phys. Rev. **156**, 487 (1967). An error in this paper has been pointed out by Swihart and Shaw, Ref. 22.  
<sup>24</sup>The author is indebted to W. Shaw and J. C. Swihart for sending a copy of an unpublished calculation based on Nam's theory which shows these effects quite clearly.  
<sup>25</sup>S. Nakajima and M. Watabe, Progr. Theoret. Phys. (Kyoto) **29**, 341 (1963).  
<sup>26</sup>The author is indebted to Dr. S. J. Allen for pointing this out.  
<sup>27</sup>The tunneling technique at present has been used in only one transition metal, Ta [L. Y. L. Shen, Phys. Rev. Letters **24**, 1104 (1970)], and for nontransition metals with the coupling parameter  $\lambda > 0.6$ .  
<sup>28</sup>For example, J. Labbé, S. Barisic, and J. Friedel, Phys. Rev. Letters **19**, 1039 (1967).  
<sup>29</sup>I. P. Ipatova, A. A. Maradudin, and D. L. Mills, Solid State Commun. **8**, 561 (1970).  
<sup>30</sup>L. J. Sham and J. M. Ziman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963).  
<sup>31</sup>J. M. Ziman, *Electrons and Phonons* (Oxford U. P., Oxford, England, 1960).  
<sup>32</sup>T. M. Rice, Phys. Rev. **175**, 858 (1968).  
<sup>33</sup>C. Y. Young and L. J. Sham, Phys. Rev. **188**, 1108 (1969); G. Grimvall, Solid State Commun. **7**, 1629 (1969).  
<sup>34</sup>W. L. McMillan, Phys. Rev. **167**, 331 (1968).

## Spin Relaxation Time of Conduction Electrons in Bulk Sodium Metal\*

W. Kolbe

Department of Physics, University of California, Berkeley, California 94720

(Received 13 July 1970)

A remeasurement of the temperature dependence of the conduction-electron spin relaxation time in sodium is reported. These experiments were made using high-purity bulk sodium. They agree with previous data using dispersions of small particles but extend the results to much lower temperatures.

### I. INTRODUCTION

The first measurements of the temperature dependence of the electron spin relaxation time  $T_1$  in

sodium metal were made by Feher and Kip.<sup>1</sup> They concluded from their data that  $T_1$  was proportional to  $1/T$  over the entire temperature range from 300 to 4 °K. At that time, theoretical calculations of

the relaxation time were at variance with this result. Using free-electron wave functions, Overhauser<sup>2</sup> concluded that  $T_1$  was proportional to  $1/(T \log T)$ , while Elliot<sup>3</sup> predicted a  $1/T^3$  dependence at low temperatures. More recently, Yafet<sup>4</sup> has reexamined these theories and obtained the result that  $T_1$  was proportional to  $1/T$  above an appropriate Debye temperature and was proportional to  $1/T^5$  at low temperatures.

Vescial *et al.*<sup>5</sup> measured  $T_1$  as a function of temperature using a dispersion of small particles of sodium, and obtained results supporting Yafet's theory. In a recent series of experiments in this laboratory using bulk samples of sodium, spin-resonance lines were seen which were significantly narrower (40 mG) at low temperatures than those reported by Vescial.<sup>5</sup> It was therefore felt that a remeasurement of  $T_1$  would be profitable since it would make possible a test of Yafet's<sup>4</sup> theory over a wider range of temperatures than previously obtained. In addition, the question exists whether a dispersion of small particles of sodium comparable in size to the skin depth is truly representative of the bulk properties of sodium. In the absence of extreme care one would expect such particles to be oxidized over a significant portion of their volume. In bulk samples this is not a problem.

Discussed below are the experimental results, a comparison with Yafet's theory, and some of the experimental techniques and precautions employed.

## II. EXPERIMENTAL

### A. Microwave Spectrometer

All measurements were made at  $K$  band (24 GHz) using a conventional bridge-type microwave reflection spectrometer. The static magnetic field was produced by a low-impedance magnet with 12-in. Armco-iron pole faces and a 3-in. gap. To improve the field homogeneity, copper shims were placed between the magnet poles and the pole faces. These were carefully adjusted to maximize the field uniformity. The field was stable to a few parts in  $10^6$  and varied less than 40 mOe over the sample volume. Signals proportional to the derivative of the real part of the sample's surface impedance were obtained by locking the microwave klystron to the cavity-resonance frequency and by modulating the magnetic field at 100 Hz.

The sodium samples were mounted in a rectangular  $TE_{102}$  cavity. As the cavity was one full wavelength long it was possible to locate the samples at positions of maximum rf magnetic field by placing them either at the center or at one end. The rf magnetic field was polarized in the vertical direction at the sample location and was therefore always perpendicular to the dc field which was horizontal and could be rotated in the horizontal plane.

### B. Temperature Control and Measurement

The microwave cavity, enclosed in a metal can, was surrounded by two concentric glass Dewars filled with liquid nitrogen and liquid helium. In order to operate at temperatures intermediate between 4.2 and 77 °K, the inner Dewar was filled with activated charcoal<sup>6</sup> surrounding the microwave gear. Liquid helium was then transferred to cool the apparatus to 4.2 °K. To raise the temperature heat was applied to the system until all or most of the liquid helium was boiled away. Helium gas absorbed by the charcoal remained to provide a large thermal reservoir. With this arrangement it was possible to warm the system to an elevated temperature, and after waiting for equilibrium to be established, sweep through the resonance line at nearly constant temperature. In practice, however, a temperature regulator employing feedback was used to maintain the cavity and sample at a constant but slightly higher temperature than the charcoal-helium bath. In this way it was possible to obtain regulated temperatures as high as 50 °K. Above 50 °K the absorbed helium no longer provided any regulation, and the temperature rapidly increased to 77 °K.

An Allen-Bradley  $\frac{1}{10}$ -W carbon resistor attached to the side of the cavity, was used as a thermometer to measure and control the temperature. The resistor was calibrated at the boiling points of liquid  $N_2$ ,  $H_2$ , and He. The sample, mounted inside the cavity, was supported by Styrofoam and surrounded by helium-exchange gas. Care was taken to avoid heating the sodium by reducing the microwave power to a safe level (at least 6 dB below the power at which any broadening of the resonance line could be seen), and it is believed that the specimen temperature was no more than 1 or 2 degrees above that recorded by the resistance thermometer.

### C. Sample Preparation

The high-purity sodium used in these experiments was provided by C. E. Taylor at the Lawrence Radiation Laboratory, Livermore, Calif. It was prepared by triple distillation in a stainless-steel still and had an estimated purity of 99.999%. Resistivity measurements of the material by the eddy-current decay method<sup>7</sup> gave a resistivity ratio [(resistivity at 300 °K)/(resistivity at 4.2 °K)] of approximately 6000.

The samples were slabs with dimensions approximately  $0.1 \times 2.5 \times 8$  mm and were cut to size under mineral oil with a razor blade. Experiments with such samples indicated that this treatment did not appreciably strain the material, and that room-temperature annealing for a few hours was sufficient to eliminate any damage that was produced. Since the properties of sodium are isotropic, it was

not necessary to select single crystals or to orient them. Most samples, however, consisted of no more than two or three individual crystals.

To minimize oxidation, the mineral oil was purified by placing in it freshly cut scraps of sodium and pumping on it overnight to remove dissolved gases before use. Samples prepared in this oil remained shiny and free of oxidation tarnish for several hours.

The sodium samples were sealed in a small Mylar packet to protect them from the effects of oxygen and moisture. A square of 0.001-in. Mylar plastic film was folded to enclose the sample and heat sealed around the edges. The sample was then mounted in the apparatus and cooled as rapidly as possible with liquid nitrogen.

### III. RESULTS AND DISCUSSION

Since spin relaxation times of the order of  $10^{-6}$ – $10^{-7}$  seconds are difficult to measure directly,  $T_1$  was calculated from the observed resonance linewidths making use of the fact that in cubic metals the longitudinal relaxation time  $T_1$  is equal to the transverse relaxation time  $T_2$ .<sup>8</sup> Such a calculation depends upon the resonance line shape. The theory of the spin-resonance line shape derived originally by Dyson<sup>9</sup> assumed the classical skin effect and was therefore not valid at low temperatures. More recently, Lampe and Platzman<sup>10</sup> have extended this calculation to the case of arbitrary surface impedance. Their result for the microwave power absorbed in the neighborhood of the spin resonance is as follows:

$$P \propto \text{Re}(Z_0^2 \cot 2W/W), \quad (1)$$

where  $Z_0$  is an adjustable parameter expressing the complex surface impedance for "spinless" electrons. The resonance term  $W$  is given by

$$W = \frac{1}{2} a^2 [i T_2 \gamma (H - H_0) - 1], \quad (2)$$

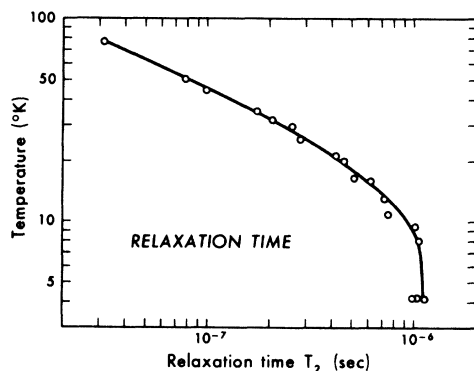


FIG. 1. Conduction-electron spin relaxation time  $T_2$  as a function of temperature.

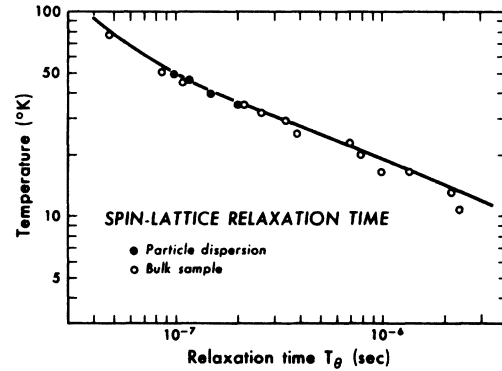


FIG. 2. Spin-lattice relaxation time  $T_\theta$ . The solid circles are Vescial's particle-dispersion data and the open circles are the present results. Yafet's theoretical curve, calculated using the parameters described in the text is also shown.

where  $H_0$  is the resonance field and  $a = L/\delta_{\text{eff}}$  is the ratio of the thickness of the sample (assumed to be a flat plate) to the average distance traveled by the diffusing electrons during their spin lifetime  $T_1$ . The surface impedance  $Z_0$  seen by the diffusing electrons as they enter the region of microwave penetration affects the line shape by mixing the real and imaginary parts of the resonance expression  $\cot 2W/W$ . Hence, in pure materials as the sample is cooled, and  $Z_0$  changes from  $(1+i)$  to the anomalous limit of  $(1+\sqrt{3}i)$ , the line shape will change.

A least-squares technique was used to fit the observed data at each temperature to Eq. (1), thus accounting for changes in both the line shape and linewidth. In most cases, experimental values were selected from 20 magnetic field points in the neighborhood of the resonance. The parameters of Eq. (1) were then adjusted by computer to obtain the best fit.

The results for  $T_2$  are shown in Fig. 1. As can be seen,  $T_2$  is a constant below about 10°K. This residual relaxation time  $T_0$  resulting from impurity effects can be subtracted from the observed relaxation time to obtain the spin-lattice contribution  $T_\theta$ :

$$1/T_\theta = 1/T_{\text{obs}} - 1/T_0.$$

The spin-lattice relaxation time is plotted as a function of temperature in Fig. 2. In the figure the present results are denoted by open circles, and Vescial's<sup>5</sup> particle-dispersion data are indicated by solid circles. The theoretical curve derived from Yafet's calculation is also shown.

Yafet's<sup>4</sup> theory contains three adjustable parameters. Its derivation, which is similar to Ziman's<sup>11</sup> calculation of the electrical resistivity, breaks quite naturally into two parts, one to describe normal phonon processes and one to describe Umklapp processes. The Debye model is used to ap-

proximate the phonon spectrum but two Debye temperatures are employed,  $\theta_N$  for normal processes and  $\theta_U$  for Umklapp. In addition to  $\theta_N$  and  $\theta_U$ , a third parameter is used to adjust the strength of the spin-lattice interaction.

The theoretical curve shown in Fig. 2 was obtained by choosing  $\theta_N = 250^\circ\text{K}$  and  $\theta_U = 150^\circ\text{K}$  as suggested by Vescial *et al.*,<sup>5</sup> and the amplitude of the spin-lattice interaction was adjusted to fit the data at  $40^\circ\text{K}$ . It is, perhaps, not worthwhile to attach too much significance to these parameters as the theory itself is based on the rather approximate Debye model. However, it should be pointed out that the choice of a low-temperature value for  $\theta_U$  is supported by the fact that transverse phonon modes with a low Debye temperature have been observed in sodium-neutron diffraction experiments.<sup>12</sup> According to Yafet's<sup>4</sup> theory, these transverse modes contribute to the relaxation primarily through Umklapp processes and not through normal processes.

Returning to Fig. 2, it is apparent that both the data of Vescial and the present results agree rather well with the theoretical calculation. The limited range of the Vescial results is due to the fact that they were unable to observe sufficiently narrow lines at low temperatures. This is presumably be-

cause of the presence of impurities in their small particles and as the authors point out, partly because of a lack of magnetic field homogeneity. In the bulk experiments these problems were not present.

#### IV. CONCLUSION

The temperature dependence of the spin-relaxation time in bulk sodium is dominated by a weak spin-orbit coupling together with a strong electron-phonon interaction as predicted by Yafet.<sup>4</sup> Below about  $10^\circ\text{K}$  impurity effects predominate, yielding a residual spin lifetime of about  $10^{-6}$  sec for the material available. In dispersions of sodium similar results have been obtained<sup>5</sup> with the exception that impurities limited the spin lifetime to  $5 \times 10^{-7}$  sec.

#### ACKNOWLEDGMENTS

The author would like to thank Professor A. F. Kip for his continuing encouragement and guidance throughout this work. Thanks are also due to Dr. Y. Yafet for supplying the unpublished results of his calculation of the spin-lattice relaxation time, and to Dr. Daniel Ch'en and Dr. James LePage for many useful discussions.

\*Work supported in part by Grant No. AF-68-1352 from the U. S. Air Force Office of Scientific Research.

<sup>1</sup>G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

<sup>2</sup>A. W. Overhauser, Phys. Rev. **89**, 689 (1953).

<sup>3</sup>R. J. Elliot, Phys. Rev. **96**, 266 (1954).

<sup>4</sup>Y. Yafet, *Solid State Physics* (Academic, New York, 1963), Vol. 14, p. 1.

<sup>5</sup>F. Vescial, N. S. Vander Ven, and R. T. Schumacher, Phys. Rev. **134**, A1286 (1964).

<sup>6</sup>G. White, *Experimental Techniques in Low Temperature Physics* (Oxford U. P., Oxford, England, 1959), p. 213.

<sup>7</sup>C. P. Bean, R. W. DeBlois, and L. B. Nesbit, J. Appl. Phys. **30**, 1976 (1959).

<sup>8</sup>D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

<sup>9</sup>F. Dyson, Phys. Rev. **98**, 349 (1955).

<sup>10</sup>M. Lampe and P. M. Platzman, Phys. Rev. **150**, 340 (1966).

<sup>11</sup>J. M. Ziman, Proc. Roy. Soc. (London) **A226**, 436 (1954).

<sup>12</sup>A. D. B. Woods, B. N. Brockhouse, R. K. March, and R. Bowers, Proc. Phys. Soc. (London) **79**, 440 (1962).