ter, for the use of his low-temperature facilities and for his interest and advice. We are particularly grateful to H. Konrad Schürmann of the University of Rochester for his patient assistance in the operation of the demagnetization cryostat.

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Role of Effective Mass in Interpreting the Knight Shift in Cadmium upon Melting

P. Jena and N. C. Halder
Department of Physics, State University of New York, Albany, New York 12203

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The abrupt changes of Knight shift K_s and nuclear spin relaxation time T_1 in Cd upon melting have been examined by studying the spin susceptibility χ_s and spin density S at the melting point. It is found that the density-of-states effective mass m^*/m in Cd changes by 27% upon melting while the spin density changes by only 8%. Both of these changes combined satisfactorily explain the abrupt changes of K_s and T_1 upon melting.

In solid Cd, the Knight shift K_s strongly depends on temperature[1] and undergoes a fractional increase of about 70% in the temperature range from 4°K to the melting point (594°K). Furthermore, at the melting point K_s suffers an abrupt increase of 34% and remains constant thereafter in the liquid state. Recently, the unusually strong temperature dependence of K_s in solid Cd has been explained[2] by including the effects of electron-phonon interaction in the one-electron Hamiltonian and evaluating the spin density and density-of-states effective mass m^*/m at the Fermi surface at various temperatures. On the other hand, the temperature independence of K_s in liquid Cd has been explained[3] by the weak (or negligible) temperature dependence of the liquid interference function[4] $I(q)$. However, the question of the abrupt change of K_s at the melting point has not yet been looked into in quantitative detail. The purpose of this Letter is to report a quantitative study of the spin susceptibility χ_s and the spin density S in Cd just before and after melting. An analysis of these two quantities which are directly responsible for the change of K_s will lead, as we shall see later, to an understanding of this abrupt change of K_s at the melting temperature.

The Knight shift in metals can be written as

$$K_s = \tfrac{8}{3}\pi N\Omega_0 \chi_s S, \qquad (1)$$

where $N\Omega_0$ is the volume of the metal (Ω_0 being the volume per atom) and χ_s is the spin paramagnetic susceptibility. The spin densities S have been calculated with a fair degree of accuracy for both the solid[5] and liquid[3] metals. However, theoretical calculation of χ_s is particularly difficult due to nonavailability of a practicable procedure to incorporate the exchange effect among the Bloch electrons. We can incorporate the effect of the periodic potential in the susceptibility through an effective-mass m^*/m approximation and treat the exchange enhancement η_s of the susceptibility by an adjustable parameter.[2] Thus,

$$\chi_s = \chi_s^{\text{free}}(m^*/m)\eta_s, \tag{2}$$

where χ_s^{free} is the free-electron value of the spin susceptibility. We will first concentrate on the change of m^*/m upon melting.

We define the effective mass to be used in this paper by

$$m^*/m = g(E_\text{F})/g_0(E_\text{F}), \tag{3}$$

where $g(E_\text{F})$ is the density of states of conduction electrons at the Fermi surface and $g_0(E_\text{F})$ is the corresponding free-electron value. Assuming the Fermi surface in the liquid state to be spherical, one can show that

$$g(E)/g_0(E) = 2[(1/k)\partial E/\partial k]^{-1}, \tag{4}$$

where k and E are expressed in atomic units ($\hbar = 1$, $m = \frac{1}{2}$, $e^2 = 2$). The density of states in the liquid has been calculated by Ballentine[6] using the Green's-function approach due to Edwards.[7] Weaire[8] and Shaw and Smith[9] have utilized perturbation theory to calculate the effective mass. In this calculation, we have utilized the latter approach and the recent nonlocal pseudopotential[10] of Cd.

The energy values E_k can be expressed up to second order in perturbation theory, namely,

$$E_k = E_k^{(0)} + E_k^{(1)} + E_k^{(2)}, \tag{5}$$

where the individual terms are

$$E_k^{(0)} = k^2, \quad E_k^{(1)} = \langle \vec{k}| W(\vec{r})|\vec{k}\rangle, \tag{6}$$

and

$$E_k^{(2)} = {\sum_{k'}}' |\langle \vec{k}'| W(\vec{r})|\vec{k}\rangle|^2/(k^2-k'^2)$$
$$= {\sum_{k'}}'[|\langle \vec{k}'|\omega|\vec{k}\rangle|^2/(k^2-k'^2)]I(|\vec{k}-\vec{k}'|),$$

where the pseudopotential $W(\vec{r})$ can be expressed as a sum of the potentials centered at each of the ionic sites $\vec{R}_\nu$, namely, $W(\vec{r}) = \sum_\nu w(\vec{r}-\vec{R}_\nu)$. Introducing the nonlocal pseudopotential $W(\vec{r})$ of Stark and Falicov,[10] the corresponding form factors can be obtained as

$$\langle \vec{k}'|\omega|\vec{k}\rangle = \frac{4\pi}{\Omega_0}\sum_{n,l} v_l(2l+1)P_l(\cos\theta_{k'k}) \times T_{nl}(k)T_{nl}(k'), \tag{7}$$

in which v_l are constants, the summation over n and l is confined to the outermost core functions[11] (4s, 4p, 4d) of Cd, and P_l is the Legendre polynomial of order l. The functions $T_{nl}(k)$ are the Bessel transforms of the radial core functions, $P_{nl}(r)$:

$$T_{nl}(k) = \int_0^\infty j_l(kr)P_{nl}(r)r\,dr. \tag{8}$$

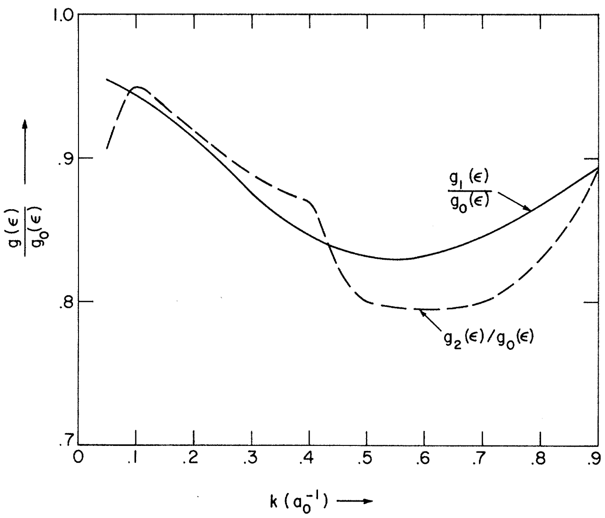

FIG. 1. Normalized electron density of states $g(E)/g_0(E)$ of liquid Cd at 350°C. $g_1(E)/g_0(E)$ is obtained by expanding the energy E up to first order in perturbation theory while $g_2(E)/g_0(E)$ is obtained with E taken up to second order.

Using the above form factors the values of $E_k^{(1)}$ and $E_k^{(2)}$ were calculated from Eq. (6). For $E_k^{(2)}$ we have carried out the principal-value integration as suggested earlier.[3]

The density of states $g(E)$ normalized to the free-electron value $g_0(E)$ is plotted in Fig. 1 by including energies up to first and second order separately. The first-order correction $g_1(E)/g_0(E)$ shows slower variation with k than that of the second-order result $g_2(E)/g_0(E)$. From the latter curve the effective mass m^*/m at 623°K was found to be

$$m^*/m = 0.827.$$

This calculation was repeated for other temperatures up to 900°K by using the appropriate experimental[4] $I(q)$. The values of m^*/m at higher temperatures were found to be constant (0.827). Thus, it is reasonable to conclude that at the melting temperature as well,

$$(m^*/m)^{\text{liq}} = 0.827. \tag{9}$$

For the solid state, m^*/m has been theoretically calculated[2] at 0, 298, and 462°K. We have plotted these values in Fig. 2 and extrapolated the curve up to the melting point. Thus, for the sol-

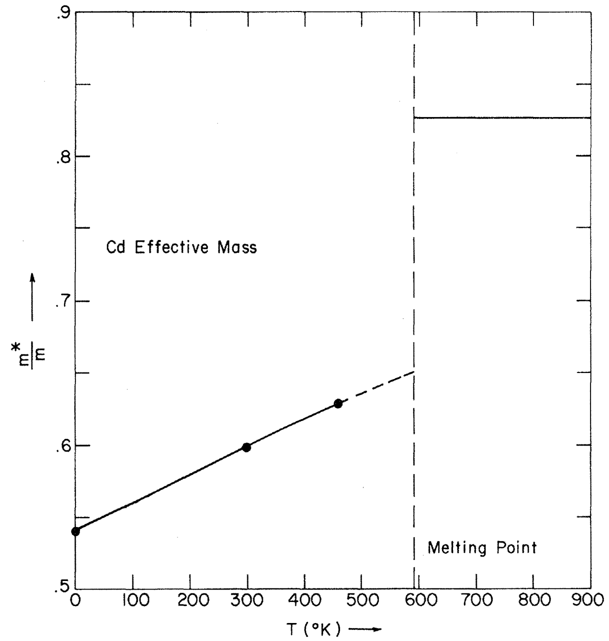

FIG. 2. Density-of-states effective mass m^*/m of solid and liquid Cd as functions of temperature.

id at the melting point,

$$(m^*/m)^{\rm sol} = 0.650. \tag{10}$$

Using Eqs. (9) and (10) and assuming that η_s does not change upon melting, the change of χ_s at the melting point can be obtained from Eq. (2). Thus,

$$\chi_s^{\rm liq}/\chi_s^{\rm sol} = (m^*/m)^{\rm liq}/(m^*/m)^{\rm sol} = 1.27. \tag{11}$$

To determine the change of K_s upon melting, we also need to investigate the change of the spin density S at the melting point. The spin densities have been obtained both in solid[2, 12] and liquid[3] Cd as functions of temperature. Following an analysis similar to that of the m^*/m, we find

$$S^{\rm liq}/S^{\rm sol} = 1.08. \tag{12}$$

Combining Eqs. (11) and (12), the change of K_s upon melting is

$$(K_s^{\rm liq}/K_s^{\rm sol})_{\rm theor} = 1.37. \tag{13}$$

From experimental measurements of K_s at the melting point, we get

$$(K_s^{\rm liq}/K_s^{\rm sol})_{\rm expt} = 1.34. \tag{14}$$

The good agreement between Eqs. (13) and (14) indicates that the change in η_s at the melting point is not appreciable and can be neglected.

A further check on this analysis can be obtained by studying the relaxation time T_1. Since

$$(T_1 T)^{-1} \propto [g(E_{\rm F})S]^2,$$

we can write

$$T_1^{\rm sol}/T_1^{\rm liq} = \left[\left(\frac{m^*}{m}\right)^{\rm liq} \Big/ \left(\frac{m^*}{m}\right)^{\rm sol}\right]^2 \left(\frac{S^{\rm liq}}{S^{\rm sol}}\right)^2. \tag{15}$$

Using Eqs. (11) and (12), we have

$$(T_1^{\rm sol}/T_1^{\rm liq})_{\rm theor} = 1.88. \tag{16}$$

On the other hand, from the experimentally reported values[13] we obtain

$$(T_1^{\rm sol}/T_1^{\rm liq})_{\rm expt} = 1.59. \tag{17}$$

As we can see, the results in Eqs. (16) and (17) are not in good agreement with each other, and therefore need some explanation. It should be noted that we have not considered the change of the exchange enhancement η_M of the nonuniform susceptibility which is relevant to the discussion of relaxation rate. Dickson[13] had noticed empirically that the change of T_1 between solid and liquid Cd due to the exchange enhancement is 0.83. Using this value for the exchange enhancement factor and Eq. (16), we find

$$(T_1^{\rm sol}/T_1^{\rm liq})_{\rm theor}^{\rm exchange} = 1.56. \tag{18}$$

This result is in very good agreement with the experimental result in Eq. (17). It is interesting to note that if one uses $m^*/m = 1$ for liquid Cd, as is usually assumed to be the case for liquid metals in general,[14] the changes in K_s and T_1 (including exchange enhancement) due to change in m^*/m alone are 1.54 and 1.97, respectively. Both of these values are substantially larger than the experimental values in Eqs. (14) and (17). This would indicate that the spin density S has to decrease upon melting. This seems rather unphysical since the potential that characterizes the strength of the angular component of the conduction-electron wave function is expected to be weaker in the liquid than that in the solid because of the increased thermal motion of the ions. This would generally result in an increase of the spin density in the liquid instead of a decrease as we just observed.

In summary, we can conclude that the changes of K_s and T_1 in Cd at the melting point are mainly due to the change in the density of states brought about by the disappearance of the long-range order in the solid state. Similar calculations for other metals, where such an abrupt jump of Knight shift occurs at the melting point, will be helpful in substantiating the present viewpoint emphasized in this note.

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Temperature-Dependent Activation Volumes in Zinc*

H. M. Gilder and L. C. Chhabildas
Rensselaer Polytechnic Institute, Troy, New York 12181

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Precision measurements of self-diffusion in zinc as a function of pressure indicate that the activation volumes ΔV_c and ΔV_b respectively associated with the nonbasal and basal vacancy jumps have a temperature dependence given by $(\partial \Delta V_c/\partial T)_p = (6.2 \pm 1.9) \times 10^{-3}$ cm^3/mole °K and $(\partial \Delta V_b/\partial T)_p = (7.6 \pm 3.4) \times 10^{-3}$ cm^3/mole °K. A model calculation based on a Morse-like potential indicates that the frequencies of atomic vibrations in the vicinity of the defect vary with pressure in a way that is consistent with these experimentally measured quantities.

According to the usual assumptions of the validity of reaction rate theory and thermodynamics[1] in describing the diffusion jump of an atom in a crystal, the study of the effect of hydrostatic pressure on the self-diffusion coefficient D of a pure metal gives information on the sum, ΔV, of the volume changes ΔV_f and ΔV_m that are, respectively, associated with the creation and motion of those defects participating in the diffusion process. On thermodynamic grounds we would expect the activation volume ΔV to be temperature dependent, since, according to one of Maxwell's thermodynamic equations,

$$(\partial \Delta V/\partial T)_p = -(\partial \Delta S/\partial p)_T = -[\partial(\Delta S_f + \Delta S_m)/\partial p]_T, \tag{1}$$

where T is the absolute temperature, p is the pressure, and ΔS is the sum of the entropy changes ΔS_f and ΔS_m respectively associated with the formation and motion of the defect that is responsible for the volume change ΔV. As ΔS depends on the way each perfect-crystal normal-mode frequency is changed by the presence and motion of the defect,[2] we would expect $(\partial \Delta S/\partial p)_T$ and hence $(\partial \Delta V/\partial T)_p$ to be nonzero, since the pressure derivatives of the perfect and altered frequencies for each mode should in general be different. However, the typical precision of ~10% to which the self-diffusion activation volume has been measured for a variety of metals has always precluded the unambiguous observation of a temperature-dependent activation volume. Curiously enough, in those experiments[4,5] where $(\partial \Delta S/\partial p)_T$ has been estimated, Eq. (1) has never been invoked to indicate a possibly temperature-dependent activation volume ΔV, possibly because the apparent trend of ΔV with T falls within the experimental uncertainty in ΔV. It is the primary purpose of this Letter to report recent precision measurements of self-diffusion in zinc as a function of pressure which indicate that