time approximation.

Finally we note that the characteristic length in Eq. (11) is of the order of the phonon mean free path. It is within this distance that the electron heat current rises from its surface to bulk value. This is independent of the α's and is much shorter than the electron mean free path. We expect this conclusion to be approximately valid in three dimensions as well, so that the large temperature gradients are within a distance of order l_p from the surface. Further on the temperature gradient is approximately constant and therefore one essentially observes bulk behavior for distances greater than l_p. This is perhaps an explanation of why measurements of ∇T in metals have failed to show any mean-free-path effects since the relevant distance l_p is much shorter than l_e.

---

[1] G. L. Pollack, Rev. Mod. Phys. 41, 48 (1969).

[2] J. D. N. Cheeke, J. Phys. (Paris) 31, Suppl. 10, 129 (1970).

[3] W. A. Little, Phys. Rev. 123, 435 (1961), and 130, 596 (1963).

[4] A. F. Andreev, Zh. Eksp. Teor. Fiz. 43, 1535 (1962) [Sov. Phys. JETP 16, 1084 (1963)].

[5] J. M. Ziman, *Principles of the Theory of Solids*, (Cambridge U. Press, Cambridge, England, 1965), p. 181.

[6] P. Morse and H. Feshbach, in *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 978.

[7] D. Davison, *Neutron Transport Theory* (Clarendon, Oxford, England, 1957), p. 67.

[8] C. Mark, Phys. Rev. 72, 558 (1947).

Pseudopotential Calculation of the Latent Heats of Melting of Simple Metals[*]

W. M. Hartmann
Michigan State University, East Lansing, Michigan 48823

(Received 19 April 1971)

The latent heats of melting for simple metals at normal pressure are calculated by the pseudopotential method. The Percus-Yevick hard-sphere model is used for the liquid-structure factor, and an uncorrelated harmonic oscillator model is used for the solid-structure factor. Numerical results agree well enough with experiment and are sufficiently stable against changes in the parameters to make further calculations of the latent heat seem worthwhile.

In this Letter we propose that the latent heat of melting may be calculated for simple metals by the pseudopotential method. Along the melting curve the Gibbs functions for liquid and solid phases must be equal. Therefore, the latent heat of melting L is

$$L = T_m \Delta S = \Delta U + p\Delta V,$$

where Δ denotes the difference between liquid and solid quantities. At atmospheric pressure $p\Delta V$ is entirely negligible, and the latent heat is given by the difference in internal energies ΔU.

The internal energy of a simple metal, in rydbergs per ion, includes the kinetic, exchange, and correlation energies of the electron gas[1]:

$$U_g = 2.21Z/r_s^2 - 0.916Z/r_s - (0.115 - 0.031 \ln r_s)Z,$$

where r_s is the Wigner-Seitz radius in atomic units and we have used the Nozières-Pines interpolation formula for the correlation energy.[2]

The energies of the conduction electrons are changed by interaction with the ions, and the treatment of this interaction by the pseudopotential method makes the calculation tractable. Because of macroscopic charge neutrality the homogeneous parts of the bare electron-ion interaction, electron-electron direct interaction, and interionic direct interaction sum to a finite result, the Hartree energy:

$$U_{\mathrm{H}} = \lim_{q \to 0} [w_b(q) + 8\pi Z/q^2] Z \Omega_0^{-1},$$

where Ω_0 is the volume per ion and $w_b(q)$ is the bare ion pseudopotential. The contribution to the latent heat from the above terms depends only upon the volume change on melting and is independent of structure. Since the kinetic energies of the ion cores at melting are $U_K = \frac{3}{2}k_{\mathrm{B}}T_m$ for both liquid and solid, only two important contributions to the system energy remain.

The difference between the direct ion interaction $V_D(q) = 8\pi Z^2/q^2$ for the structure of the system and that of the homogeneous jellium is, for

$x = L$ (liquid) or S (solid),

$$U_D{}^x = \tfrac{1}{2}(2\pi)^{-3}\int V_D(q)[a^x(\vec{q})-1]\,d^3q,$$

where $a^x(q)$ is the appropriate structure factor

$$\langle N^{-1}\sum_{l,l'} \exp[i\vec{q}\cdot(\vec{R}_l-\vec{R}_{l'})]\rangle.$$

For a small local pseudopotential the nonhomogeneous contribution to the electron energy bands is given by second-order perturbation theory and is called the band-structure energy:

$$U_{\mathrm{BS}}{}^x = \tfrac{1}{2}(2\pi)^{-3}\int V_{\mathrm{BS}}(q)a^x(\vec{q})\,d^3q,$$

where

$$V_{\mathrm{BS}}(q) = C(q)V_D(q).$$

The Cochran function $C(q)$ is defined in terms of the electron-gas dielectric function[3] $\epsilon(q)$:

$$C(q) = w_b{}^2(q)[1-\epsilon^{-1}(q)][\lim_{q\to 0} w_b{}^2(q)]^{-1}.$$

The difference between the structural factors in the integrands for U_D and U_{BS} results from the fact that whereas an ion interacts only with *other* ions an electron is scattered by all the ions of the system. For liquid or solid we may calculate either the total energy U^x or

$$U^x - U_K = U_g{}^x + U_{\mathrm{H}}{}^x + U_D{}^x + U_{\mathrm{BS}}{}^x.$$

For numerical calculations we use the simplest reasonable models. The bare ion pseudopotential is of the Ashcroft form[4]

$$w_b(q) = (8\pi Z/q^2)\cos(qr_c)$$

with a single parameter r_c. We correct the dielectric function for exchange and correlation by using the Gaussian interpolation formula for the Hubbard G function given by Singwi *et al.*,[5] evaluated at $r_s{}^* = r_s m^*/m$ appropriate to liquid and solid densities.

For the liquid-structure factor $a^L(q)$ we take the analytic form of the hard-sphere Percus-Yevick model given by Ashcroft and Lekner.[6] The solid-structure factor is

$$a^S(\vec{q}) = N^{-1}\sum_{l,l'} \exp[i\vec{q}\cdot(\vec{R}_l{}^0-\vec{R}_{l'}{}^0)]\,\langle \exp[i\vec{q}\cdot\vec{u}_l(0)]\exp[-i\vec{q}\cdot\vec{u}_{l'}(0)]\rangle$$

where $\vec{R}_l{}^0$ is the equilibrium position for the lth ion and $\vec{u}_l(t)$ is the displacement from this position at time t. If we assume that the ions of the melting solid vibrate as uncorrelated ($\langle\vec{u}_l\vec{u}_{l'}\rangle = 0$, $l \neq l'$) oscillators, harmonic in a self-consistent phonon sense, then

$$a^S(\vec{q}) = N^{-1}\sum_{l,l'} \exp[i\vec{q}\cdot(\vec{R}_l{}^0-\vec{R}_{l'}{}^0)][e^{-2W(q)} + \delta_{l,l'}(1-e^{-2W(q)})] = \frac{(2\pi)^3}{\Omega_0}\delta(\vec{q}-\vec{G})\,|f(\vec{G})|^2 e^{-2W(G)} + 1 - e^{-2W(q)},\quad \vec{G}\neq 0,$$

and

$$2W(q) = 6\left(\frac{m}{M}\right)\left(\frac{T_m}{\Theta_{\mathrm{D}}}\right)\left(\frac{\frac{1}{2}e^2a_0{}^{-1}}{E_{\mathrm{D}}}\right)(qa_0)^2.$$

The factors in the Debye-Waller factor are the ratios of the electron mass to ion mass, the melting temperature to Debye temperature, the rydberg to Debye energy, and the wave vector to the inverse Bohr radius. The form factor for the unit cell, $f(\vec{G})$, differs from unity only for the hexagonal metals. Calculations of $U_D{}^S$ and $U_{\mathrm{BS}}{}^S$ then reduce to sums over nonzero reciprocal-lattice vectors $\vec{G}$ and integrals, all of which converge rapidly except for the band-structure integral which converges rather slowly because of the slow convergence of $C(q)$. But because

$$\lim_{q\to\infty} a^L(q) = 1,$$

the difference between liquid and solid band-structure energies does converge rapidly.

Input parameters and the calculated and experimental results are shown in Table I. Macroscopic data were taken from the *Liquid Metals Handbook*,[7] and Θ_{D} from Kittel[8] and from neutron-scattering data.[9] Since phonon energies in Cd are not well known, Θ_{D} was determined by requiring the critical displacement in the Lindemann criterion to scale with those for Mg and Zn.[10] For all elements, m^*/m was taken to be unity. Otherwise the calculations for the alkali metals parallel those of Price, Singwi, and Tosi[11] for the mechanical properties of the alkalis and include the approximate modification of the Hartree energy [their Eq. (19b)] for stability at zero pressure. For the polyvalent metals no correction was made to the Hartree energy. Core radii for Pb, Zn, Tl, and Al are those for which calculated band structure and liquid resistivities agree with experiment.[12] Core radii for Mg and Cd were taken from band-structure data.[13] The agreement between theory and experiment is remarkably good considering the approximations made and the numerical difficulties.[14]

Because L is a small difference between two

Table I. Input parameters and the calculated and experimental latent heats in millirydbergs per ion. For all elements $m^*/m=1$. The c/a ratios for Mg, Zn, and Cd are assumed unchanged from their room-temperature values 1.624, 1.856, and 1.886, respectively.

	density ($\mathrm{g\ cm^{-3}}$)	$\Delta\Omega_0/\Omega_0$(solid)	r_c(a.u.)	T_m(K)	Θ_D(K)	L,th. (mRy/ion)	L,exp (mRy/ion)
Li	0.519	0.015	1.40	452	335	-1.12	3.49
Na	0.928	0.025	1.69	371	156	1.48	1.98
K	0.825	0.024	2.226	337	91.1	1.69	1.82
Rb	1.475	0.025	2.40	312	55.5	1.88	1.66
Cs	1.84	0.026	2.62	302	39.5	1.88	1.60
Mg	1.572	0.042	1.38	924	370	9.7	6.37
Zn	6.92	0.069	1.27	693	235	6.2	5.08
Cd	8.02	0.047	1.405	594	143	6.6	4.73
Aℓ	2.38	0.066	1.117	933	428	15.5	8.25
Tℓ	11.29	0.032	1.033	576	78.5	4.3	3.28
Pb	10.59	0.036	1.48	600	104	15.7	10.49

large numbers it is necessary to investigate the dependence of L on the input parameters. Table II, for Al, demonstrates that there is no pathological sensitivity to changes in the parameters, except possibly for changes in m^*/m. Because Al has the smallest r_s of the simple metals, it provides a severe test for the calculations. We believe that the observed insensitivity indicates that the calculated values of L are physically meaningful.

Of the many assumptions implicit in the above calculations perhaps the most suspect is that of the hard-sphere model. However, the well-known discrepancy between the hard-sphere values for $a^L(0)$ and $k_B T_m \chi_T/\Omega_0$, where χ_T is the isothermal compressibility,[16] may not be very important. As $a^L(0)$ is decreased, the liquid band-structure energy becomes less negative and the direct ion energy more negative by almost the same amount. We estimate that if $a^L(0)$ is decreased from the hard-sphere value of 0.025 to 0.014 with $a^L(q) \geq a^L(0)$, then the value of L for Al will change by less than 1.0 mRy/ion. The most serious difficulty presented by the calculated results would seem to be that the variation of L among the alkalis is opposite to that observed experimentally. Hopefully the use of better liquid-structure factors will remedy this difficulty, though it may be necessary to do the calculation in real space.[17]

We wish to thank D. Stroud, D. L. Price, T. O. Woodruff, S. D. Mahanti, F. Toigo, and A. Rahman for useful comments on this work.

Table II. For changes in the input parameters listed, the latent heat of aluminum is decreased from the value 15.5 mRy/ion by ΔL. The effective mass $m^*/m = 1.04$ is suggested in Ref. 15; the resulting change in L brings it into close agreement with experiment.

Parameter	Change (%)	ΔL (mRy/ion)
Density	−10	−0.6
$\Delta\Omega_0/\Omega_0$(solid)	−10	−1.3
r_c	−10	−5.1
Θ_D	−10	−3.2
m^*/m	+ 4	−6.8

---

*Work partially supported by the National Science Foundation Science Development Grant No. GU2648.

[1] Our analysis of the total energy follows that of N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967). All quantities except for energy are given in atomic units.

[2] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966), Vol. I.

[3] W. Cochran, Proc. Roy. Soc., Ser. A 276, 308 (1963).

[4] N. W. Ashcroft, Phys. Lett. 23, 48 (1966).

[5] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970).

[6] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

[7] *Liquid Metals Handbook* (U. S. Office of Naval Research and Atomic Energy Commission, Washington, D. C., 1952).

[8] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), 3rd ed., p. 180.

[9] Pb: R. Stedman, L. Almqvist, and G. Nilsson, Phys. Rev. 162, 549 (1967). Mg, Zn: G. Gilat, G. Rizzi, and G. Cubiotti, Phys. Rev. 185, 971 (1969); N. H. Nachtrieb, Advan. Phys. 16, 309 (1967).

[10] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U. Press, London, 1964), p. 63.

[11] D. L. Price, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 2, 2983 (1970).

[12] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967). The core radius for Al also leads to excellent phonon energies: D. C. Wallace, Phys. Rev. 187, 991 (1969); W. M. Hartmann and T. O. Milbrodt, Phys. Rev. B (to be published).

[13] Y. Fukai, Phys. Rev. 186, 697 (1969); J. C. Kimball, R. W. Stark, and F. M. Mueller, Phys. Rev. 162, 600 (1967); R. W. Stark and L. M. Falicov, Phys. Rev. Lett. 19, 795 (1967).

[14] For Pb, for example, $U^L - U_K = -6769.9$ and $U^S - U_K = -6785.6$.

[15] D. Weaire, Proc. Phys. Soc., London 92, 956 (1967).

[16] P. Ascarelli, Phys. Rev. 173, 271 (1968).

[17] D. L. Price has performed the integral for liquid energies in real space to calculate the difference in energy of liquid Na and the solid at $T = 0$ (to be published).

Measurement of Hyperfine Structure in the Relaxed-Excited State of the *F* Center in KI by Optical Triple Resonance*

L. F. Mollenauer, S. Pan, and A. Winnacker†
Department of Physics, University of California, Berkeley, California 94720

(Received 26 April 1971)

An optical method for detection of electron-nuclear double spin resonance in the relaxed-excited state of *F* centers is described. It has been successfully applied to KI. The hyperfine splittings inferred from these measurements indicate a relatively compact wave function for the relaxed-excited state.

For the *F* center in KI we have detected electron-nuclear double spin resonance (ENDOR) in the relaxed-excited state by a special optical triple-resonance technique. As in our earlier work[1] on the electron spin resonance (ESR) of the relaxed-excited state, the method relies on the large electron-spin memory exhibited by the *F* center in an entire pumping cycle. By subjecting the relaxed-excited state to resonant microwave (ESR) fields H_1 and radio-frequency (ENDOR) fields H_{11} while the *F* center is being pumped with σ^+ or σ^- (circularly polarized) light, the spin memory can be partially erased. As a consequence, the *rate* of pumping of the ground-state spin polarization P_e is increased. [$P_e \equiv (n^+ - n^-)/(n^+ + n^-)$, where n^+ and n^- are the $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ populations, respectively.] Changes in P_e thus induced by the resonant effects in the excited state are measured (and hence the signal is detected) by continuous monitoring of the magnetic circular dichroism (MCD) of the absorption band. Thus the fundamental detector in these experiments is the ground-state spin system itself.

In our earlier work, P_e was the product of dynamic equilibrium between unsaturated optical pumping and ground-state spin-lattice relaxation. With the optical-pump intensity adjusted to give optimum sensitivity, P_e can change at a rate no greater than $\sim 2/T_1$ in response to the application of H_1 fields resonant with the relaxed-excited state. Here, T_1 is the spin-lattice relaxation time. (For appropriate rate equations, see Ref. 1.) Since T_1 is of the order of seconds,[2] the resultant slow detector response time mitigates against the use of lock-in detection on the ESR or ENDOR effect itself.

To circumvent the above limitation, our present experiment uses saturated optical pumping. A high-intensity optical pump tuned to one MCD peak of the absorption band is switched symmetrically between σ^+ and σ^- polarizations at a 50-kHz rate. It is well known[2-4] that either σ^+ or σ^- alone would produce $P_e \sim +40\%$ or $P_e \sim -40\%$, respectively, for the *F* center in KI. Now, with rapid and symmetrical switching of the light polarization, and in the absence of resonance effects on the excited state, only the time-average value $P_e = 0$ is produced. But suppose a microwave H_1 field, resonant with the relaxed-excited state, were switched on and off synchronously