the value of the Korringa product in the alkali metals is almost constant. As a further test of the theory, it would be desirable to have experimental data for the ratio of Zeeman to dipolar spin-lattice relaxation times in other alkali metals. Applicability of the theory in its present form to metals for which band effects are significant is somewhat questionable. For such cases a crude approximation is to assume an effective band mass for the electrons.

---

*Work supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center and by the National Science Foundation under Contract No. GP-11054.

†Present address: Physics Department, Punjab University, Chandigarh, India.

[1] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1955).

[2] J. Korringa, Physica 16, 601 (1950).

[3] A. Narath and H. T. Weaver, Phys. Rev. 175, 373 (1968).

[4] T. Moriya, J. Phys. Soc. Japan 18, 516 (1963).

[5] P. A. Wolff, Phys. Rev. 129, 84 (1963).

[6] D. P. Tunstall and D. Brown, Phys. Rev. B 1, 2881 (1970).

[7] G. Allan, W. M. Lomer, R. D. Lowde, and C. G. Windsor, Phys. Rev. Letters 20, 933 (1968); R. D. Lowde (private communication).

[8] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B1, 1044 (1970).

[9] D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Soviet Phys. Usp. 3, 320 (1960)].

[10] P. A. Wolff, Phys. Rev. 120, 814 (1960).

[11] R. Lobo, K. S. Singwi, and M. P. Tosi, Phys. Rev. 186, 470 (1969).

[12] K. A. Brueckner and K. Sawada, Phys. Rev. 112, 328 (1958).

[13] T. M. Rice, Phys. Rev. 175, 858 (1968).

[14] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 87.

[15] T. Moriya, Progr. Theoret. Phys. (Kyoto) 16, 23 (1956).

[16] L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 504 (1959); see also, A. G. Anderson and A. G. Redfield, *ibid.* 116, 583 (1959).

[17] J. Poitrenaud and J. M. Winter, Phys. Letters 17, 199 (1965).

PHYSICAL REVIEW B VOLUME 3, NUMBER 5 1 MARCH 1971

Pressure Dependence of the Knight Shift in Al and Nb Metal

Toshimoto Kushida and J. C. Murphy
Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

(Received 21 August 1970)

The pressure dependence of the Knight shift K of Al and Nb metals was measured with a digitally slaved signal averager. The maximum hydrostatic pressure utilized was 8000 kg/cm^2. The observed value of $d\ln K/d\ln V$ is -1.01 ± 0.02 and -0.29 ± 0.02 for Al and Nb, respectively. Since it is essential to know the volume dependence of the (electron-electron-enhanced) spin susceptibility $d\ln\chi^*_{\mathrm{sp}}/d\ln V$ in order to analyze the observed $d\ln K/d\ln V$, the theoretical implication of the previously proposed methods to estimate $d\ln\chi^*_{\mathrm{sp}}/d\ln V$ was explored. The linearly temperature-dependent thermal expansion at low temperature α_e gives rise to the volume dependence of electron-phonon-enhanced density of states at the Fermi surface. α_e includes only a temperature-independent part of the enhancement factor $1+\lambda$. The pressure dependence of the superconductor parameters renders the volume dependence of the density of states clothed with a full electron-phonon interaction, which includes the temperature-independent part as well as a possible temperature-dependent part. A semiempirical scheme to deduce the volume dependence of $1+\lambda$, the density of states for the bare electrons $N(E_F)_{\mathrm{BS}}$, and the band-structure effective mass m^* is proposed. These values are derived from the pressure dependence of the superconducting transition temperature and α_e. The volume dependence of χ^*_{sp} is deduced from $d\ln N(E_F)_{\mathrm{BS}}/d\ln V$ by taking into account the effect of the electron-electron enhancement factor. The volume dependence of the density of wave function at the Fermi surface $\langle|\psi(0)|^2\rangle$ was deduced for Al as $d\ln\langle|\psi(0)|^2\rangle/d\ln V=-2.12$. The volume dependence of the orbital Knight shift K_0 for Nb is estimated as $d\ln K_0/d\ln V\simeq 0.4$ (or 0.1). The possible origin of the discrepancy between the density of states derived from α_e and from the pressure dependence of the superconductor parameters is discussed. The origin of inconsistency in the previously reported temperature dependence of K for Al is also suggested.

I. INTRODUCTION

The Knight shift K and the spin-lattice relaxation time T_1 of metals are directly associated with the properties of the electronic wave functions. The three main contributions to K and T_1 are the contact (hyperfine) interaction with the conduction electrons at the Fermi surface, the contact interaction with the core electrons, and the orbital interactions. Because of advances in first-principles calculations of wave functions of electrons in metals, the interpretation of K and T_1 is found to be more complicated than has been thought traditionally. An electron-electron and an electron-phonon interaction have to be properly taken into account in the analysis of the experimental data. Possible additional contributions to the Knight shift have also been proposed.[1]

It is rather obvious at this stage that the first-principles calculation of the wave functions is essential to the interpretation of the experimental results. Unfortunately, however, the results of the band-structure calculations usually list only the information about the eigenvalue $E(\vec{k})$. No information is usually available for the associated wave functions $\Psi_{\vec{k}}$. This is mainly because such calculations have been performed by people who are predominantly interested in the eigenvalues. Another, probably more pertinent, reason is that the information derived from the resonance experiment is usually an average value over the Fermi surface such as $\langle |\Psi(0)|^2\rangle$, whereas more detailed experimental information is available for $E(\vec{k})$. Nevertheless, it is clear that the knowledge of $\Psi_{\vec{k}}$ is as important as the information about $E(\vec{k})$ for the understanding of the electronic structure of metals in general.

The most obvious method to increase the experimentally available information for the metal is to study the effect of alloying. A great deal of knowledge has been accumulated from the nuclear-magnetic-resonance (NMR) study of alloys. Another technique to enhance the experimental information is a study of pressure dependence of K and T_1 in metals. In principle, such information as $\langle |\Psi(0)|^2\rangle$ and $d\langle |\Psi(0)|^2\rangle/dV$ is more suitable for purposes of comparison with the first-principles calculation than the concentration dependence of this quantity in alloys, although, in practice, the range of available volume change caused by the applied pressure is limited.

Among the three major contributions to K, the first is most important for alkali metals. Since the compressibility of alkali metals is large, the detailed relation between K and the volume V could be studied.[2] A reassessment of the pressure results for the alkali metals[3] is interesting in view of (i) the recent advance in the calculation of the wave function and (ii) the results of the many-body effect which seems to be sizable in alkali metals.[4] The second contribution to the Knight shift plays the dominant role for Pt metal.[5] The first-principles calculation[1] indicates that the effect of the core polarization is not negligible even for Be. The third contribution is dominant for V and Nb.[6] The pressure experiment was carried out for the Pt and the V Knight shifts.[7,8]

In this paper a similar experiment has been extended to Al and Nb metal. The earlier attempt[2] to measure dK/dV for Al was not successful because of the relatively primitive technique available at that time. The recently developed signal-enhancement technique[9] enabled us to obtain a reliable magnitude of shift in K under a moderately high pressure. For Al, a band-structure calculation seems to give good agreement with the Fermi-surface experiment.[10,11] A detailed calculation of the Knight shift has been carried out by Das and his group.[12] The analysis of the Knight shift in the transition metals such as V and Nb is more complicated. If one attempts to solve this type of problem experimentally, the number of unknown parameters is much larger than that of the measurable parameters. One of the approaches taken to such problems is "a chemist's method," which is to compare similar results for the different elements in the same column of the Periodic Table. This is the reason why the Nb experiment was undertaken.

When the observed volume dependence of K is to be analyzed, it is necessary to estimate $d\ln\chi_{sp}/d\ln V$, where χ_{sp} is the (volume) Pauli susceptibility.[8] Since very few direct measurements for this quantity are available,[8] one has to depend on an indirect derivation from the available experimental data. A naive estimate based on a simple free-electron model is usually unsatisfactory.[8] The two groups of values derived from different types of experiments do not seem to reconcile with each other.[8] A possible origin of the discrepancy will be discussed.

A semiempirical method to derive the volume dependence of the following parameters is proposed: (i) the electron-phonon interaction parameter, (ii) a band-structure density of states at the Fermi surface, (iii) a band-structure effective mass, and finally (iv) the spin susceptibility. These values are derived from the low-temperature thermal-expansion data and the pressure dependence of the critical temperature for superconductivity by using McMillan's theory of superconductivity[13] and Silverstein's calculation for the many-body electron-electron interaction.[14]

II. EXPERIMENTAL PROCEDURE AND RESULTS

The hydrostatic pressure was generated with a Bridgman-type hydraulic ram which was purchased from Harwood Engineering Co. A considerable modification of the original package was required to obtain satisfactory operation. The compressed liquid was led through flexible stainless tubing $\frac{1}{8}$-in. o.d., $\frac{1}{40}$-in. i.d.) to a Be-Cu pressure bomb[2] in a magnet. The bomb contained an rf coil and the finely powdered sample.[2,7,8] The magnetic field generated with a 12-in. Varian magnet was stabilized using F^{19} NMR in a piece of Teflon. The F^{19} resonance was detected with another frequency-stabilized marginal oscillator detector, and the resonance signal was fed back to the power supply of the magnet in such a way as to lock the strength of the magnetic field to the center of the F^{19} NMR line.[8]

The F^{19} monitor spectrometer is a simple one-tube spectrometer described elsewhere.[15] The frequency of the spectrometer was locked[16] to a precision pulse train which was synthesized from the output of a crystal oscillator. A simple automatic oscillation-level control was added to the spectrometer. The rf level picked up by a loosely coupled loop was amplified with a wide-band amplifier (Hewlett Packard HP 461A) and detected with an rf diode. The difference between the detected level and a standard voltage was fed back to a programmable B-voltage regulator. The regulator consisted of an operational amplifier (Philbrick SK2V) as a noninverting amplifier and two 12AU7 cathode followers as a power booster. The automatic level control was necessary in order to keep the oscillation level low enough to avoid saturation of the F^{19} NMR signal. The Al^{27} or the Nb^{93} NMR was observed with a modified Pound-Knight-Watkins spectrometer.

The phase-detected NMR signal was sent to a time averager (TMC CAT 1000) in order to enhance the signal-to-noise ratio S/N. Without the signal averaging, the S/N ratio was not sufficient to detect a small pressure shift in the resonance frequency. Although the S/N ratio can be improved indefinitely, in principle, with this technique, the conventional CAT system is not sufficient for the present purpose.[9] The frequency of the sample spectrometer must be precisely slaved to the channel number (ADDRESS) of the signal averager. In the presently available averager system, the slaving is achieved with an analog system. The analog slaving accuracy is typically ± 0.1% or ± one channel. Therefore the tradeoff for signal enhancement is the loss in the frequency scale accuracy, which cannot be tolerated for the present measurement.[9] Therefore, the frequency of the sample spectrometer was digitally slaved to the ADDRESS location.

The digital slaving could be achieved by a frequency synthesizer with a fast remote-control capability combined with a small computer. The present slaving system was, however, assembled mainly using DEC (Digital Equipment Corp.) R-series module cards. Since these discrete-component logic units are now obsolete, the detailed circuit is not described here.[17]

The operation of the digital slaver is summarized as follows. (i) The binary ADDRESS information of the signal averager is transferred into a register. (ii) Crystal-controlled clock pulses are sent into this register, which is now acting as an up-counter. (iii) When the register counter is filled up, the oncoming clock pulse train is turned off. The number of pulses sent to the register counter is the complement[18] of the ADDRESS number. These processes are repeated exactly 122 times a second. (iv) The train of pulses thus generated is sent to an up-count input of an up-down counter. (v) The spectrometer frequency is beaten against a crystal-controlled fixed frequency. The difference between the spectrometer and the fixed frequency is fed into a down-count input of the up-down counter. The content of the counter is transferred READ OUT after each counting sequence into another register. The content of this register is a time integral of the frequency difference between the spectrometer frequency and the pulse train corresponding to the ADDRESS location. (vi) The binary content of the register is converted into an analog signal with a DAC (digital-to-analog converter) and fed back to a frequency control circuit of the spectrometer.

The spectrometer frequency is thus slaved to the ADDRESS location digitally. In a practical circuit the ADDRESS register counter is "complemented"[18] when the ADDRESS location is in a more-than-half range. This is detected simply by the state "1" at the most significant bit of the ADDRESS binary. Thereby the direction of the spectrometer-frequency sweep is reversed at the center of the ADDRESS. The triangular sweep generated by this process was found to be more convenient for the present purpose than the sawtooth sweep generally available from the analog output of the averager. The time lag between an up-sweep and a down-sweep signal can be checked conveniently. If the time lag is within the acceptable range, it is averaged out after the signal accumulation.

Another function which was found to be very useful is a skipping capability of the frequency sweep. The particular parts of the resonance line such as the tail and the center zero-crossing region can be accumulated in the averager. The unimportant parts of the line are quickly swept through without being registered. This skipping process reduces the measurement time a great deal and makes the measurement with acceptable accuracy practical. Signal averaging for more than several hours under high pressure is uncomfortable, to say the least. The "skipping" is accomplished by deleting a certain number of pulses from the pulse train for the down-input of the up-down counter, when the ADDRESS location is in certain ranges (for instance, the center of the line or the upper tail region). The spectrometer frequency has to make up the deleted pulses by increasing its frequency.

The F^{19} spectrometer frequency can be trimmed digitally by using a simple digital frequency synthesizer in the present unit so as to locate the Al or the Nb NMR frequency at the proper position of the memory of the averager.

The entire line shape was accumulated first at atmospheric pressure and 8000 kg/cm^2. If no asymmetry in the line shape is noticed, it is safe to assume that the pressure shift of the zero-crossing frequency represents the pressure dependence of the resonance frequency. The digital slaver was programmed in such a way as to accumulate the center zero-crossing region and the tails (the higher- and the lower-frequency tail) of the line.[9] The signal of the center and the tails was accumulated for 3–4 h in the morning at a given pressure, and the signal at atmospheric pressure was accumulated for about the same period in the afternoon. The procedure was repeated for several days to get the pressure shifts for several pressure values.

Al powder was purchased from Gallard Schlesinger Chem. MFC (Carle Place, N. Y.). Nominal purity is 99.995%. Following the recommendation in the literature,[19] we obtained Nb powder from Johnson Matthey Chem. Ltd. The claimed impurities are Ta (0.01%), Si (200 ppm), and Fe (200 ppm).

Since there is some discrepancy in the temperature dependence of the Al Knight shift reported in the literature, the resonance frequency of Al^{27} was measured at room temperature and at liquid-N_2 temperature. Since Al^{27} resonance in Al metal has been used frequently for the purpose of calibrating magnetic fields,[20,21] there is some importance in clarifying the origin of such discrepancy. Borsa and Barnes[22] reported a 5% *increase* in the Knight shift $K(T)$ as the temperature was reduced from 300 to 77 °K. Knight reported a small decrease in K, when T was reduced from room temperature to 1.2 °K.[23] Other workers[20,24] reported no temperature dependence within their experimental accuracy.

The present measurement indicates a *decrease* in Al^{27} frequency as T is reduced,

$$\nu_{300} - \nu_{77} = 210 \pm 30 \text{ Hz},$$

where

$$\nu_{300} = 10\,789.16 \text{ kHz}.$$

If the Knight shift is taken as 0.161%,

$$(K_{300} - K_{77})/K_{300} = 1.21\%.$$

This value is consistent with Feldman's result for the wider temperature range,[25]

$$(K_{\text{room}} - K_{1.2})/K_{\text{room}} = 1.75\% .$$

A possible magnetic effect caused by the Dewar was not corrected in this measurement. The F^{19} sample was placed outside the Dewar. Since the Dewar is made of glass and the result is consistent with Feldman's value, the Dewar effect may be very small, if it exists.

A possible origin of the discrepancy in the published values for $K(T)$ was studied as follows: The samples used for the early studies[26] of the Knight shift in metals and alloys were traditionally prepared by filing a piece of ingot with a steel file. The trace of the steel powder in the sample was picked up with a small magnet. In order to test the possible effect of the residual iron impurity on the observed $K(T)$, a small amount of fine iron powder was mixed with the aluminum powder, and the iron powder was picked up with a small magnet. The sample thus prepared would contain a trace of iron powder. The iron content could, however, be smaller than that for the samples prepared in the traditional way. The apparent temperature dependence of this sample was

$$\nu_{300} - \nu_{77} = 60 \text{ Hz} .$$

The second sample, which would simulate the traditional preparation more closely, was made as follows: The Al powder was bonded with Epoxy glue. Then this solid piece was filed down with a steel file and cleaned with the magnet. The temperature dependence for this sample was

$$\nu_{300} - \nu_{77} = 25 \text{ Hz}.$$

The effect of the residual iron powder impurity seems to increase the resonance frequency at low temperature. The large increase reported by Borsa and Barnes[22] could have been, at least partially, due to the effect of a relatively large amount of residual steel powder in their sample. Their samples were prepared with the traditional filing method.

A typical accumulated signal for the Al line is shown in Fig. 1. The lower-frequency tail LT, the center part CT, and the higher-frequency tail UT of the derivative of the resonance curve are shown on the left half of the figure. On the right half UT$'$, CT$'$, and LT$'$ are similar data for the reversed frequency sweep. The triangular sweep was used as mentioned before. The frequency markers shown in the figure were made as follows: After the data were accumulated, the signal gate of the averager was closed, a display output was connected to an XY recorder, and the channel advance pulses were sent to the slaver system. While the recorder displayed the accumulated data, the advancement of the channels was stopped several times near the center crossing points. The sweep of the spectrometer frequency which had been slaved to the channel advance stopped accordingly. The frequency of the spectrometer locked to the particular channel where the advance was stopped was measured with a frequency counter and printed.

The pressure dependence of the Al^{27} NMR frequency is shown in Fig. 2. The resonance frequency increases with pressure,

$$\frac{d\ln K}{dP}=+\frac{(1.31\pm 0.02)\%}{10\,000\ \mathrm{kg/cm^2}}\ .$$

The Nb^{93} line of the present sample had a slight asymmetry. The higher-frequency deflection was about 6% larger than the lower-frequency deflection in the derivative curve. The degree of the asymmetry, however, remained unchanged under a pressure of 8000 kg/cm^2.

The linewidth defined as the distance between the maximum and the minimum of the derivative curve was 8.0 kHz. This is in reasonable agreement with the previously reported values.[27-29] The linewidth of the Nb NMR sharply depends on the quality of the sample.[27] The linewidth of the present sample is close to the best samples reported. The narrowest linewidth observed by Butterworth[27] using a pulsed free-induction decay method is 7.8 kHz. A single crystal of Nb of the highest quality (the resistivity ratio $R_{300}/R_{4.2}$ is reported to be 500) gave 4.5 and 9.5 kHz for [100] and [110] directions.[28] If one assumes the corresponding powder linewidth to be $\frac{1}{3}(\Delta\nu[100]+2\Delta\nu[110])$, one obtains 7.8 kHz.

The small asymmetry observed in the present sample could be explained by a second-order quadrupole effect,[27,30] although Schone suggested[28] that only a first-order quadrupole effect would be observed for the high-quality sample.

Strictly speaking, if the line shape has asymmetry, the zero-crossing point is not a good measure of the resonance frequency. It is not practical for the present case, however, to display the total profile of the line and calculate the center of gravity. Since the S/N ratio of Nb is relatively poor, it would take at least 30–40 h to accumulate the signal, if the total line shape were swept. The S/N ratio must be enhanced a great deal in order to measure the small pressure shift. Therefore it was decided to measure the pressure dependence of the zero-crossing point using the "skipping" sweep. Since the asymmetry was small and the degree of the asymmetry did not change with the pressure, this procedure was considered to be acceptable.

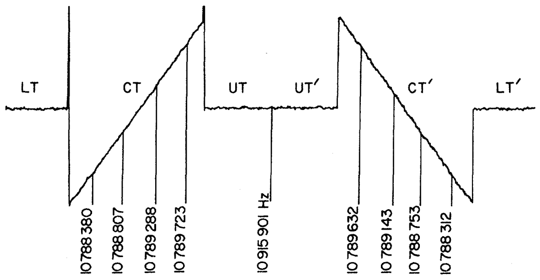

FIG. 1. Accumulated NMR signal in a digitally slaved signal averager. The center zero-crossing part CT, the lower-frequency tail LT, and the higher-frequency tail UT of the derivative curve are accumulated in the memory of the averager. The rest of the resonance curve was skipped by using the skipping mode of the digital slaver. The direction of the frequency sweep is reversed at the center.

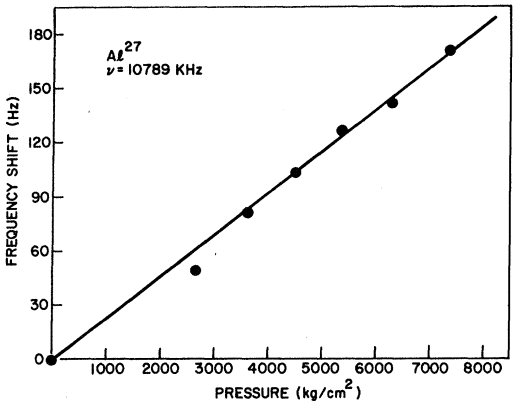

FIG. 2. NMR frequency of Al^{27} in Al metal as a function of hydrostatic pressure.

The result is shown in Fig. 3. Since the amount of the pressure shift is smaller and the S/N ratio is poorer than the Al^{27} line, the scatter of the data is larger than that in Fig. 2. If the Knight shift of Nb^{93} is taken as 0.821%,[31,32] the pressure dependence of the Knight shift is[33]

$$\frac{d\ln K}{dP}=+\frac{(0.16\pm 0.01)\%}{10\,000\ \mathrm{kg/cm^2}}\ .$$

Slightly different values for the Nb Knight shift have been reported in other sources.[23,34,35]

If one uses Bridgman's value of compressibility,[36] the volume dependence of the Knight shift is derived as

$$\frac{d\ln K}{d\ln V}=-1.01\pm 0.02\ \text{ for Al}, \tag{1}$$

$$\frac{d\ln K}{d\ln V}=-0.29\pm 0.02\ \text{ for Nb}. \tag{2}$$

The temperature dependence of the Nb Knight shift was reported to be unobservable,[31] although the earlier measurement suggested a slight decrease with a decrease of temperature.[23] We noticed a slight decrease in K as the temperature was reduced from room to liquid-nitrogen temperature:

$$(K_{300}-K_{77})/K_{300}=0.16\%\ .$$

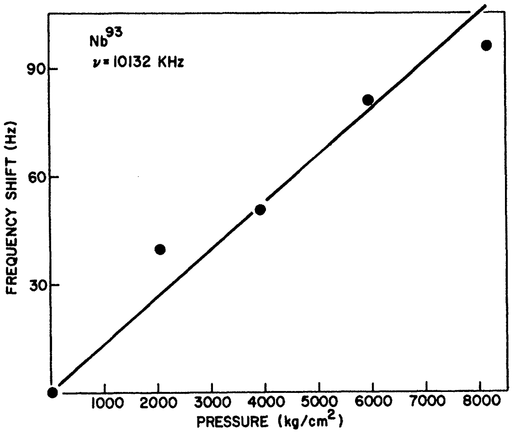

FIG. 3. NMR frequency of Nb^{93} in Nb metal as a function of hydrostatic pressure.

The observed value is somewhat smaller than the theoretical estimate, $(K_{20^\circ C} - K_{-150^\circ C})/K_{20^\circ C} = -0.61\%$, and its sign is opposite. Since the possible Dewar effect was not corrected and the sample contained some iron impurity (200 ppm), this observed temperature dependence should not be taken seriously.

III. SEMIEMPIRICAL DERIVATION OF $d\ln(1+\lambda)/d\ln V$, $d\ln V(E_F)_{\rm BS}/d\ln V$, $d\ln m^*/d\ln V$, AND $d\ln\chi^*_{\rm SP}/d\ln V$

The three major contributions to the Knight shift K are, as mentioned previously,

$$K = K_s + K_d + K_0 , \tag{3}$$

where

$$K_s = \tfrac{8}{3}\pi\langle\,|\Psi(0)|^2\rangle\,\chi_s\,\Omega , \tag{4}$$

$$K_d = \tfrac{8}{3}\pi\langle\rho(0)\rangle_d\,\chi_d\,\Omega , \tag{5}$$

and

$$K_0 \simeq 2\,\langle r^{-3}\rangle_D\chi_0\Omega \ . \tag{6}$$

Here K_s is the Knight shift due to the contact interaction between the pertinent nucleus and the conduction electrons at the Fermi surface.[37] χ_s is the volume susceptibility of s-p band, Ω is the atomic volume, and $\langle\,|\Psi(0)|^2\rangle$ is the probability density for s electrons at the nucleus, averaged over the Fermi surface. K_d represents the shift due to the core-electron polarization.[38] $\langle\rho(0)\rangle_d$ is the net unpaired density at the nucleus caused by d-electron spins averaged over the d state at the Fermi surface. χ_d is the volume susceptibility of the d band. K_0 is the orbital contribution to the Knight shift.[39–41] χ_0 is the orbital paramagnetism and $\langle r^{-3}\rangle_D$ is the average of r^{-3} over all contributing states in the band.

The volume dependence of K is

$$\frac{d\ln K}{d\ln V} = \frac{K_s}{K}\,\frac{d\ln K_s}{d\ln V} + \frac{K_d}{K}\,\frac{d\ln K_d}{d\ln V} + \frac{K_0}{K}\,\frac{d\ln K_0}{d\ln V} \ . \tag{7}$$

If K_d and K_0 are negligible compared with K_s, one obtains

$$\frac{d\ln K}{d\ln V} = \frac{d\ln\langle\,|\Psi(0)|^2\rangle}{d\ln V} + \frac{d\ln(\chi_s\Omega)}{d\ln V} \ . \tag{8}$$

This is a good approximation for most of the simple metals such as Al and alkali metals.[2,12,42] Since the estimate of $d\ln(\chi_s\Omega)/d\ln V$ based on a free-electron model, which is $\frac{2}{3}$, is not appropriate,[8,22,43] one has to use a more realistic value, either deduced semiempirically or derived from a reliable first-principles calculation.

If K_0 is negligible compared with K_s and K_d and if K_d has an appreciable temperature dependence, one can separate the first two contributions in Eq. (7) by using the temperature dependence of the second term. This is the case for Pt metal.[7] For V metal K_0 is most important, $K_0 > |K_d| \gg K_s$. Here a reliable estimate for $d\ln(\chi_d\Omega)/d\ln V$ was essential in order to deduce the volume dependence of K_0.[8]

In any case it is highly desirable to have a semiempirical method of deriving the volume dependence of the spin susceptibility $\chi_{\rm sp}$, since very few direct measurements of $d\chi_{\rm sp}/dP$ for paramagnetic metals have been reported.[44] It is the purpose of this section to propose a new systematic method of tackling this problem and discuss the previously suggested methods critically. As a by-product it is also pointed out that the volume dependence of (i) the electron-phonon interaction parameter, (ii) the band-structure density of states, and (iii) the band effective mass can be deduced semiempirically. It would be interesting to compare the volume derivatives of these parameters with *ab initio* calculations or with directly measured quantities such as the pressure dependence of the cyclotron resonance or of the tunneling spectrum.

A. Effect of Electron-Electron and Electron-Phonon Interactions on c_e and $\chi_{\rm sp}$

If one neglects the electron-phonon and the electron-electron interaction, $\chi_{\rm sp}$ can be derived from the specific-heat measurement at low temperature. The linearly temperature-dependent part of the low-temperature specific heat c_e is proportional to the density of states of the electrons at the Fermi surface $n(E_F)$,[45]

$$c_e/T \equiv \gamma = \tfrac{2}{3}\pi^2k^2n(E_F) , \tag{9}$$

where c_e and $n(E_F)$ refer to the values per unit volume. The spin susceptibility $\chi_{\rm sp}$ is also proportional to $n(E_F)$,[46]

$$\chi_{\rm sp} = 2\mu_0^2\,[n(E_F) + O((kT/E_F)^2)] , \tag{10}$$

where μ_0 is the magnetic moment of the electron.

The second term in Eq. (10) is usually negligible.[47] The spin susceptibility is, therefore,

$$\chi_{\rm sp} = 3(\mu_0/\pi k)^2 \gamma \;. \qquad (11)$$

If the electron-phonon interaction is turned on, γ will be enhanced appreciably. The enhancement factor is given by McMillan[13] as $1+\lambda$. λ is a dimensionless electron-phonon coupling constant, which corresponds roughly to $N(E_F)V$ of the BCS model of superconductivity.[48] λ for various metals derived from superconducting properties are listed in Ref. 13.

γ could be affected by the electron-electron interaction (exchange and correlation interaction).[49] This effect is appreciable for such low-density metals as Rb and Cs, but it does not seem to be important for Al and Nb. Therefore, the band-structure density of states $n(E_F)_{\rm BS}$ can be obtained from[13]

$$n(E_F)_{\rm BS} = 3\gamma/2\pi^2 k^2(1+\lambda) \;, \qquad (12)$$

where λ for Al and Nb is 0.38 and 0.82, respectively.[13] λ could be determined from the ratio between the cyclotron mass and the band mass.[1]

It is well known that $\chi_{\rm sp}$ is enhanced by electron-electron interaction,[46] the most obvious and striking example being a ferromagnet. The exchange-enhanced susceptibility is often described by a Stoner form,[4,46]

$$\chi^*_{\rm sp} = \chi_{\rm sp}/(1-\alpha) \;, \qquad (13)$$

where $\chi^*_{\rm sp}$ is the enhanced susceptibility and α is proportional to $\chi_{\rm sp}$ itself. A more specific form derived from many-body formalism is given by Silverstein[14] as

$$\chi^*_{\rm sp} = \frac{\chi_0}{1+(m/m^*-1)(\chi_0/\chi_{\rm free})} \;, \qquad (14)$$

where $\chi_{\rm free}$ is the free-electron susceptibility. χ_0 is the enhanced susceptibility in the free-electron approximation, which is given in Fig. 4 of Ref. 14. m^* is the band effective mass,[1]

$$m^*/m = n(E_F)_{\rm BS}/n(E_F)_{\rm free} \;. \qquad (15)$$

It is noted that Eq. (14) is valid only for a nearly-free-electron case, which seems to be justifiable for Al but doubtful for Nb. An obvious catastrophe will be encountered if m^*/m is equal to or larger than a certain value, since the denominator of Eq. (14) becomes

$$1+(m/m^*-1)(\chi_0/\chi_{\rm free}) \le 0$$
$$\text{for } m^*/m \ge \chi_0/(\chi_0-\chi_{\rm free}) \;.$$

The relation between the spin susceptibility and the electronic specific heat, Eq. (11), will be modified by the electron-phonon and the electron-electron enhancement factor:

$$\chi^*_{\rm sp} = 3(\mu_0/\pi k)^2 \gamma (1-\alpha)^{-1}(1+\lambda)^{-1} \;. \qquad (16)$$

Since the effects of λ and α tend to cancel each other, it is noticed that the bare-one-electron derivation, Eq. (11), is sometimes a fair approximation. In the case of Al, for instance, $\chi^*_{\rm sp} = \chi_0/0.91 = 1.37\chi_{\rm free}$ [Eq. (14)] and $\gamma = 1.49(\frac{2}{3}\pi^2 k^2 n_{\rm free})$, obtained by using[13] $m^*/m = 1.08$, $\lambda = 0.38$, and $\chi_0/\chi_{\rm free} \simeq 1.24$,[14] gives us $(1-\alpha)^{-1}(1+\lambda)^{-1} \simeq 0.9$. Probably this is the reason why Shu *et al.*[12] could get a very good agreement between the calculated Knight shift of Al and its experimental value using relation (11). Rohy and Cotts also noticed the similar cancellation for a V-Cr alloy.[50]

B. Previous Attempts to Derive $d\ln(\chi^*_{\rm sp}\Omega)/d\ln V$ and Their Evaluation

A few attempts have been tried to derive $d\ln(\chi^*_{\rm sp}\Omega)/d\ln V$ semiempirically.[8,22,43] It has been noticed, however, that the consistency among the values derived from the different methods is relatively poor.[8] It is the purpose of this subsection to consider their theoretical background more carefully and to evaluate their reliability in deducing the pertinent parameters.

1. *Magnetostriction*

Fawcett and White[51] derived the volume dependence of susceptibility from magnetostriction measurements for a few metals. The details have not been published.

2. $(\partial S_e/\partial V)_T$

Two independent methods have been used to obtain $(\partial S_e/\partial V)_T$, where S_e is molar electronic entropy and V is molar volume. They gave different answers. The reason has not been well understood. In any case one can deduce the volume dependence of the density of states from $\partial S_e/\partial V$. From Eq. (9) the phonon-corrected electronic specific heat (per mole) C_e is

$$C_e/T = \tfrac{2}{3}\pi^2 k^2 N(E_F)_{\rm BS}(1+\lambda) \;, \qquad (17)$$

where $N(E_F)_{\rm BS}$ is the density of states per mole for bare electrons. If a possible temperature dependence of λ, which will be discussed later, is neglected, a thermodynamical relation,

$$\frac{C_e}{T} = \frac{\partial S_e}{\partial T} \;, \qquad (18)$$

leads to $S_e = C_e$.

The volume dependence of the density of state is

$$\left(\frac{\partial \ln(E_F)_{\rm BS}}{\partial \ln V}\right)_T + \left(\frac{\partial \ln(1+\lambda)}{\partial \ln V}\right)_T = \left(\frac{\partial \ln S_e}{\partial \ln V}\right)_T$$
$$= \frac{V}{C_e}\left(\frac{\partial S_e}{\partial V}\right)_T \;. \qquad (19)$$

The electronic Grüneisen's constant, $(V/C_e)(\partial S_e/\partial V)_T \equiv g_e$, gives the volume dependence of the phonon-enhanced density of states, $N(E_F)_{\rm BS}(1+\lambda)$.

a. $(\partial S_e/\partial V)_T$ *derived from low-temperature thermal expansion.* An elementary thermodynamics relation[52] gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa}, \tag{20}$$

where S, α, and κ are molar entropy, the (volume) thermal-expansion coefficient, and the compressibility, respectively. Varley[53] and Andres[54] considered an electronic and a lattice contribution to S and α at low temperature:

$$\left(\frac{\partial S_l}{\partial V}\right)_T + \left(\frac{\partial S_e}{\partial V}\right)_T = \kappa^{-1}(\alpha_l + \alpha_e), \tag{21}$$

where l and e refer to the lattice and the electronic contribution, respectively. It is a general practice to identify α_e as a linearly temperature-dependent part of the thermal expansion at low temperature,[54, 55]

$$\left(\frac{\partial S_e}{\partial V}\right)_T = \frac{\alpha_e}{\kappa} . \tag{22}$$

The electronic Grüneisen's constant g_e given in Eq. (19) or by $\partial \ln n(E_F)_{\mathrm{BS}}\, \Omega(1+\lambda)/\partial \ln V$ obtained from the thermal-expansion data at low temperature is[55,56]

$$g_e = 1.8 \pm 0.1 \quad \text{for Al}, \tag{23}$$

$$g_e = 1.5 \pm 0.2 \quad \text{for Nb}. \tag{24}$$

b. $(\partial S_e/\partial V)_T$ *derived from volume dependence of parameters in superconducting state.* From the thermodymanical relation of the superconductor,[57]

$$\Delta S = S - S_s = -\frac{V}{4\pi} H_c \left(\frac{\partial H_c}{\partial T}\right)_P, \tag{25}$$

where S and S_s are molar entropy for the normal and the superconducting state. H_c is the critical field. At low temperature, $T \lesssim \frac{1}{10} T_c$,

$$\Delta S = (S_l + S_e) - (S_{sl} + S_{se}) = S_e , \tag{26}$$

where the additional subscript s refers to the superconducting state. The assumptions used in deriving Eq. (26) are (i) $S_l = S_{sl}$ and (ii) S_{se} goes to zero faster than S_e as the temperature is reduced. The volume dependence of S_e can be obtained from the volume dependence of H_c and $\partial H_c/\partial T$,

$$\left(\frac{\partial S_e}{\partial V}\right)_T = -\frac{1}{4\pi} \frac{\partial}{\partial V} \left[V H_c \left(\frac{\partial H_c}{\partial T}\right)_P \right]_T, \qquad T \lesssim T_c/10 . \tag{27}$$

Harris and Mapother[58] obtained g_e for Al using a similar method. Since they could not perform the pressure experiment at low enough temperature, they had to use a semiempirical relation (a similarity principle) in order to deduce g_e. The result is

$$g_e = 6.65 \pm 3 \quad \text{for Al}. \tag{28}$$

The discrepancy between (23) and (28) does not seem to be due to the similarity principle used. Garfinkel and Mapother[59] observed the same discrepancy for Pb, where they could use relation (27) directly, since T_c for Pb is higher than for Al. Similar data for some other metals are tabulated in the review article by Brandt and Ginzburg (Table 3).[60] It may be possible to disregard g_e given by (28) because of the large experimental error.[61] The discrepancy seems to be real, however, for Pb. g_e for Pb derived from relation (27) is[59]

$$g_e = 5.0 \pm 0.7 \quad \text{for Pb}, \tag{29}$$

where κ is taken as 2.1×10^{-6} atm^{-1}. The thermal-expansion data give[56]

$$g_e = 1.7 \pm 0.5 \quad \text{for Pb}. \tag{30}$$

The discrepancy of a factor of about 3 cannot be explained by the naive quasiparticle picture of the electron-phonon interaction given in Eqs. (17) and (19). The enhancement factor $1+\lambda$ has not been taken into account in most of the published works,[54,56,58] however. It is noted that the electron-phonon interaction can be important in deriving $\partial \ln N(E_F)_{\mathrm{BS}}/\partial \ln V$ from Eq. (19). For Al, λ is only 0.38 as stated before, but the volume derivative of λ is $\partial \ln\lambda/\partial \ln V = 3.0$, $[\partial \ln(1+\lambda)/\partial \ln V = 0.84]$, as will be derived later. The phonon clothes can be softer than the electrons themselves. The pressure dependence of the phonon spectrum of Pb from tunneling experiments suggests that $\partial \ln(1+\lambda)/\partial P$ is almost eight times as large as $\partial \ln N(E_F)_{\mathrm{BS}}/\partial P$.[62] The numerical value itself may not be taken too seriously, however, because of the assumptions involved. Trofimenkoff and Carbotte estimated $\partial \ln\lambda/\partial \ln V$ as 2.7 for Pb.[63] The results by McMillan[13] indicate that λ changes a great deal with the change in composition of Nb-Mo alloys. We are also aware of the danger of using the naive quasiparticle picture indiscriminately.[64]

It may be considered intuitively that the large value derived from relation (27) is the volume dependence of the fully dressed entropy and the smaller value derived from (22) is for the partially stripped electron entropy.

c. Tentative explanation for discrepancy. A tentative interpretation of the discrepancy mentioned in the previous sections is proposed here based on Éliashberg's[65] and Grimvall's[66] theory of the electron-phonon interaction. Éliashberg derived the entropy due to the electron-phonon interaction as

$$S' = \gamma T + \beta T^3 \ln(\Theta_D/T), \tag{31}$$

where γ and β are constants, and Θ_D is the Debye temperature. It is noted that the first term is a "pseudoelectron"-type entropy, since it is proportional to T, and the second contribution has a "pseudolattice" form because $\ln(\Theta_D/T)$ is nearly constant in the pertinent temperature range.

The total specific heat C is

$$C=T\left(\frac{\partial S_l}{\partial T}\right)_V+T\left(\frac{\partial S_e}{\partial T}\right)_V+T\left(\frac{\partial S'}{\partial T}\right)_V . \tag{32}$$

The contribution from the electron-phonon interaction C' is

$$C'=\gamma T+\beta[3\ln(\Theta_D/T)-1]T^3 \quad , \tag{33}$$

which also consists of the pseudoelectron and the pseudolattice term.

If one takes the difference between the specific heat of the normal state and of the superconducting state at low temperature,

$$\Delta C=(C_l-C_{sl})+(C_e-C_{se})+(C'-C_s'), \quad T<T_c \tag{34}$$

where s refers to the superconducting state. Since $C_l=C_{sl}$ [65] and C_{se} as well as C_s' go as $\exp(-T_c/T)$, ΔC will be

$$\Delta C=C_e+C' \quad \text{at } T<\tfrac{1}{10}T_c . \tag{35}$$

Bryantand Keesom[67] noticed that ΔC for In contains the pseudolattice term as is expected from Eqs. (33) and (35).[68]

The thermal-expansion coefficient α is

$$\frac{\alpha}{\kappa}=\left(\frac{\partial S_l}{\partial V}\right)_T+\left(\frac{\partial S_e}{\partial V}\right)_T+\left(\frac{\partial S'}{\partial V}\right)_T , \tag{36}$$

where

$$\left(\frac{\partial S'}{\partial V}\right)_T=\left(\frac{\partial\gamma}{\partial V}\right)_T T+\frac{\beta}{V}\left(\frac{\partial\ln\beta}{\partial\ln V}\ln\frac{\Theta_D}{T}+\frac{\partial\ln\Theta_D}{\partial\ln V}\right)_T T^3 . \tag{37}$$

Here we find the T and the T^3 term again.

The volume derivative of Eq. (25) is

$$\frac{\partial}{\partial V}\left(-\frac{VH_c}{4\pi}\frac{\partial H_c}{\partial T}\right)=\frac{\partial\Delta S}{\partial V}=\left(\frac{\partial S_e}{\partial V}\right)_T+\left(\frac{\partial S'}{\partial V}\right)_T, \quad T\lesssim\tfrac{1}{10}T_c . \tag{38}$$

The linear part (in T) of the thermal expansion represents the bare-electron contribution and the pseudoelectronic part of the electron-phonon interaction (the partially stripped electrons). The volume derivative of the superconducting parameter, Eq. (38), gives the fully clothed results (with the pseudoelectronic and the pseudolattice effect). The discrepancy between these two measurements is due to the pseudolattice contribution, the second term in Eq. (37). The magnitude of $(\partial S'/\partial V)_T$ could be comparable with or larger than $(\partial S_e/\partial V)_T$ mentioned before. The T^3 term in Eq. (37) could be larger than the T term, depending on $\partial\ln\beta/\partial\ln V$ and T. The temperature where the pressure experiments of the superconductor are usually performed is not much lower than T_c, the exception being the case of Pb.[59] Therefore the T^3 term in Eq. (37) can be appreciable. Since the accuracy of these measurements is relatively poor, the expected T^3 dependence was not detected.

The pseudolattice term can be taken into account as the temperature dependence of λ. λ in Eq. (17) is then the sum of the temperature-independent part and a $T^2[\ln(\Theta_D/T)-\frac{1}{3}]$ term. The temperature dependence of λ was observed as the temperature-dependent cyclotron effective mass.[69,70]

3. *Microsopic Theory of Superconductivity*

The thermodynamical relation (25) is independent of the detailed mechanism of superconductivity. The combination of the semiempirical relations and the thermodynamical relations have been used extensively for the purpose of deriving the electronic Grüneisen's constant from the pressure dependence of the superconductor parameters.[58,60,71] These relations generally do not depend on the microscopic mechanism of the superconductivity.

Since the first successful microscopic theory of superconductivity (BCS theory[48]) contains the density of states $N(E_F)$ explicitly in the expression for T_c,

$$T_c=0.85\Theta_D e^{-1/N(E_F)V} , \tag{39}$$

a few attempts have been made to retrieve the volume dependence of $N(E_F)$ out of $\partial T_c/\partial P$.[8,72] A more refined theory,[13] however, seems to discourage these attempts strongly.

McMillan[13] gave the following expression for T_c:

$$T_c=\frac{\Theta_D}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] , \tag{40}$$

where μ^* is the Coulomb pseudopotential of Morel and Anderson.[73] It is generally believed that μ^* is insensitive to the volume change.[63,74-77] The electron-phonon coupling constant λ, which has been discussed in Sec. III A, is expressed as[13]

$$\lambda=N(E_F)\langle\mathscr{I}^2\rangle/M\langle\omega^2\rangle , \tag{41}$$

where $\langle\mathscr{I}^2\rangle$ is the average electronic matrix elements of the deformed crystal potential and $\langle\omega^2\rangle$ is an average of the square of the phonon frequency. It is also known that the product $N(E_F)\langle\mathscr{I}^2\rangle$ is insensitive to $N(E_F)$ itself. This is particularly the case for materials having a high density of d states at the Fermi surface.[13,78] The product is also believed to be insensitive to the volume change.[79] Therefore it may be concluded that $\partial N(E_F)/\partial P$ cannot be derived from $\partial T_c/\partial P$ with confidence based on the present microscopic theory of superconductivity. First-principles calculations for $\partial T_c/\partial P$ [63,74-76] also indicate that the phonon spectrum change is the dominant factor in the observed pressure dependence of T_c. The volume derivative of Eq. (40) is, however, very useful in deriving the volume dependence of the phonon-electron enhancement factor as will be shown in Sec. III C.

It is concluded that the best available information to deduce $d\ln\chi_{sp}^{*}\Omega/d\ln V$ from is, in general, the low-temperature thermal expansion. The correction due to the volume dependence of the enhancement factors ought to be included however. The detailed study of the low-temperature magnetostriction (Sec. III B 1) is not available at the moment. The theoretical implication of the electronic thermal expansion is simple and the experimental accuracy is high. The linear part of the observed thermal expansion does not contain the pseudolattice-type electron-phonon interaction, whose behavior is not well known. The pressure dependence of the superconductor parameters is more difficult to measure, and the experimental uncertainty is much larger than the thermal-expansion results. The theoretical implication for most of the measurements where the semiempirical relations and the similarity principle are used is less clear. The simplest case expressed by Eq. (27) is only applicable to Pb. The result derived from Eq. (27) could contain the effect of the pseudolattice contribution of the electron-phonon interaction.

C. Newly Proposed Method

We propose a systematic scheme to estimate the volume dependence of χ_{sp}^{*} from the electronic thermal-expansion coefficient α_e. The basic scheme is as follows: $d\ln N(E_F)_{BS}/d\ln V$ is derived from α_e, which is proportional to the volume dependence of the phonon-clothed density of states [Eqs. (19) and (22)], by stripping off the phonon-cloth effect. The volume dependence of the phonon clothes is derived from Eq. (40). The volume derivative of the bare density of states thus obtained will be clothed with the electron-electron interaction effect.

The volume derivative of Eq. (40) is

$$\frac{d\ln T_c}{d\ln V}=\frac{d\ln\Theta_D}{d\ln V}+\ln\left(\frac{\Theta_D}{1.45T_c}\right)\varphi\,, \tag{42}$$

where

$$\varphi=d\ln\left(\frac{\lambda-\mu^{*}(1+0.62\lambda)}{1.04(1+\lambda)}\right)\Big/\,d\ln V\,. \tag{43}$$

One can evaluate φ from the observed value of $d\ln T_c/d\ln V$, Grüneisen's constant $d\ln\Theta_D/d\ln V$, and Θ_D/T_c. The volume derivative of the phonon enhancement factor is

$$\frac{d\ln(1+\lambda)}{d\ln V}=\frac{\lambda-\mu^{*}(1+0.62\lambda)}{1+0.38\mu^{*}}\,\varphi\,, \tag{44}$$

where $d\mu^{*}/dV$ is assumed to be zero.[63,74–77] μ^{*} is almost constant for the same series of metals ($\mu^{*}=0.13$ for transition metals, $\mu^{*}=0.1$ for polyvalent metals).[13]

From Eq. (19) the volume derivative of the band-structure density of states is derived as

$$\frac{d\ln N(E_F)_{BS}}{d\ln V}=g_e-\frac{d\ln(1+\lambda)}{d\ln V}\,, \tag{45}$$

where g_e is obtained from α_e,

$$g_e=V\alpha_e/C_e\kappa\,. \tag{46}$$

From Eq. (15) and the relation $N(E_F)_{BS}=Vn(E_F)_{BS}$, the volume dependence of the band effective mass m^{*} is obtained as

$$\frac{d\ln m^{*}}{d\ln V}=\frac{d\ln N(E_F)_{BS}}{d\ln V}-\frac{2}{3}\,. \tag{47}$$

The proposed scheme to derive the volume derivative of $1+\lambda$, $N(E_F)_{BS}$, and m^{*} has a wide applicability, the important exception being for nonsuperconducting metals. The parameters required for the present derivation are available for most of the polyvalent metals. The validity and the reliability of the present method may, however, have to be evaluated more carefully in the future when first-principles calculations of $N(E_F)_{BS}$ and m^{*} are performed as a function of V and/or direct measurements for the derived parameters are available.

The next step is to derive $d\ln\chi_{sp}^{*}/d\ln V$ from the volume derivative of the stripped density of states given by Eq. (45). This is more subtle than the previous process, however, since the electron-electron enhancement does not seem to be completely understood. Silverstein's relation, Eq. (14), is legitimate only for the nearly-free-electron case. The alternative, Eq. (13),[4,46,80] contains a molecular field parameter α whose exact expression depends on *ad hoc* models.

If one uses Eq. (14), the volume derivative of the electron-electron-enhanced susceptibility is

$$\frac{d\ln\chi_{sp}^{*}}{d\ln V}=\left(1+\frac{(m/m^{*}-1)\chi_0}{\chi_{free}}\right)^{-1}\times\left[\frac{d\ln\chi_0}{d\ln V}+\frac{\chi_0}{\chi_{free}}\,\frac{m}{m^{*}}\,\frac{d\ln m^{*}}{d\ln V}-\frac{1}{3}\,\frac{\chi_0}{\chi_{free}}\left(\frac{m}{m^{*}}-1\right)\right]\,, \tag{48}$$

where the semiempirical value for $d\ln m^{*}/d\ln V$ is available in Eq. (47). Figure 4 in Ref. 14 gives us $d\ln\chi_0/d\ln V$ corresponding to the pertinent r_s. The second term in the square bracket is usually larger than the other terms because $d\ln\chi_0/d\ln V\simeq-\frac{1}{3}$ and $m\simeq m^{*}$ for the free-electron approximation to be valid. This is consistent with the assumption made by Weaver and Narath.[4] They assumed that the dominant volume dependence comes from dm^{*}/dV, although they utilized a different expression for χ_{sp}^{*}.

If one uses the Stoner-type expression for the susceptibility,

$$\chi_{sp}^{*}=(1-\alpha'\chi_{sp})^{-1}\chi_{sp}\,,\quad \alpha=\alpha'\chi_{sp} \tag{49}$$

one obtains

$$\frac{d\ln\chi_{sp}^{*}}{d\ln V}=(1-\alpha'\chi_{sp})^{-1}\,\frac{d\ln\chi_{sp}}{d\ln V}\,, \tag{50}$$

where the volume dependence of α' is neglected.[4]

It is noted that $d\ln\chi_{sp}^*/d\ln V$ is enhanced by the same factor, $(1-\alpha'\chi_{sp})^{-1}$, as for χ_{sp}. From Eq. (10) we have

$$\frac{d\ln\chi_{sp}}{d\ln V}=\frac{d\ln n(E_F)_{BS}}{d\ln V}=\frac{d\ln N(E_F)_{BS}}{d\ln V}-1\,. \tag{51}$$

Since $d\ln N(E_F)_{BS}/d\ln V$ is obtainable semiempirically as stated above, one can get $d\ln\chi_{sp}^*/d\ln V$, if the enhancement factor for χ_{sp} itself is known. For instance, the temperature dependence of the susceptibility would give some information about the molecular field parameter α'.[81]

IV. ANALYSIS OF $d\ln K/d\ln V$ FOR Al

The volume dependence of the Al Knight shift, Eq. (1), is the sum of two contributions as is shown in Eq. (8). The second term, $d\ln\chi_s\Omega/d\ln V$, will be evaluated semiempirically using the scheme mentioned in Sec. III.

Olsen *et al.*[79] obtained φ as defined by Eq. (43) from essentially the same equation as Eq. (42),

$$\varphi=3.4 \text{ for Al.} \tag{52}$$

Equation (44) leads to

$$\frac{d\ln(1+\lambda)}{d\ln V}=0.84 \tag{53}$$

or

$$\frac{d\ln\lambda}{d\ln V}=3.0\ . \tag{54}$$

Using the Grüneisen's constant g_e obtained from the electronic thermal-expansion coefficient [Eq. (23)], we get the volume dependence of the bare-electron density of states [Eq. (45)] as

$$\frac{d\ln N(E_F)_{BS}}{d\ln V}=1.0\pm0.1\ . \tag{55}$$

It is noted that $d\ln(E_F)_{BS}/d\ln V$ thus obtained is about 30% larger than the free-electron value $\frac{2}{3}$. The volume dependence of the band-structure effective mass is from Eq. (47),

$$\frac{d\ln m^*}{d\ln V}=0.3\pm0.1\ . \tag{56}$$

Since the free-electron model is believed to be a fair approximation in evaluating the electron-electron enhancement for the susceptibility, $d\ln\chi_{sp}^*/d\ln V$ is estimated from Eq. (48) as

$$\frac{d\ln\chi_{sp}^*}{d\ln V}=+0.14\ , \tag{57}$$

where m^*/m is taken as 1.08.[13] As stated before, the second term in the square bracket is largest. $d\ln\chi_{sp}^*\Omega/d\ln V$, which is to be used for the second term in Eq. (8), is

$$\frac{d\ln\chi_s\Omega}{d\ln V}=\frac{d\ln\chi_{sp}^*\Omega}{d\ln V}=1.11\ . \tag{58}$$

From Eqs. (1), (8), and (58) one can derive the volume dependence of $\langle|\Psi(0)|^2\rangle$ as

$$\frac{d\ln\langle|\Psi(0)|^2\rangle}{d\ln V}=-2.12\ . \tag{59}$$

The uncertainty of the value derived above is difficult to estimate. The error is probably not more than ± 0.2.

The precise physical implication of the volume dependence of $\langle|\Psi(0)|^2\rangle$ has to wait for the first-principles calculation. It is noted, however, that (i) it has the same sign and the same order of magnitude as is expected from the simple uniform scaling of the wave function; (ii) its size is one order of magnitude larger than the corresponding value for Na, but it is about the same as Cs,[2] although we are aware of the crudeness of the estimate in Ref. 2 which was available at that time; and (iii) it is not inconsistent with the recent pressure-dependence experiments of the Fermi surface.[82] The volume dependence of the cross-sectional area of the Fermi surface is usually somewhat larger than is expected from the simple scaling. Particularly the "neck" area for Cu has ~ 4–5 times larger volume dependence than the scaling prediction.[82]

V. ANALYSIS OF $d\ln K/d\ln V$ FOR Nb

The volume dependence of the Nb Knight shift, which is expressed by Eq. (7), will be analyzed using a similar method as was utilized for V metal.[8] The result of the analysis is, however, less clear cut. Since the V Knight shift is dominated by K_0 and K_s is almost negligible, the derivation of $d\ln K_0/d\ln V$ was not very difficult. Since McMillan's theory[13] was not available and the physical implications of (i) the low-temperature thermal expansion and (ii) the various enhancement factors were not clear when Ref. 8 was prepared, there was some confusion in the estimate for $d\ln K_d/d\ln V$. Nevertheless, it is our belief that the deduced value for V, $d\ln K_0/d\ln V=-0.49\pm0.10$, is basically correct.

The partition of the Nb Knight shift into its components is[83]

$$K_s=0.37\%,\quad K_d=-0.23\%,\text{ and }K_0=0.74\%$$

These values are essentially derived from theoretical estimates. The total calculated Knight shift K_{calc} (= 0.88%) is slightly larger than the experimental value 0.85% quoted in Ref. 83. It is, however, closer to the experimental value 0.87% by Drain.[84,85] The semiempirical partition of the Nb Knight shift into two parts, K_s+K_d and K_0, has also been reported[86]:

$$\frac{d\ln K}{d\ln V}=\frac{K_s}{K}\frac{d\ln K_s}{d\ln V}+\frac{K_d}{K}\frac{d\ln K_d}{d\ln V}+\frac{K_0}{K}\frac{d\ln K_0}{d\ln V}$$

$$=0.42\frac{d\ln K_s}{d\ln V}-0.26\frac{d\ln K_d}{d\ln V}+0.84\frac{d\ln K_0}{d\ln V}\ . \quad (60)$$

Since the weight of the first term, 0.42, is comparable to the weight of the other terms, the estimate of $d\ln K_s/d\ln V$ is important for the derivation of the rest of the terms. Unfortunately there seems to be no reliable way to estimate this term, except probably for a first-principles calculation. The recent APW calculation results for Nb metal[87] do not include any information about the wave functions nor their volume derivatives. One has to depend on some educated guess. The electronic configuration of the Nb s-p band suggests using the $d\ln K_s/d\ln V$ value for Rb. If this is an acceptable analogy, one gets from Ref. 2

$$\frac{d\ln K_s}{d\ln V}\simeq-0.1\ . \quad (61)$$

Another guess is to estimate the components of Eq. (8) as follows: We assume that $d\ln\chi_s\Omega/d\ln V$ is roughly equal to the electronic Grüneisen's constant for the s-p band. The implication is that the effect of the electron-phonon enhancement factor roughly cancels the susceptibility enhancement factor. Since g_e is empirically known to be in the neighborhood of 1.5,[72] the second term of Eq. (8) would be

$$\frac{d\ln\chi_s\Omega}{d\ln V}=+1.5\ . \quad (62)$$

The first term would be of the order of −1. Note that this value would be smaller than $d\ln\langle|\Psi(0)|^2\rangle/d\ln V$ for Al, since the number of the s-p band electrons in Nb is less than in Al. $d\ln K_s/d\ln V$ would be

$$\frac{d\ln K_s}{d\ln V}\simeq+0.5. \quad (63)$$

The second contribution in Eq. (60) is expressed by

$$\frac{d\ln K_d}{d\ln V}=\frac{d\ln\langle\rho(0)\rangle_d}{d\ln V}+\frac{d\ln\chi_d^*\Omega}{d\ln V}\ . \quad (64)$$

The first term of Eq. (64) is estimated from the pressure-dependence results of Fe metal as is shown in Ref. 8,

$$\frac{d\ln\langle\rho(0)\rangle_d}{d\ln V}\simeq-0.2\ . \quad (65)$$

It seems that we have some empirical clue for the estimate of the second term of Eq. (64). Fawcett and White[51] derived the volume dependence of the spin susceptibility from the low-temperature magnetostriction,

$$\frac{d\ln\chi_{sp}^*\Omega}{d\ln V}=+2.4\ . \quad (66)$$

Since the d-band susceptibility χ_d^* is much larger than the s-p-band susceptibility χ_s^*, one may take

$$\frac{d\ln\chi_d^*\Omega}{d\ln V}=+2.4\ . \quad (67)$$

It is interesting to compare the value given above and the corresponding value deduced from the scheme proposed in Sec. IV. Although the derivation of $d\ln N(E_F)_{\mathrm{BS}}/d\ln V$ and $d\ln m^*/d\ln V$ is legitimate for Nb, Eq. (48) is hardly applicable since the free-electron model is a poor approximation for the d-band electrons. In the following estimates, the distinction between the s-p and the d band is neglected. The parameters derived, therefore, refer to an average over the two bands. The weight for the d band is dominant.

The value for φ derived from Eq. (42) is

$$\varphi=-0.32\ , \quad (68)$$

where the following values for the parameters were utilized: $dT_c/dP=(1.2\pm0.2)\times10^{-5}$ °K/bar,[88] $T_c=9.2$ °K, $\Theta_D=252$ °K, and $d\ln\Theta_D/d\ln V=-1.35$.[72] The present value for φ is different from the previously reported value by Olsen *et al.*[71] because the new value for dT_c/dP was used. Equation (44) yields

$$\frac{d\ln(1+\lambda)}{d\ln V}=-0.19\ , \quad (69)$$

where $\lambda=0.82$ and $\mu^*=0.13$ were used.[13] From g_e for Nb, 1.5 ± 0.2,[56] one gets

$$\frac{d\ln N(E_F)_{\mathrm{BS}}}{d\ln V}=1.7\ , \quad (70)$$

$$\frac{d\ln m^*}{d\ln V}=1.0\ . \quad (71)$$

If one uses expression (50) for the volume dependence of the enhanced susceptibility, one obtains

$$\frac{d\ln\chi_{sp}^*\Omega}{d\ln V}=(1-\alpha)^{-1}\frac{d\ln\chi_{sp}\Omega}{d\ln V}=(1-\alpha)^{-1}\frac{d\ln N(E_F)_{\mathrm{BS}}}{d\ln V}\ . \quad (72)$$

In order for the two experimentally derived values (66) and (70) to be compatible, the enhancement parameter α must be about 0.3, which seems to be reasonable.[89]

If one uses Eq. (48), one obtains

$$\frac{d\ln\chi_{sp}^*\Omega}{d\ln V}=1.8\ , \quad (73)$$

where m^*/m was assumed to be 0.7 based on the APW calculation.[87] The result is in poor agreement with the value given in (66). This is not surprising because (48) is not valid for Nb. If one adopts the semiempirical value for $d\ln\chi_0/d\ln V$ derived from (70),

$$\frac{d\ln\chi_0}{d\ln V}=\frac{d\ln n(E_F)_{\mathrm{BS}}}{d\ln V}=0.7,$$

instead of Silverstein's *ab initio* value,[14] the situation is more favorable, although the theoretical justification is not clear. The result is

$$\frac{d\ln\chi_{\mathrm{sp}}^{*}\Omega}{d\ln V}=2.5,$$

where $\chi_0/\chi_{\mathrm{free}}$ was assumed to be $1.2\simeq 1.3$.

The last term in Eq. (60) can be derived from the estimates for the first and the second term given above. The estimated value for $d\ln K_d/d\ln V$ is relatively reliable, since the dominant component, the second term in Eq. (64), was derived semiempirically. The estimate of the first term in Eq. (60) is, however, unreliable, and unfortunately its contribution to $d\ln K/d\ln V$ is sizable. Therefore, the deduced value for $d\ln K_0/d\ln V$ has a considerable uncertainty. If one uses the estimate for $d\ln K_s/d\ln V$ given in Eq. (61), one obtains

$$\frac{d\ln K_0}{d\ln V}=+0.4. \tag{74}$$

If the value in Eq. (63) is used, the result is

$$\frac{d\ln K_0}{d\ln V}=+0.1. \tag{75}$$

The volume dependence of K_0 consists of two terms,[8]

$$\frac{d\ln K_0}{d\ln V}=\frac{d\ln\langle r^{-3}\rangle_D}{d\ln V}+\frac{d\ln\Delta^{-1}}{d\ln V}\ . \tag{76}$$

Here Δ is the average bandwidth of the d band. Since the first term is most likely negative and the second term is positive,[8] the small positive value for $d\ln K_0/d\ln V$ given in Eq. (74) or (75) implies that the magnitude of the $d\ln\Delta^{-1}/d\ln V$ is somewhat larger than the (absolute) magnitude of the first term. More specifically, since it is expected that[8]

$$0\gtrsim\frac{d\ln\langle r^{-3}\rangle_D}{d\ln V}\gtrsim-1\ , \tag{77}$$

the second term is

$$0.1\lesssim\frac{d\ln\Delta^{-1}}{d\ln V}\lesssim1.4, \tag{78}$$

which seems to be reasonable and compatible with the results for V.[8]

VI. CONCLUSION

The pressure dependence of the Al and the Nb Knight shifts was measured with a digitally slaved time averager. The previously proposed methods to derive $d\ln\chi_{\mathrm{sp}}^{*}\Omega/d\ln V$ were discussed critically. Particular attention was paid to the effect of the electron-phonon and the electron-electron enhancement factor. It is pointed out that the volume dependence of $1+\lambda$, $N(E_F)_{\mathrm{BS}}$, and m^* can be deduced semiempirically. $d\ln\chi_{\mathrm{sp}}^{*}/d\ln V$ was also deduced from these parameters based on the expression for the electron-electron-enhanced susceptibility. A possible origin of the discrepancy between $\partial S_e/\partial V$ derived from the low-temperature thermal expansion and from the pressure dependence of the superconductor parameters was discussed in terms of the Éliashberg's theory of the electron-phonon interaction. The volume derivative of $\langle|\Psi(0)|^2\rangle$ for Al was derived from the measured value of dK/dP using the scheme proposed here. The origin of the discrepancy among the reported values of $K(T)$ for Al was also suggested. From the observed value of $d\ln K/dP$ for Nb, the volume dependence of the orbital Knight shift for this metal was deduced.

ACKNOWLEDGMENTS

The authors are indebted to Dr. A. W. Overhauser and Dr. K. J. Duff for helpful discussions with respect to the electron-phonon interaction presented in Secs. III B 2 *a*–III B 2 *c*.

---

[1] P. Jena, T. P. Das, and S. D. Mahanti, Phys. Rev. B <u>1</u>, 432 (1970).

[2] G. Benedek and T. Kushida, J. Phys. Chem. Solids <u>5</u>, 241 (1958).

[3] E. T. Micar, G. M. Stocks, and W. H. Yong, J. Phys. C <u>2</u>, 1661 (1969).

[4] H. T. Weaver and Albert Narath, Phys. Rev. B <u>1</u>, 973 (1970).

[5] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. <u>134</u>, A650 (1964).

[6] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters <u>9</u>, 262 (1962).

[7] Toshimoto Kushida and Lajos Rimai, Phys. Rev. <u>148</u>, 593 (1966).

[8] Toshimoto Kushida and J. C. Murphy, Phys. Rev. <u>178</u>, 433 (1969).

[9] J. T. Hickmott, Jr., T. Kushida, and J. C. Murphy, Rev. Sci. Instr. <u>38</u>, 29 (1967).

[10] V. Heine, Proc. Roy. Soc. (London) <u>A240</u>, 354 (1957).

[11] W. A. Harrison, Phys. Rev. <u>118</u>, 1182 (1960).

[12] Wei-Mei Shu, T. P. Das, and G. D. Gaspari, Phys. Rev. <u>152</u>, 270 (1966).

[13] W. L. McMillan, Phys. Rev. <u>167</u>, 331 (1968).

[14] S. D. Silverstein, Phys. Rev. <u>130</u>, 1703 (1963).

[15] Terry Cole, Toshimoto Kushida, and Hanan C. Heller, J. Chem. Phys. <u>38</u>, 2915 (1963).

[16] Arnold H. Silver and Toshimoto Kushida, J. Chem. Phys. <u>38</u>, 865 (1963).

[17] The authors will be glad to send a complete circuit diagram on request.

[18] A logic operation, $(a_1, a_2, \ldots)\rightarrow(\bar{a}_1, \bar{a}_2, \ldots)$, is called complementing, where $(a_1, a_2, \ldots)$ represents a binary number, a_i's being 1 or 0. $\bar{a}_i$ is NOT*ai*. For example, the complement of (11001) is (00110).

[19] R. J. Noer, Proc. Phys. Soc. (London) <u>86</u>, 309

(1965).

[20] Albert Narath and H. T. Weaver, Phys. Rev. 175, 373 (1968).

[21] R. W. Weinert and R. T. Schumacher, Phys. Rev. 172, 711 (1968).

[22] F. Borsa and R. G. Barnes, J. Phys. Chem. Solids 27, 567 (1966).

[23] W. D. Knight, Phys. Rev. 96, 861 (1954).

[24] L. E. Drain, Proc. Phys. Soc. (London) 83, 755 (1964).

[25] D. W. Feldman, Ph. D. thesis, University of California, Berkeley, 1959 (unpublished).

[26] For instance, N. Bloembergen, and T. J. Rowland, Acta Met. 1, 731 (1953); D. Weinberg and N. Bloembergen, J. Phys. Chem. Solids 15, 240 (1960).

[27] J. Butterworth, Proc. Phys. Soc. (London) 85, 735 (1965).

[28] Harlan E. Schone, Phys. Rev. 183, 410 (1969).

[29] T. J. Rowland, *Nuclear Magnetic Resonance in Metals*, *Progress in Materials Science*, edited by B. Chalmers (Pergamon, New York, 1961), Vol. 9, p. 45.

[30] For instance, M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 420.

[31] D. O. Van Ostenburg, D. J. Lam, Masao Shimizu, and Atsushi Katsuki, J. Phys. Soc. Japan 18, 1744 (1963).

[32] D. J. Lam, J. J. Spokas, and D. O. Van Ostenburg, Phys. Rev. 156, 735 (1967).

[33] A private communication from Dr. A. C. Gossard indicates that their independent measurement rendered $d\ln K/dp = +(1.01 \pm 0.20)\%/26$ kbar. This is appreciably larger than the present result, although the sign is the same. The reason for the discrepancy is not understood. Their pressure is quasihydrostatic.

[34] 0.87%, quoted as private communication from L. E. Drain in Ref. 27.

[35] 0.85%, W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic , New York, 1956), Vol. 2, p. 122.

[36] P. W. Bridgman, *The Physics of High Pressure* (Bell, London, 1952), p. 160.

[37] C. H. Towns, C. Herring, and W. D. Knight, Phys. Rev. 77, 852 (1950).

[38] T. Muto and S. Kobayasi, J. Phys. Soc. Japan 19, 1837 (1964); see also Ref. 5.

[39] Ryogo Kubo and Yukio Obata, J. Phys. Soc. Japan 11, 547 (1956).

[40] L. E. Orgel, J. Phys. Chem. Solids 21, 123 (1961).

[41] D. S. Schreiber, Phys. Rev. 137, A860 (1965).

[42] All the simple metals are not necessarily expressed by Eq. (8), however. A first-principles calculation for Be indicates that K_d is more important than K_s for this metal, because of the lack in the s-rich segments of the Fermi surface. See Ref. 1.

[43] G. A. Matzkanin and T. A. Scott, Phys. Rev. 151, 360 (1966).

[44] To the authors' knowledge the only published measurements so far are for Mn and Sc: I. V. Svechkarev and A. S. Panfilov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 2, 501 (1965) [Soviet Phys. JETP Letters 2, 313 (1965)].

[45] For instance, R. E. Peierls, *Quantum Theory of Solids* (Oxford U. P., Oxford, England, 1955), p. 94.

[46] A. H. Wilson, *The Theory of Metals*, 2nd ed. (Cambridge U. P., Cambridge, England, 1958), p. 151.

[47] It is noted, however, that the second term has an important contribution to the Knight shift of Pt at higher temperature. See Ref. 7.

[48] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[49] S. D. Silverstein, Phys. Rev. 128, 631 (1962).

[50] David Rohy and R. M. Cotts, Phys. Rev. B 1, 2070 (1970).

[51] E. Fawcett and G. K. White, Bull. Am. Phys. Soc. 11, 78 (1966).

[52] For instance, F. W. Sears, *An Introduction to Thermodynamics, The Kinetic Theory of Gases and Statistical Mechanics*, 2nd ed. (Addison-Wesley, Reading, Mass., 1952), p. 149.

[53] J. H. O. Varley, Proc. Roy. Soc. (London) A237, 413 (1956).

[54] K. Andres, Physik Kondensierten Materie 2, 294 (1964).

[55] G. K. White, Cryogenics 2, 292 (1962).

[56] J. G. Collins and G. K. White, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1964), Vol. 4, p. 465.

[57] D. Shoenberg, *Superconductivity*, 2nd ed. (Cambridge U. P., Cambridge, England, 1962), p. 58.

[58] E. P. Harris and D. E. Mapother, Phys. Rev. 165, 522 (1968).

[59] M. Garfinkel and D. E. Mapother, Phys. Rev. 122, 459 (1961).

[60] N. B. Brandt and N. I. Ginzburg, Contemp. Phys. 10, 355 (1969).

[61] R. W. Munn, Phys. Rev. 178, 677 (1969).

[62] J. P. Franck, W. J. Keeler, and T. M. Wu, Solid State Commun. 7, 483 (1969).

[63] P. N. Trofimenkoff and J. P. Carbotte, Phys. Rev. B 1, 1136 (1970).

[64] Leo P. Kadanoff, Phys. Rev. 132, 2073 (1963). It is shown that a naive quasiparticle picture introduced in the nuclear relaxation rate in metals renders a false prediction, $(T_1T)^{-1} = kC[N(E_F)(1+\lambda)]^2$, where $\lambda(T) \to 0$ at $T > \Theta_D$. Such temperature dependence has never been observed. It is pointed out in this paper that the factor $1+\lambda$ in the effective density of states cancels by a wave-function renormalization factor. The calalog of the phenomena which either do or do not exhibit the many-body electron-phonon interaction is shown in R. E. Prange and L. P. Kadanoff, Phys. Rev. 134, A566 (1964).

[65] G. M. Éliashberg, Zh. Eksperim. i Teor. Fiz. 43, 1005 (1962) [Soviet Phys. JETP 16, 780 (1963)].

[66] Göran Grimvall, Physik Kondensierten Materie 9, 283 (1969).

[67] C. A. Bryant and P. H. Keesom, Phys. Rev. Letters 4, 460 (1960).

[68] Boorse *et al.* first reported a similar effect for Nb: H. A. Boorse, A. T. Hirshfeld, and H. Leupold, Phys. Rev. Letters 5, 246 (1960). But they found later that the effect was spurious: H. A. Leupold and H. A. Boorse, Phys. Rev. 134, A1322 (1964). The In result was re-examined more carefully and confirmed to be real: C. A. Bryant and P. H. Keesom, *ibid.* 123, 491 (1961).

[69] Jesse J. Sabo, Jr., Phys. Rev. B 1, 1325 (1970).

[70] P. B. Allen and M. L. Cohen, Phys. Rev. B 1, 1329 (1970).

[71] J. L. Olsen and H. Rohrer, Helv. Phys. Acta 30, 49 (1957); 33, 872 (1960); J. L. Olsen, E. Bucher,

M. Levy, J. Muller, E. Corenzwit, and T. Geballe, Rev. Mod. Phys. 36, 168 (1964).

[72] V. G. Bar'yakhtar and V. I. Makarov, Zh. Eksperim. i Teor. Fiz. 49, 1934 (1965) [Soviet Phys. JETP 22, 1320 (1966)].

[73] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[74] P. N. Trofimenkoff and J. P. Carbotte, Solid State Commun. 7, 661 (1969).

[75] Robert E. Hodder, Phys. Rev. 180, 530 (1969).

[76] P. E. Seiden, Phys. Rev. 179, 458 (1969).

[77] Since μ^* is related to the isotope shift α as shown in Ref. 13, Bucher *et al.* attempted to correlate α with the volume dependence of the exponent in Eq. (39), in order to investigate a possible volume dependence of μ^*: E. Bucher, J. Müller, J. L. Olsen, and C. Palmy, Cryogenics 5, 283 (1965).

[78] J. J. Hopfield, Phys. Rev. 186, 443 (1969).

[79] J. L. Olsen, K. Andres, and T. H. Gevalle, Phys. Letters 26A, 239 (1968).

[80] P. A. Wolff, Phys. Rev. 129, 84 (1963), Eq. (40).

[81] For instance, A. H. Wilson, *The Theory of Metals*, 2nd ed. (Cambridge U. P., Cambridge, England, 1958), p. 155. See also Ref. 31.

[82] For instance, W. J. O'Sullivan and J. E. Schirber, Phys. Rev. 170, 667 (1968).

[83] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yaffet, Rev. Mod. Phys. 36, 170 (1964).

[84] Quoted in Ref. 27 as the private communication from L. E. Drain.

[85] Slightly different experimental values have been reported as follows: (0.830 ± 0.004)% at 8.08 kOe, (0.825 ± 0.007)% at 11.0 kOe, and (0.821 ± 0.004)% at 14.0 kOe, in Ref. 31; and (0.821 ± 0.004)%, in Ref. 32.

[86] $K_s + K_d = -0.101\%$ and $K_0 = 0.931\%$ in Ref. 31.

[87] L. F. Mattheiss, Phys. Rev. B 1, 373 (1970).

[88] D. Köhnlein, Z. Physik 208, 142 (1968). It is also pointed out in this article that dT_c/dP for V and Nb is very structure sensitive. The previously reported values of dT_c/dP, which are negative or approximately zero, are for the strained samples.

[89] For $Nb_{0.75}Mo_{0.25}$ alloy, Van Ostenberg *et al.* estimated α as 0.24 based on the temperature dependence of the susceptibility. See Ref. 31.

PHYSICAL REVIEW B VOLUME 3, NUMBER 5 1 MARCH 1971

Temperature Dependence of the Positron-Annihilation Angular Correlation in Metals*

Birger Bergersen
Department of Physics, McMaster University, Hamilton, Ontario, Canada
and
Erkki Pajanne
Department of Theoretical Physics, University of Helsinki, Siltavuorenpenger 20, Helsinki 17, Finland

(Received 6 July 1970)

The thermal smearing of the positron-annihilation–angular-correlation curves is studied. In the case where the medium is a homogeneous interacting electron gas in thermal equilibrium, the analysis applied by Stewart and co-workers to the thermal smearing is shown to correctly give the effective mass. In conjuction with previous calculations of the effective mass, our results indicate that the observed thermal smearing cannot be explained as mainly caused by electron-gas effects. It is shown how the model can be modified to take into account the positron-phonon interaction. This reduces the discrepancy between theory and experiment, but not sufficiently to account fully for the experimental data. It is argued that new experiments are needed before one can decide whether it is necessary to consider new mechanisms in order to explain the effect. A convenient formalism is presented, which allows one to calculate all positron quantities at moderate nonzero temperatures within a given approximation scheme. The "ladder" approximation is used to illustrate the argument and to estimate correction terms.

I. INTRODUCTION

The temperature dependence of the 2γ angular correlation from positrons annihilating in alkali metals has been studied experimentally by Stewart and co-workers.[1,2] Employing a model described in detail by Kim,[2] they used their data to determine the ratio m^* of the effective and bare masses, and found the values 1.8 ± 0.3, 1.8 ± 0.2, 2.1 ± 0.3, 2.3 ± 0.3, respectively in Li, Na, K, and Rb. Calculations of the electron-positron,[3,4] positron-phonon,[5,6] and, in the case of Na, the band effective mass[2,7] all tend, however, to give values of m^* close to unity. This discrepancy makes it desirable to reexamine whether the experiment actually can be expected to give the positron effective mass.

The main purpose of the present paper is to demonstrate that, in the idealized case of a thermalized positron annihilating at moderate temperatures in an interacting electron gas, the above-mentioned