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Thermopower of the alkali metals at high temperatures

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An empirical calculation is presented of the thermopower of the alkali metals at the melting temperature for both the liquid phase and the solid phase. The overall agreement between the calculated and the measured values is very good. The first-principles Shukla-Taylor form factor is used for Na and K and an empirical form factor is used for Li, Rb, and Cs. The energy dependence of the form factor, required for the calculation of the thermopower, is obtained directly from the form factor itself by means of an approximate procedure based on a phase-shift expansion. The approximation is shown to be reliable. The structure factor was obtained for both the solid and the liquid phases by means of a scaling procedure. The scaling procedure is shown to be reliable. Finally, a qualitative discussion is presented of various aspects of the thermopower calculation.

I. INTRODUCTION

The calculation of the thermopower $Q(T)$ of the alkali metals has long been regarded[1-3] as one of the fundamental problems in the transport theory of metals. The theoretical difficulties associated with the problem are well known.[1-5] However, there has been considerable recent progress regarding the high-temperature calculation. In fact, there now exist first-principles calculations[6,7] of $Q(T)$ at high temperatures that are in quantitative agreement with experiment. As would be expected, first-principles calculations are rather complex and the results are thus far restricted to Na and K.

We shall here adopt the different approach of calculating $Q(T)$ at high temperatures by an empirical method. The input data required for the calculation are the measured phonon spectrum for the structure factor and available screened electron-ion matrix elements (on-Fermi-surface pseudopotential matrix elements) for the form factor. The energy derivative of the screened pseudopotential matrix elements, a quantity required for the calculation of $Q(T)$, will be obtained directly from the form factor by a modification of an approximation proposed by Young *et al.*[8] The approximation is shown to be quite good and has the important advantage of avoiding entirely the complicated calculation[9] of the energy dependence of the off-Fermi-surface screened pseudopotential matrix elements.

Although empirical calculations, such as the one described here, are not, of course, intended to replace first-principles calculations, they do offer several advantages. First, they are easy to carry out. Indeed, we have carried out the calculation of $Q(T)$ for all the alkali metals for both the solid and liquid[10] phases. Very good overall agreement with experiment is found. Second, the required input data are readily available, usually from experiment. Third, performing a calculation of $Q(T)$ for a series of metals within a single unified framework permits one to analyze trends from metal to metal within an entire chemical group and thereby to get a "feel" for the calculation, which is not always easily obtained from a complicated calculation specific to each metal. Such trends will be discussed in some detail when comparison is made between the results for the different alkali metals.

In Sec. II, the procedure is described for obtaining the input data required for the calculation of $Q(T)$. In particular, a scaling procedure is introduced for obtaining the high-temperature structure factor. In Sec. III, an approximate method is proposed for obtaining the energy derivative of the form factor from the form factor itself. The results of the calculation of $Q(T)$ at the melting temperature are presented in Sec. IV and comparison is made with experiment. In Sec. V, a simplified one-parameter model is introduced for the form factor. The model permits a fairly complete qualitative discussion of the general features of the thermopower calculation. The summary follows in Sec. VI.

II. INPUT DATA FOR CALCULATION

According to standard theory,[11,12] the high-temperature thermopower is given by

$$Q(T)=-(\pi^2 k_B T/3eE_F)\xi(T)\,, \tag{2.1}$$

$$\xi(T)=3-2q(T)-\tfrac{1}{2}r(T)\,, \tag{2.2}$$

$$q(T)=\frac{k_F^4 w^2(2k_F,k_F)S(2k_F,T)}{4\int_0^{2k_F} dK\,K^3 w^2(K,k_F)S(K,T)}\,, \tag{2.3}$$

$$r(T)=\frac{k_F\int_0^{2k_F} dK\,K^3 S(K,T)\,\partial[w^2(K,k_F)]/\partial k_F}{\int_0^{2k_F} dK\,K^3 w^2(K,k_F)S(K,T)} \tag{2.4}$$

where $S(K,T)$ is the temperature-dependent angular average of the structure factor and $w(K,k_F)$ is the form factor. The k_F dependence of $w(K,k_F)$ arises from the fact that the form factor derives from an energy-dependent, nonlocal pseudopotential operator, and thus depends not only on the momentum transfer upon scattering $\hbar K$, but also on the energy $\hbar^2 k_F^2/2m$ of the electron being scattered. It should be noted that the temperature dependence of the thermopower parameter $\xi(T)$ is rather weak because the temperature dependences of the numerator and denominator of $q(T)$ and $r(T)$ tend to cancel at high temperatures.

Equations (2.1)–(2.4) for $Q(T)$ are based on the lowest-order variational solution to the Boltzmann equation. It has been repeatedly demonstrated over the last decade by explicit calculation that the lowest-order solution (relaxation-time approximation) provides a very accurate value at high temperatures for both the electrical resistivity[13-19] and the thermal resistivity[20-23] of the alkali metals. A similar direct proof does not exist for $Q(T)$ because the thermopower does not satisfy a variational principle.[12] Nevertheless, there is no reason to doubt that the lowest-order variational calculation is also very reliable for $Q(T)$ at high temperatures. The derivation of (2.1)–(2.4) also depends on the assumption of a spherical Fermi surface and single-plane-wave pseudo-wave-functions. The Fermi surface is indeed very nearly spherical for all the alkalis.[24] However, the approximation of single-plane-wave pseudo-wave-functions is questionable for lithium.[25,26] Nevertheless, in the interest of simplicity, we adopt the single-plane-wave model for all the alkalis.

As seen from (2.3) and (2.4), the input data needed for the calculation of $Q(T)$ consist of two items, the form factor $w(K,k_F)$ and the angular-averaged structure factor $S(K,T)$. We shall consider each of these items in turn.

A. Form factor

For two of the alkali metals (Na and K), there are available recent accurate calculations[27] of the form factor $w(K,k_F)$. For the other alkali metals (Li, Rb, and Cs), we used an empirical potential. Kaveh[28] has shown how to construct an accurate empirical form factor for the alkali metals from the electrical resistivity data. Thus, for each of the alkali metals, the form factor we used leads to accurate values for the electrical resistivity over a wide temperature range for the solid phase.

The form factor is needed at the atomic volume corresponding to the melting temperature for both the solid and the liquid phase. Although the volume change upon melting is fairly small, it should be included. For Na and K, the form factor was calculated[27] as a function of volume, and thus, one has directly the required volume dependence. For the other alkali metals, the volume dependence of $w(K,k_F)$ is readily obtained by means of the procedure described by Wiser and Greenfield,[29] the essence of which is the following. Wherever k_F or the atomic volume Ω_0 occur explicitly in the form factor, one adjusts them to the required value, i.e., to the value appropriate to the melting point in the solid or liquid phase. Whenever the k_F dependence is only implicit, it is ignored. Since the explicit k_F dependence of the form factor is easily shown[30] to be much stronger than the implicit k_F dependence, this procedure should be more than adequate, especially since the volume dependence of $w(K,k_F)$ is rather small.

The accuracy of this procedure was first established by Harrison[31] for Al by explicit calculation. We have also confirmed the accuracy of this procedure for Na and K by comparing the approximate volume dependence of $w(K,k_F)$ predicted by this procedure with that obtained by Shukla and Taylor[27] from a full pseudopotential calculation. The results agree to within 0.001 Ry for all K for both sodium and potassium. Therefore, adjusting the form factor of the metal to the required atomic volume is readily and accurately carried out.

The energy derivative of the form factor appearing in expression (2.4) for $r(T)$ will be obtained by an approximate procedure which does not require any additional input data. The procedure will be described in the next section.

B. Structure factor

The structure factor can be obtained directly from experiment. For the liquid phase, neutron or x-ray scattering data[32] directly measure $S(K,T)$. For the solid phase, one may use the standard[12] one-phonon approximation for the structure factor

$$S(\vec{K},T)=\frac{\hbar^2}{Mk_BT}\sum_{\lambda}\frac{[\vec{K}\cdot\hat{\xi}_\lambda(\vec{K})]^2}{\{\exp[\hbar\omega_\lambda(\vec{K})/k_BT]-1\}\{1-\exp[-\hbar\omega_\lambda(\vec{K})/k_BT]\}}, \tag{2.5}$$

where M is the ionic mass and $\omega_\lambda(\vec{K})$ and $\hat{\xi}_\lambda(\vec{K})$ are the frequency and polarization vector, respectively, of the phonon of branch λ and wave vector $\vec{K}$. The values of $\omega_\lambda(\vec{K})$ and $\hat{\xi}_\lambda(\vec{K})$ can be obtained directly from the measured interatomic force constants by a Born–von Kârmân analysis.

An important simplification occurs in the determination of $S(\vec{K},T)$ because we are considering only high temperatures, essentially the melting point. For all the alkali metals, the ratio Θ_D/T_m is significantly smaller than unity, where Θ_D is the Debye temperature and T_m is the melting temperature. In Table I are listed the values[33] for Θ_D, T_m, and k_F at T_m in the liquid phase for all the alkali metals. As the fourth row of the table shows, for all metals the ratio Θ_D/T_m is sufficiently small that one may expand the exponentials of (2.5) to obtain

$$S(\vec{K}, T_m) \simeq \frac{k_B T_m}{M} \sum_\lambda \frac{[\vec{K}\cdot\hat{\xi}_\lambda(\vec{K})]^2}{[\omega_\lambda(\vec{K})]^2}. \tag{2.6}$$

Even for Li, for which $\Theta_D/T_m = 0.73$, the expansion is quite good. Even for Θ_D/T_m as large as 0.73, the value of $[\exp(\Theta_D/T_m)-1][1-\exp(-\Theta_D/T_m)]$ differs from the value of $(\Theta_D/T_m)^2$ by only 5%. Moreover, one notes[34] that the phonons that are most important for the calculation of $\rho(T)$ for the alkali metals are not the most energetic ones, $\hbar\omega_{\max} = k_B\Theta_D$, but rather those for which $\omega_\lambda(\vec{K}) \simeq 0.5\omega_{\max}$. Therefore, it is clear that the approximation (2.6) for $S(\vec{K}, T_m)$ is very good for all the alkali metals.

The next step is to exploit the fact that $\omega_\lambda(\vec{K})$ scales fairly closely with Θ_D for all the alkali metals. This leads one to write

$$\hbar\omega_\lambda(\vec{K}) = \alpha_\lambda(\hat{K}, K/K_{\max}) k_B \Theta_D, \tag{2.7}$$

where $\alpha_\lambda(\hat{K}, K/K_{\max})$ is a dimensionless geometrical factor that depends on λ, on the direction $(\hat{K})$ of $\vec{K}$, and on the fraction of the distance that $\vec{K}$ lies from the Brillouin-zone boundary $(K/K_{\max})$. The assumption of scaling for $\omega_\lambda(\vec{K})$ lies in assuming that $\alpha_\lambda(\hat{K}, K/K_{\max})$ is only weakly dependent on the particular alkali metal under consideration. The essence of (2.7) for the alkali metals is based on the work of Copley and Brockhouse.[35] They showed by an explicit calculation that for a pair of alkali metals [denoted metal (1) and metal (2)], the mean frequency ratio $\langle\omega_\lambda^{(1)}/\omega_\lambda^{(2)}\rangle$ equals the ratio of the Debye temperatures $\Theta_D^{(1)}/\Theta_D^{(2)}$ to within 3%. Copley and Brockhouse[35] verified this result for each pair of alkali metals, except for Cs, for which the experimental data for $\omega_\lambda(\vec{K})$ were not available. We shall here assume that (2.7) is also valid for Cs.

TABLE I. Values for the melting temperature T_m, the Debye temperature Θ_D, and the Fermi momentum k_F for the liquid phase at the melting temperature. The scale factor is defined in the text. The source of the data is given in Ref. 33.

Metal	T_m(K)	Θ_D(K)	k_F(a.u.)	Θ_D/T_m	Scale factor
Li	453	335	0.578	0.73	1.32
Na	371	156	0.474	0.42	1.00
K	337	91	0.382	0.27	1.01
Rb	312	56	0.357	0.17	1.02
Cs	303	40	0.332	0.13	1.08

Inserting (2.7) into (2.6) yields

$$S(\vec{K}, T_m) \simeq \frac{\hbar^2 T_m}{M k_B \Theta_D^2} \sum_\lambda \frac{[\vec{K}\cdot\hat{\xi}_\lambda(\vec{K})]^2}{[\alpha_\lambda(\hat{K}, K/K_{\max})]^2}, \tag{2.8}$$

where the sum over λ is taken to be independent of the particular alkali metal. On the basis of (2.8), a scaling procedure can be proposed for the angular-averaged structure factor $S(K, T_m)$. One notes that by transforming the variable of integration in the thermopower integrals (2.3) and (2.4) from K to $x = K/2k_F$, one obtains the same limits of integration, from 0 to 1, for all metals. Therefore, a comparison of structure factors for different metals requires the angular-averaged structure factor as a function of x, rather than as a function of K. Thus, the factor $[\vec{K}\cdot\hat{\xi}_\lambda(\vec{K})]^2$ of (2.8), which is proportional to $K^2 = (2k_F)^2 x^2$, becomes proportional to k_F^2 for given x. One next recalls that after factoring out this k_F^2, the sum over λ has been assumed independent of the particular metal, and that the ratio $K/K_{\max}$ is proportional to x. It then follows that the variation of $S(x, T_m)$ from metal to metal occurs only through the variation of $k_F^2 T_m/M\Theta_D^2$. As a result, one needs to calculate $S(x, T_m)$ in detail for only one metal, which we take to be Na. According to the scaling procedure, one obtains $S(x, T_m)$ for the other alkali metals by multiplying $S(x, T_m)$ for Na by the following:

$$\text{scale factor} = \frac{(k_F^2 T_m/M\Theta_D^2)_{\text{metal}}}{(k_F^2 T_m/M\Theta_D^2)_{\text{Na}}}, \tag{2.9}$$

whose value is given for the liquid phase in the last row of Table I.

For both Na and K, the values for $S(x, T_m)$ have been analyzed[34] in detail using the full expression (2.5) and including the important anharmonic correction. Thus, one can compare the results for $S(x, T_m)$ for K obtained by explicit calculation with those obtained using the scaling procedure. We find that for K, the scaling procedure reproduces the values of $S(x, T_m)$ to within 5% for all but the lowest values of x, which are unimportant anyway for $\xi(T)$. This good agreement could, of course, have been anticipated from the work of Copley and Brockhouse.[35] Since the error introduced into $\omega_\lambda(\vec{K})$ by the assumption of (2.7) is about 3% for potassium,[27] and since $\omega_\lambda(\vec{K})$ appears squared in $S(\vec{K}, T_m)$, one may expect that the scaling procedure will introduce an error into $S(x, T_m)$ of about 5–10%.

So far, we have been discussing $S(x, T_m)$ for the solid phase. For the liquid phase, $S(x, T_m)$ is obtained, in principle, directly from a scattering experiment. However, for some metals, experimental difficulties[32] have led to serious discrepancies between the various sets of available data for $S(x, T_m)$. Therefore, we again turn to the scaling procedure to obtain $S(x, T_m)$, again choosing Na as the standard metal, because of the availability of a very accurate measurement[32] of $S(x, T_m)$ for Na. The accuracy of the scaling procedure for liquid alkali metals can be estimated by comparing the measured values[32] for $S(x, T_m)$ for K with the results obtained with the scaling procedure. Such a comparison shows that for K, using the scaling procedure for the liquid phase leads to a comparable error as for the solid phase.

In summary, the estimated error for $S(x, T_m)$ resulting from the scaling procedure is 5–10% for both the solid phase and the liquid phase. It should be noted that the thermopower parameter $\xi(T_m)$ contains $S(x, T_m)$ both in the numerator and in the denominator of both the terms $q(T_m)$ and $r(T_m)$. Therefore, a partial cancellation of errors may be expected.

III. ENERGY DERIVATIVE OF FORM FACTOR

The energy derivative of the form factor, by which one means $\partial w(K, k_F)/\partial k_F$, occurs in the term $r(T)$, as given by (2.4). The calculation of $r(T)$ has an uneven history, with the early calculations[36] of $\xi(T)$ generally omitting this term altogether because of a lack of knowledge of $\partial w(K, k_F)/\partial k_F$. However, it is easy to show that the approximation of neglecting $r(T)$ is inadequate, even for the simplest case of the alkali metals. Consider the metal potassium. The experimental value of $\xi(T_m)$ is 3.7. However, from (2.2), it follows at once that if one were to neglect the term $-\frac{1}{2}r(T)$, then $\xi(T)<3$, because the term $-2q(T)$ is negative, according to (2.3). Thus, for K, the term $-\frac{1}{2}r(T)$ must make a significant positive contribution to $\xi(T)$. If this is the case for K, then there is no reason *a priori* to ignore $-\frac{1}{2}r(T)$ for any alkali metal. On the other hand, the spirit of the present approach is to avoid all complex calculations, such as that of the energy derivative[9] of $w(K, k_F)$. Therefore, we shall rely on an approximation scheme which has the twin advantages of simplicity and reasonable accuracy.

The first step in the development of the approximation scheme is to write $w(K, k_F)$ in terms of a scattering amplitude $f(K, k_F)$, whose phase-shift expansion[37] is given in the usual form

$$f(K, k_F) = (2ik_F)^{-1} \sum_{\lambda} (2l+1)(e^{2i\eta_l(k_F)} - 1) \times P_l(1 - K^2/2k_F^2)\,, \qquad (3.1)$$

where $P_l(\cos\theta)$ is the Legendre polynomial of order l and the scattering angle θ ranges from 0° ($K=0$) to 180° ($K=2k_F$). The phase shifts $\eta_l(k_F)$ depend on the energy $\hbar^2 k_F^2/2m$ of the electron being scattered. The normalization constant $-2\pi\hbar^2/m\Omega_0$ relates the scattering amplitude to the form factor

$$w(K, k_F) = -(2\pi\hbar^2/k_F m\Omega_0) \sum_l (2l+1)\eta_l(k_F) \times P_l(1 - K^2/2k_F^2) \qquad (3.2)$$

where we have expanded the exponential because, for a simple metal, the assembly of ions embedded in a screening charge implies weak scattering. The detailed justification for this important result has been given by Greene and Kohn.[13] A basic consequence of the linear relationship (3.2) between the form factor and the phase shifts is seen by considering the zero-scattering-angle limit $K=0$. The property of Legendre polynomials that $P_l(1)=1$ for all l reduces (3.2) to

$$w(0, k_F) = -(2\pi\hbar^2/k_F m\Omega_0) \sum_l (2l+1)\eta_l(k_F)\,. \qquad (3.3)$$

Use of the Friedel sum rule,[12] which is an exact relation satisfied by the phase shifts

$$\sum_l (2l+1)\eta_l(k_F) = \tfrac{1}{2}\pi z\,, \qquad (3.4)$$

where z is the valence of the ions, leads immediately to the well known result

$$w(0, k_F) = -\tfrac{2}{3}E_F\,. \qquad (3.5)$$

This exact result[12] for plane-wave pseudo-wavefunctions, derived here through the Friedel sum rule, is a direct consequence of the fact that $w(K, k_F)$ is a linear function of the $\eta_l(k_F)$.

It is a straightforward matter to obtain the $\eta_l(k_F)$ corresponding to any given $w(K, k_F)$ by inversion of (3.2) through the orthogonality properties of the Legendre polynomials

$$\eta_l(k_F) = -(m\Omega_0/4\pi\hbar^2) \times \int_0^{2k_F} dK\, K w(K, k_F) P_l(1 - K^2/2k_F^2)\,. \qquad (3.6)$$

In practice, the $\eta_l(k_F)$ decrease rapidly with increasing l, and one may safely ignore the phase shifts for which $|\eta_l(k_F)| < 0.001$. This corresponds to $l > 3$ for all the alkalis. Thus, (3.2) constitutes a known expansion for $w(K, k_F)$, consisting of four terms.

We now turn to the determination of $\partial w(K, k_F)/\partial k_F$. In (3.2) there appear three sources of k_F dependence for $w(K, k_F)$. There is no difficulty in evaluating the contribution to $\partial w(K, k_F)/\partial k_F$ arising from the k_F^{-1} factor before the sum over l and from the k_F^2 in the argument of $P_l(1-K^2/2k_F^2)$. The difficulty lies in the unknown k_F dependence of $\eta_l(k_F)$. Here, we make the approximation suggested by the work of Young, Meyer, and Kilby[8] (YMK). For a particular model potential, Meyer *et al.*[38] calculated explicitly both the phase shifts and their energy derivatives $\partial\eta_l(k_F)/\partial k_F$. YMK (Ref. 8) noticed that for all the alkalis, the energy derivatives of the phase shifts were reasonably well approximated (to about 20%) by the large-l expression (Ref. 37) $\eta_l(k_F)\propto k_F^{2l+1}$ for $l \geq 1$ and by the high-energy expression $\eta_0(k_F)\propto k_F^{-1}$ for $l=0$. Using these two expressions leads to

$$\begin{aligned} k_F\frac{\partial\eta_l(k_F)}{\partial k_F} &= (2l+1)\eta_l(k_F)\,, \quad l \neq 0 \\ k_F\frac{\partial\eta_0(k_F)}{\partial k_F} &= -\eta_0(k_F)\,. \end{aligned} \tag{3.7}$$

This constitutes a complete determination of the energy derivative of the form factor and thus permits an explicit calculation of $r(T_m)$ in terms of the form factor and the structure factor.

One can test the present phase-shift calculation of the term $-\frac{1}{2}r(T_m)$ by comparing with the results of the complete, many-body pseudopotential calculation.[9] Leavens and Taylor[6] list in their Table I the values they obtained for $\frac{1}{2}r(T)$ for both Na and K. As expected, the value for $-\frac{1}{2}r(T_m)$ for Na is quite small (0.07) and therefore of less interest than the result for K. For K, Leavens and Taylor find $-\frac{1}{2}r(T_m)=1.72$, whereas we find the value 1.61. This close agreement is particularly satisfying and increases our confidence in the use of an empirical phase-shift approach to calculate $-\frac{1}{2}r(T_m)$.

IV. RESULTS AND COMPARISON WITH EXPERIMENT

In the previous two sections, the methods were presented for determining the structure factor and the form factor, including its energy dependence, for the alkali metals. With this information, one is in a position to evaluate (2.3) and (2.4) and thus obtain the calculated values for the thermopower of all the alkali metals, for both the solid and the liquid phases.

For comparison with the calculated values, we use the recent thermopower measurements of Kendall[39] for both ξ_S and ξ_L for all the alkali metals, where the subscripts S and L denote solid and liquid phase, respectively, at the melting temperature. Of particular importance is the fact that the same worker measured both ξ_S and ξ_L on the same apparatus. Thus, one can be confident of the reliability of the experimental values of the solid-to-liquid difference $\xi_S-\xi_L$. Similarly, the volume derivative of the thermopower for the solid phase, $\partial(\ln Q_S)/\partial(\ln V)$, was measured by Dugdale and Mundy[40] for all the alkali metals. Although the volume derivative was measured[40] at 0 °C and our calculation refers to the melting temperature, one would not expect any significant change in the volume derivative over the relatively short temperature interval from 0 °C to T_m. In fact, $\xi_S(T)$ itself varies[39] by less than 10% over this interval for all alkalis.

In Fig. 1, we compare the experimental results (solid circles) with our calculated results (open circles) for ξ_S and ξ_L. For each alkali metal, the results are given for both the solid (S) phase and the liquid (L) phase. In Table II, we present the results for $\xi_S-\xi_L$ and for $\partial(\ln Q_S)/\partial(\ln V)$ for the alkali metals. For each entry in Table II, the calculated value is listed directly below the experimental value. Before discussing the table and the figure in some detail, we note that the overall agreement between the calculated and experimental values is quite good. This illustrates once again the power of the empirical approach.

Consider first the solid-to-liquid difference. For all the alkali metals, the calculated values of $\xi_S-\xi_L$ are within 0.2 of the experimental values. Such close agreement between theory and experiment has not characterized previous studies. Turning now to the values for ξ_S and ξ_L individually, for Na, K, and Rb, there is very good agreement between theory and experiment for both ξ_S and ξ_L. Note in particular that the results for K, for which the calculated value of $\xi(T_m)$ is greater than 3, point to the ability of the empirical approach to calculate accurately the term $-\frac{1}{2}r(T_m)$. For Li and Cs, the situation is somewhat less satisfactory. The calculated values of both ξ_S and ξ_L

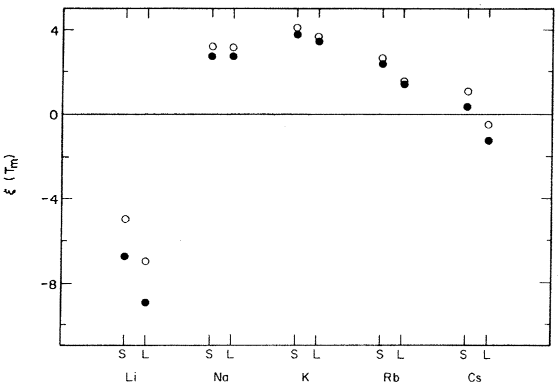

FIG. 1. Values for $\xi(T_m)$ for the alkali metals for the solid (S) phase and the liquid (L) phase. The solid circles represent the experimental values and the open circles represent the calculated values.

TABLE II. Comparison between experimental and calculated values for $\xi_S - \xi_L$ and for $\partial(\ln Q_S)/\partial(\ln V)$ for the alkali metals.

		Li	Na	K	Rb	Cs
$\xi_S - \xi_L$	expt.	2.2	0.0	0.3	1.0	1.6
	calc.	2.0	0.1	0.5	1.2	1.7
$\frac{\partial(\ln Q_S)}{\partial(\ln V)}$	expt.	0.4	2.1	−0.4	0.4	~50
	calc.	1.4	2.7	−0.5	1.0	

differ from experiment, by ~2 for Li and ~1 for Cs. However, note that for Cs, the difference in sign between ξ_S and ξ_L is successfully reproduced by the calculation.

We suggest that the source of the discrepancy for Li, and perhaps also for Cs, lies in our use of single-plane-wave pseudo-wave-functions. This is certainly a satisfactory approximation for Na, K, and Rb, for which the value of the form factor at $K = 2k_F$ is rather small. Define $\overline{w}(K) \equiv w(K, k_F)/(\frac{2}{3}E_F)$ as the normalized form factor. Then, for Na, K, and Rb, one finds $|\overline{w}(2k_F)| < 0.1$, justifying the single-plane-wave approximation. However, for Li, for which $\overline{w}(2k_F) > 0.3$, a multiple-plane-wave pseudo-wave-function is certainly required, and probably also for Cs, for which $|\overline{w}(2k_F)| = 0.14$. This point has previously been emphasized for lithium.[25,26] It would therefore be expected that the single-plane-wave approximation would affect the calculated values for ξ_S and ξ_L in about the same way. Accordingly, one expects, and finds, for both Li and Cs, that (i) the calculated values of $\xi(T_m)$ are always higher (more positive) than the experimental values and (ii) the calculated difference $\xi_S - \xi_L$ is in agreement with experiment.

We now turn to the volume derivative of the thermopower, given in the last column of Table II. One sees that, with the exception of Cs, the calculated values follow the general trend of the data. The calculated value for $\partial(\ln Q_S/\partial(\ln V)$ is largest for Na, is smaller for Li and Rb, and is negative for K. The extremely large experimental value of about 50 for Cs may possibly be related to the large d-band resonance for Cs, which is known[41] to be especially strong and close to the Fermi surface for this heaviest of the alkali metals. There is, of course, no possibility that our empirical form factor can adequately describe the volume dependence of such a resonance.

V. SIMPLIFIED MODEL

Within the present framework, it is possible to examine several general features of the thermopower calculation. We are here interested in a qualitative picture which relates the calculated results for the different alkali metals. For this purpose, it is convenient to introduce a simplified model for the form factor which, while not reliable for a quantitative calculation of $\xi(T_m)$, is very useful for a qualitative discussion. The model consists of replacing the realistic form factors that we used for our quantitative calculation by the one-parameter Ashcroft[42] model potential, whose bare potential, in terms of $x = K/2k_F$, is given by

$$w_{\text{Ash}}^{\text{bare}}(x) = \frac{-\pi e^2 \cos(2k_F R_c x)}{x^2 k_F^2 \Omega_0} . \tag{5.1}$$

In this expression for $w_{\text{Ash}}^{\text{bare}}(x)$, each alkali metal is characterized by two parameters, k_F and the core radius R_c. We wish to reduce this characterization to a single parameter. To this end, we introduce the normalized core radius $\overline{R}_c \equiv R_c k_F$. Rewriting (5.1) in terms of $\overline{R}_c$ yields

$$w_{\text{Ash}}^{\text{bare}}(x) = \frac{-e^2 \overline{R}_c \cos(2\overline{R}_c x)}{x^2 R_c} . \tag{5.2}$$

We now note that the dependence of $w_{\text{Ash}}^{\text{bare}}(x)$ on R_c is much weaker than the dependence on $\overline{R}_c$, because R_c appears only as a multiplicative factor, whereas $\overline{R}_c$ appears in the argument of the cosine. Moreover, R_c varies[43] by only about 10% for the different alkalis. Therefore, we replace R_c in (5.2) by its average value, $(R_c)_{\text{ave}} = 1.0$ Å. With this replacement, $w_{\text{Ash}}^{\text{bare}}(x)$ depends only on the single parameter $\overline{R}_c$.

To obtain the form factor, one must divide $w_{\text{Ash}}^{\text{bare}}(x)$ by the screening function $\epsilon(x)$. For $\epsilon(x)$, it is natural to use the Hartree dielectric function $\epsilon_H(x)$. Thus, our simplified expression for the Ashcroft model form factor is

$$w_{\text{Ash}}(x) = \frac{-e^2 \overline{R}_c \cos(2\overline{R}_c x)}{(R_c)_{\text{ave}} x^2 \epsilon_H(x)} . \tag{5.3}$$

The value for $\overline{R}_c$ is chosen by setting $w_{\text{Ash}}(x)$ equal, at $x = 1$, to the realistic form factor we used to calculate $\xi(T_m)$ and $\rho(T_m)$. In other words, for each alkali metal, $\overline{R}_c$ is chosen so that $w_{\text{Ash}}(x)$ gives the correct value for $\overline{w}(2k_F) \equiv w(2k_F, k_F)/(\frac{2}{3}E_F)$. Thus, for each alkali metal, the form factor is completely determined by the single parameter $\overline{w}(2k_F)$. The usefulness of this simplification will soon become apparent.

The scaling procedure we used to determine the angular-averaged structure factor $S(K, T_m)$ leads to an important result for the calculation of $\xi(T_m)$. In terms of the variable $x = K/2k_F$, for a given phase (solid or liquid), $S(x, T_m)$ is identical for each alkali metal except for the scale factor (2.9). However, the expressions for $q(T_m)$ and

$r(T_m)$ contain $S(x, T_m)$ in both the numerator and the denominator. Therefore, the scale factor (2.9) cancels out of $q(T_m)$ and $r(T_m)$ and hence does not appear at all in $\xi(T_m)$. As a result, the same structure factor enters the calculation of $\xi(T_m)$ for all the alkali metals.

In view of the above discussion, the following feature characterizes the calculation of $\xi(T_m)$ if one makes the approximation of using the Ashcroft model form factor in addition to the scaling procedure for the structure factor. For a given phase, the calculated value of $\xi(T_m)$ depends solely on the parameter R_c or, equivalently, on $\overline{w}(2k_F)$. Accordingly, we have calculated $\xi(T_m)$ as a function of $\overline{w}(2k_F)$. The results are plotted on Fig. 2, where the solid and dashed curves represent $\xi(T_m)$ for the solid and liquid phases, respectively. An arrow marks the value of $\overline{w}(2k_F)$ for each of the alkali metals. Note that $\overline{w}(2k_F)$ decreases monotonically[31] with atomic number, from $\overline{w}(2k_F)=0.35$ for Li to $\overline{w}(2k_F)=-0.15$ for Cs. [The change in $\overline{w}(2k_F)$ upon melting is very small, only about 0.005.] For comparison, the calculated values ξ_S and ξ_L for each alkali metal, as given in Table II, are also indicated on the graph by the solid and open circles, respectively.

The following interpretation may be attached to the curves in Fig. 2. One imagines a "generalized" alkali metal, characterized by a continuous variation of the value of $\overline{w}(2k_F)$. Then, the curves give the values for ξ_S and ξ_L for this generalized alkali metal within the approximation of the Ashcroft model form factor. Each of the five "real" alkali metals constitutes one point on the $\overline{w}(2k_F)$ axis.

It is natural to limit our discussion to the "physical" range of $\overline{w}(2k_F)$, which extends from about +0.4 (~Li) to about −0.2 (~Cs). Within the physical range, $\xi(T_m)$ varies from a maximum value of about +4 to a minimum value of about −8, with no qualitative difference between the solid and the liquid phases. Note that the calculated values of ξ_S and ξ_L for Li are not far from the lowest possible values for a single-plane-wave generalized alkali metal. Similarly, the calculated values of ξ_S and ξ_L for K are very close to the highest possible values. One also sees that for Li, Na, and K, the calculated values for both ξ_S and ξ_L lie quite close to the corresponding model curve. However, for Rb and Cs, the model calculation is not quantitatively reliable.

We now consider the terms $-\frac{1}{2}r(T_m)$ and $-2q(T_m)$ individually. These are plotted in Fig. 3 as a function of $\overline{w}(2k_F)$. Again, the solid and dashed curves represent the solid and liquid phases, respectively. For the term $-\frac{1}{2}r(T_m)$, there is only

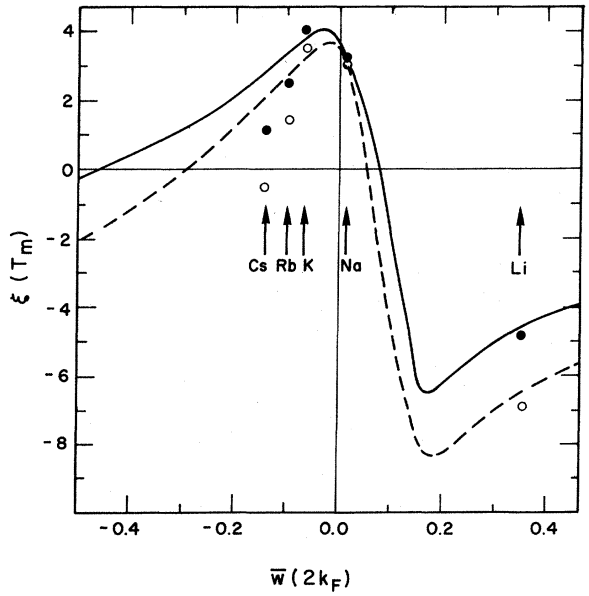

FIG. 2. Model calculation for $\xi(T_m)$ as a function of the normalized form factor $\overline{w}(2k_F)$. The solid and dashed curves denote the solid and liquid phases, respectively. The arrows indicate the value of $\overline{w}(2k_F)$ corresponding to each of the alkali metals. The solid and open circles indicate the calculated values for the solid and liquid phases, respectively.

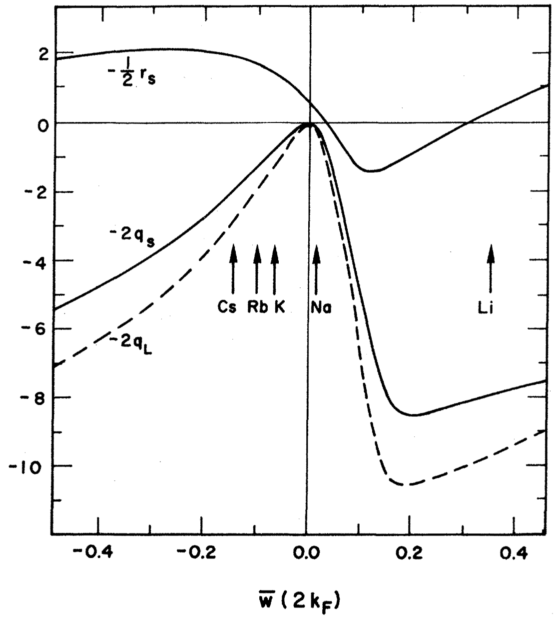

FIG. 3. Model calculation for $-2q(T_m)$ and $-\frac{1}{2}r(T_m)$ as a function of the normalized form factor $\overline{w}(2k_F)$ for the solid (S) and liquid (L) phases, respectively. Since the curve for $-\frac{1}{2}r_L$ is almost identical with the curve for $-\frac{1}{2}r_S$, it is not given. The arrows indicate the value of $\overline{w}(2k_F)$ corresponding to each of the alkali metals.

a negligible difference between the values for the two phases and, therefore, only one curve is plotted. As in Fig. 2, an arrow marks the value of $\overline{w}(2k_F)$ for each of the alkali metals.

The most interesting results are those for $-\frac{1}{2}r(T_m)$. One sees that for most of the physical range of $\overline{w}(2k_F)$, the magnitude of the contribution of this term to $\xi(T_m)$ exceeds unity. Therefore, there is no *a priori* justification for neglecting the term $-\frac{1}{2}r(T_m)$ for any metal. Indeed, the fact that $-\frac{1}{2}r(T_m)$ is quite small for both Li and Na is, in a sense, accidental. The values for $-\frac{1}{2}r(T_m)$ change sign twice within the physical range as a function of $\overline{w}(2k_F)$, and the two values of $\overline{w}(2k_F)$ for which $-\frac{1}{2}r(T_m)$ vanishes just happen to occur near the values of $\overline{w}(2k_F)$ appropriate to Li and Na. Therefore, $-\frac{1}{2}r(T_m)$ is small for those two alkalis. However, for a general value of $\overline{w}(2k_F)$, such as that corresponding to K, Rb, and Cs, the values for $-\frac{1}{2}r(T_m)$ are considerably larger than unity and clearly constitute a sizable contribution to $\xi(T_m)$.

Consider now the values for $-2q(T_m)$. For $\overline{w}(2k_F)>0.1$, the term $-2q(T_m)$ dominates $-\frac{1}{2}r(T_m)$ and is primarily responsible for the large, negative value of $\xi(T_m)$ for Li. However, for $\overline{w}(2k_F)<0.1$, the terms $-2q(T_m)$ and $-\frac{1}{2}r(T_m)$ are comparable in magnitude. Therefore, $\xi(T_m)$ is much larger for the other four alkalis, varying from about -1 to about $+4$.

A comment is in place about the minimum exhibited by $-2q(T_m)$ near $\overline{w}(2k_F)\simeq 0.15$. One might have thought that because $q(T_m)\propto|\overline{w}(2k_F)|^2$, according to (2.3) the value of $q(T_m)$ would always increase with increasing $\overline{w}(2k_F)$. However, $q(T_m)$ also contains an integral in the denominator. For large values of $\overline{w}(2k_F)$, this integral is dominated by the integrand at $K\simeq 2k_F$, and becomes nearly proportional to $|\overline{w}(2k_F)|^2$. Therefore, for $\overline{w}(2k_F)>0.2$, $q(T_m)$ becomes nearly independent of $\overline{w}(2k_F)$. Such behavior is clearly apparent in Fig. 3. For the same reasons, a minimum in $-2q(T_m)$ also occurs for large, negative values of $\overline{w}(2k_F)$. However, for negative $\overline{w}(2k_F)$, the minimum occurs far beyond the physical range of $\overline{w}(2k_F)$ and therefore does not appear in Fig. 3.

VI. SUMMARY

In this paper, we present an empirical calculation of the high-temperature thermopower of the alkali metals. Such empirical calculations complement first-principles calculations and are particularly suitable for analyzing the general features of the calculation. Our principal result are the following:

(i) The empirical calculation for the high-temperature thermopower yields results that are in very good overall agreement with the experimental values at the melting temperature. This is the case both for the solid phase and for the liquid phase, for all the alkali metals.

(ii) A scaling procedure is proposed for determining the high-temperature structure factor, which is applicable to both the solid phase and the liquid phase. The estimated error of the structure factor obtained from the scaling procedure is shown to be less than 10%.

(iii) An approximate procedure is proposed for obtaining the energy derivative of the form factor from the form factor itself, by means of a phase-shift expansion. Our results for the thermopower integral $-\frac{1}{2}r(T_m)$ that contains the energy derivative of the form factor are within 0.1 for K and 0.3 for Na of those obtained by Leavens and Taylor from the complete calculation.

(iv) A simplified one-parameter model is introduced, suitable for a qualitative discussion of the thermopower calculation. General features of the calculation are analyzed in the framework of the model, including the variation of $\xi(T_m)$ from metal to metal, the maximum and minimum possible values for $\xi(T_m)$, and the importance of the role played by the energy derivative of the form factor.

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