Change in the Pauli susceptibility of Li on melting

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The Pauli susceptibility χ_P of Li metal was measured below and above the melting point at constant pressure. χ_P increased by $(0.8 \pm 0.6)\%$ on melting. The corresponding increase at constant volume was deduced, by using the volume dependence of χ_P for solid Li, as $(0.7 \pm 0.6)\%$. From the observed change in the Knight shift on melting, the change in the electronic charge density at the nucleus P_F was also derived. P_F decreased by $(1.9 \pm 0.6)\%$ on melting at constant volume. The observed value of P_F and χ_P for solid Li does not collapse to the nearly-free-electron value, which was once postulated to characterize the liquid-metal state.

I. INTRODUCTION

The change in the Pauli susceptibility χ_P upon melting was measured accurately in Li metal. By using the present data and the previously measured change in the Knight shift K, we obtained the change in the amplitude of the wave functions at the Fermi surface, $\langle |\psi_k(0)|^2\rangle_{av} \equiv P_F$, upon melting, for the first time. The conventional Knight-shift expression

$$K = (8\pi/3)\chi_P \Omega P_F , \tag{1}$$

was used. Here Ω is atomic volume and χ_P is expressed in cgs volume units.

It is essential to obtain the values of P_F and χ_P independently (but they are rarely accessible experimentally), since they are related to the two fundamental entities of the electronic structure of metals, the wave functions and the density of states at the Fermi surface. It is not reliable to estimate the value of P_F or χ_P in order to obtain the other from a single experimental measurement, that of K, since the ambiguity in the theoretical estimate of one is not in general any better than that of the other.[1]

The change in P_F upon melting, $\Delta P_F \equiv P_{F,\text{liq}} - P_{F,\text{sol}}$, provides one with direct information about the wave-function change upon melting. This can be compared with theoretical calculations. The interpretation of the susceptibility change, $\Delta\chi_P \equiv \chi_{P,\text{liq}} - \chi_{P,\text{sol}}$, is more complicated. We feel, however, that recently developed theories[2] of χ_P are on the verge of supplying reliable information about the electronic structure from the experimental data. A knowledge of ΔP_F and $\Delta\chi_P$ is particularly useful in helping to understand the electronic states of liquid metals,[3] since these quantities may be compared directly with theoretical calculations. The effect of calculational techniques (selection of pseudopotential, etc.) tends to cancel when the differences between two states are calculated by using the same formalism.[4]

II. EXPERIMENTAL

The change in χ_P for Li metal was measured by the Schumacher-Slichter method.[5] The accuracy was improved by automating the measurements. The statistical average over hundreds of runs could be taken in a relatively short time. The procedure is essentially the same as the one used in the measurement of the pressure dependence of χ_P in solid Li and Na.[1,6] Details are given in Ref. 1. The measurements were most carefully performed just below and just above the melting point of Li in order to measure $\Delta\chi_P$.

The Li metal was purchased from Matheson, Coleman, and Bell. Its nominal purity was 99.9%. The metal was dispersed in mineral oil mechanically. The size of the dispersed particles was from 5 to 30 μm. This is sufficiently small for the rf signal of a Pound-Knight spectrometer to penetrate completely. The frequency of the spectrometer was approximately 16 MHz. The magnetic field was modulated with triangular waves at 6 Hz. The swing of the modulation was ± 20–40 G for conduction-electron spin-resonance measurements. The sample, coated with mineral oil, was sealed in vacuum. The temperature of the sample was controlled in a silicon oil bath. The line width of the conduction-electron spin-resonance line was typically 2.2 G peak to peak just below the melting point. The width increased somewhat just above the melting point. Each set of data taken under different conditions, consists of a few hundred runs.

The observed susceptibility change on melting is[7]

$$(\Delta\chi_P^A/\chi_{P,\text{sol}})_P = 0.008 \pm 0.006 . \tag{2}$$

Since the number of Li atoms does not change on melting, the observed value is the change in *atomic* susceptibility χ_P^A at constant pressure.

The estimated experimental error includes both the systematic and random error.

The volume increase on melting, 1.65%,[8] would change χ_P^A by a small amount.[6] The susceptibility change at constant volume is[9] derived as

$$(\Delta\chi_P^A/\chi_{P,\mathrm{sol}}^A)_V = 0.007 \pm 0.006 \ . \tag{3}$$

The fractional change in the atomic susceptibility at constant volume, Eq. (3), is the same as the fractional change in the volume susceptibility.

$$(\Delta\chi_P/\chi_{P,\mathrm{sol}})_V = 0.007 \pm 0.006 \ . \tag{4}$$

It is noted that the effect of the volume change on $\Delta\chi_P$ is considerably smaller than the value previously assumed.[4]

The observed Knight shift change upon melting at constant pressure is[10]

$$[(K_{\mathrm{liq}} - K_{\mathrm{sol}})/K_{\mathrm{sol}}]_P \equiv (\Delta K/K_{\mathrm{sol}})_P = -0.012 \pm 0.001 \ . \tag{5}$$

By using the pressure dependence data[11] for K_{sol}, ΔK at constant volume is derived as

$$(\Delta K/K_{\mathrm{sol}})_V = -0.013 \pm 0.001 \ . \tag{6}$$

The change in P_F at constant volume is therefore

$$(\Delta P_F/P_{F,\mathrm{sol}})_V = -0.019 \pm 0.006 \ . \tag{7}$$

If one uses the observed change in the total susceptibility χ_t on melting[12] and assumes that the ion core contribution to the total susceptibility is unchanged on melting, one obtains the change in diamagnetic susceptibility χ_d on melting as

$$[(\chi_{d,\mathrm{liq}}^A - \chi_{d,\mathrm{sol}}^A)/\chi_{t,\mathrm{sol}}^A]_P \equiv (\Delta\chi_d^A/\chi_{d,\mathrm{sol}}^A)_P = 0.001 \pm 0.007 \ . \tag{8}$$

The temperature dependence of χ_P^A was also measured from room temperature to 220 °C. The measurement consisted of two sets of runs. No temperature dependence was observed from room temperature to the melting point within the experimental error of ±1.0%. Collings[12] observed a pronounced peak in the total susceptibility just above the melting point. We noticed no temperature dependence in χ_P^A within our experimental error (±1.0%) from the melting point up to 220 °C.

III. DISCUSSION

The observed fact that $K_{\mathrm{liq}} \simeq K_{\mathrm{sol}}$ for most of the metals has been the subject of great controversy since the later 1950's.[3] Does this mean that both $\chi_P^A (= \chi_P \Omega)$ and P_F are roughly the same for liquid and solid? Or do χ_P^A and P_F change appreciably while keeping the product essentially unchanged on melting?[13] The experimental answer for Li is given in the previous section. Li is one of the best materials for the purpose of answering this question. The spin susceptibility in solid Li contains a large amount of enhancement due to the band-structure effect. If molten Li is free-electronlike, i.e., if Li ions lose their local correlation significantly on melting, one would expect a large decrease in χ_P and a substantial change in P_F on melting.

There was no rigorous way to include a large band-structure effect in the calculation of electron-electron enhanced susceptibility until recently.[14] The evaluation of ΔP_F is, at least in principle, more straightforward, although the numerical value of ΔP_F of Li has not been published.[15]

A very small change in P_F (Eq. 7) indicates that the electronic structure of Li is essentially preserved on melting. It appears to be surprising, however, that the observed ΔP_F is negative, since the average distribution of the neighboring ions about a particular ion under consideration becomes more spherically symmetric upon melting. This tendency increases the s component of the conduction-electron wave function and enhances P_F upon melting. This is indeed the case for Cd where $P_{F,\mathrm{liq}} > P_{F,\mathrm{sol}}$.[16]

Another effect of melting is to increase the amplitude of lattice vibration; this also effects P_F. In fact, ΔP_F can be written

$$(\Delta P_F)_V = (\Delta P_F)_{\mathrm{av}} + (\Delta P_F)_{\mathrm{lv}} \ . \tag{9}$$

Here $(\Delta P_F)_V$ which is the change at constant volume [Eq. (7)] represents the change in ion configuration upon melting. $(\Delta P_F)_{\mathrm{lv}}$ is the effect due to increased lattice vibration, and $(\Delta P_F)_{\mathrm{av}}$ is the effect due to the change in average equilibrium distribution (discussed in the last paragraph). The lattice-vibration effect on the Knight shift of solid metals has been observed as an explicit temperature dependence of the Knight shift.[17] Although $(\Delta P_F)_{\mathrm{av}}$ is exceptionally large[16] for Cd, the amount for most metals is believed to be comparable to that of $(\Delta P_F)_{\mathrm{lv}}$ (a few percent).

The lattice-vibration contribution affects the wave functions in two different ways depending on the correlation of the neighboring ions:

$$(\Delta P_F)_{\mathrm{lv}} = (\Delta P_F)_{\mathrm{sym}} + (P_F)_{\mathrm{asym}} \ . \tag{10}$$

(i) A spherically symmetric mode[18] (symmetric breathing mode) has negligible effect on P_F of Li [$(\Delta P_F)_{\mathrm{sym}} \simeq 0$], since a uniform compression hardly changes P_F.[1,6] This mode of vibration is, however, important for the explicit temperature dependence of P_F of other alkali metals.[17] (ii) Asymmetric modes, which reduce the instantaneous symmetry without changing local volume, increase non-s-components of the wave functions on average and decrease P_F; $(\Delta P_F)_{\rm asym} < 0$.

It is suggested, therefore, that the negative sign of $(\Delta P_F)_V$ is probably due to the increase in the amplitude of the asymmetric vibrations on melting; $|(\Delta P_F)_{\rm av}| < |(\Delta P_F)_{\rm asym}|$.

The present experimental result on $(\Delta\chi_P)_V$ clearly indicates [Eq. (4)] that a large band-structure enhancement of χ_P in solid Li is essentially unchanged on melting. The band-structure effect enhances the χ_P value of Li by $\simeq 70\%$ compared with a "jellium" susceptibility which includes exchange-correlation enhancement alone.[1,2]

A reliable numerical comparison between calculation and the observed $(\Delta\chi_P)_V$ must wait for a first-principles calculation.[2] All the calculations of χ_P in the past were based on one of the following schemes: (i) assuming that there is no band-structure effect, one uses an elaborate many-body technique to calculate the jellium susceptibility and then modifies the results with a somewhat dubious band-structure correction (an effective-mass approximation), or (ii) one starts with the susceptibility calculation based on the band structure, entirely neglecting the electron-electron interaction (step a), and adds the exchange-correlation effects later (step b). For the liquid metals the second approach is most popular, since the main interest is the effect of the liquid electronic structure compared with that of the solid lattice. Therefore, step a is most elaborate and is followed by a rather arbitrarily chosen step b. Some authors did not proceed beyond step a.

Shaw and Smith[4] calculated the density-of-states $\rho(\epsilon_F)$ for liquid and solid Li using the same pseudopotentials and the same perturbation method. This is the equivalent of step a, since χ_P for noninteracting electrons is proportional to $\rho(\epsilon_F)$. The importance of fully nonlocal pseudopotentials $\omega_q(\vec{k})$ is emphasized in deriving correct results. They used the Heine-Abarenkov model potential[19] in conjunction with the theoretically derived structure factor $a(q)$ by Ashcroft and Lekner.[20] The calculated $\rho(\epsilon)$ for both liquid and solid Li is shown in Fig. 14 of their paper.

Although the difference between $\rho(\epsilon)_{\rm liq}$ and $\rho(\epsilon)_{\rm sol}$ is prominent for a higher energy than ϵ_F, the difference is very small at the actual Fermi energy. The density of states at the Fermi level *decreases* by 1.5% on melting (at constant volume). Since they did not proceed to step b, a numerical comparison between their result, $\Delta\rho(\epsilon_F)_V[\equiv \rho(\epsilon_F)_{\rm liq} - \rho(\epsilon_F)_{\rm sol}] < 0$ (at constant volume), and the present result, $(\Delta\chi_P)_V$, is not feasible. Although the sign of these quantities is opposite, the important point is that the theory correctly predicted a very small change on melting.

A similar attempt has been made by Takahashi and Shimizu.[21] They calculated $\rho(\epsilon)_{\rm liq}$ with a Green's-function method and added the exchange-correlation effect (step b) calculated by Hedin and Lundqvist.[22] Unfortunately, since they did not calculate $\rho(\epsilon)_{\rm sol}$ using the same formalism with the same $\omega_q(\vec{k})$, it is impossible to discuss the small change in $\rho(\epsilon_F)$ and in χ_P on melting.

Timbie and White[23] obtained $\Delta\rho(\epsilon_F)$ using the Animalu-Heine pseudopotentials[19] and the Ashcroft-Lekner structure factor.[20] Their value, -4% is somewhat larger in magnitude than the Shaw-Smith value, -1.5%. They dressed a relatively old jellium susceptibility obtained by Brueckner and Sawada[24] with their band-structure effect. Their result, $(\Delta\chi_P)_V = -8\%$, is considerably larger in magnitude than the observed value and opposite in sign. Ichikawa[25] also calculated the $\rho(\epsilon)$ curve of liquid Li. He did not, however, evaluate the same curve for solid Li.

A comparison between the present experimental result on $(\Delta\chi_P)_V$ and the theoretical predictions suggests that the actual $\rho(\epsilon)$ curve near the Fermi level is close to those obtained by Shaw-Smith and by Takahashi-Shimizu, although a conversion from $(\Delta\chi_P)_V$ to $(\Delta\rho(\epsilon_F))_V$ based on a logical, rather than an *ad hoc*, theory[2] is required in order to discuss the numerical comparison between $\rho(\epsilon)_{\rm liq}$ and $\rho(\epsilon)_{\rm sol}$ by using the experimentally observed $(\Delta\chi_P)_V$.

IV. CONCLUSION

The directly observed change in χ_P and P_F in Li metal on melting is very small in spite of the fact that the electronic structure of solid Li deviates largely from the free-electron model. The decrease in P_F on melting suggests that the asymmetric breathing modes of ion motions in the liquid state are more important for ΔP_F than the average symmetric coordination of the neighboring ions. The small change in χ_P on melting is in accord with the recent calculations of the density of states for liquid Li. The difference in the sign between $\Delta\chi_{P,\rm obs}$ (>0) and $\Delta\rho(\epsilon_F)_{\rm calc}$ (<0) is probably within the uncertainty of the calculations. It is emphasized that the band-structure enhanced susceptibility in solid Li does not collapse to the nearly-free-electron value on melting as was postulated some-time ago.

[1]For the literature of recent theories of χ_P, see Toshimoto Kushida, J. C. Murphy, and M. Hanabusa, Phys. Rev. B 13, 5136 (1976).

[2]For example, S. H. Vosko and J. P. Perdew, Can. J. Phys. 53, 1385 (1975). See also Ref. 1.

[3]The electronic state of liquid metals has been a long-standing controversy. A large change in electronic states was postulated in order to explain a large change in transport properties (Ziman's model). K in most metals, however, does not change much on melting. It has been strongly suggested (Knight's model) that the electronic state is essentially unchanged on melting in these metals, since it is most unlikely that a large ΔP_F and a large $\Delta\chi_P$ accidentally cancel and yield the small ΔK. For reviews of liquid metals, see for example, J. E. Enderby, *Liquid Metals, Chemistry and Physics*, edited by S. Z. Beer (Dekker, New York, 1972), p. 585; R. Dupree and E. F. W. Seymour, *ibid.*, p. 461. V. A. Alekssev, A. A. Andreev, and V. Ya. Prokhorenko, Sov. Phys.—Usp, 15, 139 (1972).

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[7]J. E. Enderby *et al.* measured $\Delta\chi_P$; J. E. Enderby, J. M. Titman, and G. D. Wignall, Philos. Mag. 10, 633 (1964). They confirmed that the change is small. Their experimental uncertainty, $\Delta\chi_P/\chi_{P,\mathrm{sol}} = 0.04 \pm 0.05$, is, however, much too large to deduce the P_F change with a reasonable accuracy.

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[11]G. B. Benedek and T. Kushida, J. Phys. Chem. Solids 5, 241 (1958).

[12]E. W. Collings in Ref. 8.

[13]N. F. Mott, Philos. Mag. 26, 505 (1972).

[14]For detailed discussion, see Ref. 1. The Vosko-Perdew theory (Ref. 2) seems to be a most promising development. The theory is successful in calculating χ_P and its volume dependence in solid Li, although no attempt has been made to calculate $\Delta\chi_P$.

[15]A Green's-function formalism for ΔP_F was derived by Edwards, S. F. Edwards, Adv. Phys. 16, 359 (1967), Eq. (4.8). Pseudopotential methods were described in Ref. 4 and by Watabe *et al.*, Mitsuo Watabe, Minoru Tanaka, Hirohisa Endo, and B. K. Jones, Philos. Mag. 12, 347 (1965).

[16]P. Jena and N. C. Halder, Phys. Rev. Lett. 26, 1024 (1971). Their calculation shows that $\Delta P_{F,\mathrm{av}} = +8\%$.

[17]Ref. 10 (experimental evidence and general concept). T. Muto, S. Kobayasi, M. Watanabe, and H. Kozima, J. Phys. Chem. Solids 23, 1303 (1962) (detailed calculation). The explicit temperature dependence of K is comparable in magnitude to the implicit temperature dependence for solid alkali metals.

[18]It is noted that these modes are not normal modes of vibration. We expand the normal modes in terms of spherical harmonics. An s-like component gives $(\Delta P_F)_{\mathrm{sym}}$, and the rest of the components produce $(\Delta P_F)_{\mathrm{asym}}$.

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[25]K. Ichikawa, Philos. Mag. 27, 177 (1973). Ichikawa used the Shaw-Smith (Ref. 4) formalism and the same $a(q)$. The pseudopotential was, however, modified by a Singwi *et al.*'s dielectric screening function [K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970)]. The result is quite different from that obtained by Shaw-Smith and by Takahashi-Shimizu. A large bump in $\rho(\epsilon)$ is shifted below the Fermi level in the Ichikawa result, and $\rho(\epsilon_F)$ is *below* the free-electron value. The latter is difficult to reconcile with the large enhancement observed in χ_P and in the specific heat of Li.