Thermochimica Acta, 218 (1993) 1–16
Elsevier Science Publishers B.V., Amsterdam

THE ELECTRON-PHONON INTERACTION AND MELTING OF METALS

B. H. Armstrong[a]

[a]*IBM Scientific Center, Palo Alto, CA 94304, USA*

Keywords: Melting, Uncertainty Principle, Lindemann law, electron-phonon interaction.

ABSTRACT

The minimum uncertainty product form of Heisenberg's Uncertainty Principle is applied to the electron-phonon interaction in metals in the free-electron and Debye approximations. Twice the Debye frequency follows as an upper limit to the electron-phonon scattering rate. This is an extension of an earlier application to the 3-phonon anharmonic scattering rate, and Lindemann's law of melting follows in both cases. Corrections and clarifications of the earlier work are included. It is shown that the electron-phonon relaxation time, the Debye zone-boundary phonon relaxation time, the ion-ion collision time on the liquid side of melting, and the inverse of twice the Debye frequency are all approximately equal at the melting point.

INTRODUCTION

In several earlier articles, I made use of the energy-time Uncertainty Principle (UP) to obtain a number of results connected with melting (Armstrong, 1986, 1988a, 1988b, 1988c). Initially, Lindemann's law of melting was derived from the 3-phonon anharmonic transition rate of Roufosse and Klemens (1973) and, in addition, a lower bound on diffusion coefficients of simple solids at the melting point was obtained. This lower bound was found to be a good approximation to actual diffusion coefficients at the melting point of alkali metals and alkali halides. Next, it was found to also provide a good approximation for electrical conductivities and volume expansion of alkali halides at the melting point (Armstrong, 1988a). The estimates of diffusion coefficients and electrical conductivities were carried out in the Debye approximation to phonon theory, are exceedingly simple, and involve no adjustable parameters. The fusion volume expansion of alkali halides was also estimated with favorable accuracy with the replacement of the maximum frequency phonon modes by single-particle ion motion in terms of an Einstein oscillator model. Later (Armstrong, 1988c), the diffusion coefficient formula was found to provide a similarly good approximation for the more complex solids H_2 and N_2 at the melting point and to provide a well-known empirical expression for the self diffusion of liquid metals at the melting point (Iida and Guthrie, 1988). The minimum uncertainty product form of Heisenberg's Uncertainty Principle was used in the initial derivations (Armstrong, 1986, 1988a), and only later (Armstrong, 1988b) was it recognized that, for the phonon-phonon interaction case leading to Lindemann's law, one was dealing with a classical, not a quantum system, and the "Uncertainty Principle' involved was the classical Uncertainty Principle of the well-known limit on the Fourier resolution of a function of time of finite duration (See, e. g., Kramers, 1958; Papoulis, 1962). The results are the same because $\hbar$ cancels out of the equations. I am not herein attributing a quantum, character to ordinary melting, but am attempting to clarify a situation wherein quantum derivations yield classical results more readily than classical derivations. It should be noted that the Roufosse-Klemens (1973) 3-phonon anharmonic transition rate is independent of $\hbar$ even though it is derived by second quantization.

Fundamental to these earlier results is the upper limit to the anharmonic phonon transition rate established by the UP, along with the assumption that this upper limit is reached at the melting point T_m by the maximum frequency phonons in the lattice. This upper limit, where the phonon energy and linewidth become comparable, expresses the condition whereby the maximum frequency phonons lose their validity as collective excitations. The basic idea of this approach, viz., establishing a condition for loss of validity of certain phonons as collective excitations is somewhat analogous to the self-consistent-phonon (SCP) theory as represented by the work of Moleko and Glyde (1983, 1984). In that approach, an average squared phonon frequency is computed as a function of temperature. A critical temperature is found above which there are no real solutions. The phonon frequency becomes imaginary and therefore the phonon does not exist as a valid collective excitation, or travelling wave normal mode.

It is the purpose of the present article to summarize the results of the unpublished reports (Armstrong, 1988b,c) and clarify two published articles (Armstrong, 1986, 1988a). In addition to improved interpretation of earlier work, the present article presents new results for free-electron solids. In extending our earlier considerations to conduction electrons in metallic crystals, it is found that, at the melting point, electron-phonon scattering is related to phonon-phonon scattering, as well as to ion-ion scattering. These results are somewhat surprising, since there appears to be no *a priori* reason why such relationships should exist. Upon close examination, however, it appears that they may be required for consistency with a unique and sharply defined melting point. The analysis undertaken herein is limited to the free-electron approximation. Lifting this approximation would be of doubtful value unless the Debye approximation were also dispensed with. Neither of these improvements appears crucial to the concepts proposed herein, and would greatly complicate initial presentation of the theory.

ELECTRON-PHONON SCATTERING AT THE MELTING POINT

Application of the Uncertainty Principle

In the case of electron-phonon scattering, it may be recalled that the electron-phonon interaction depends on the vibration amplitude in the crystal. This is, e. g., displayed explicitly in Eq. 11.84 of Kittel (1956, p. 303) in the form

$$Q_d = (\vec{q} \cdot \vec{d})^2 Q_s \ , \tag{1}$$

where (to quote Kittel), "Q_d is the effective cross section for scattering of an electron by a displaced ion in an otherwise perfect lattice, and Q_s is the free space scattering cross section for an isolated ion". The vector with magnitude d denotes the displacement of the ion, while $\vec{q}$ is the phonon wavevector. Now if one believes, as conventionally asserted in Lindemann theory, that a critical value of d exists which marks the onset of lattice instability, then this effect should also be reflected in the electron-phonon scattering rate according to Eq. (1). This analogy suggests, but is not necessary to, the application of the UP arguments to the electron-phonon system.

In the present case, we start at the outset with the Debye approximation to phonon theory. This approach circumvents the necessity of decomposing the electron-phonon transition rate into components of the electron-phonon interaction for each wavevector. Loss of accuracy due to this approach is justified by lack of precise knowledge of that interaction term. Alternatively, we can appeal to the "dominant phonon" approximation under which we would treat the system as containing only phonons of frequency ω_D at the melting point.

We write the energy-time UP in the minimum uncertainty product form as before,

$$\frac{1}{\tau_{ep}} \leq \frac{2\Delta E_e}{\hbar} \tag{2}$$

where ΔE_e is, of course, the uncertainty in the electron energy and τ_{ep} is the electron-phonon relaxation time. This minimum-product form obtains only for the case of Gaussian distributions of the uncertainties in the relevant dynamical variables. The validity of this form is assumed herein without *a priori* justification as a fundamental premise of the approach. If it is further assumed that the electrons available to interact with phonons are on the Fermi surface with well-defined energy, we have

$$\Delta E_e \ \leq \ \hbar\omega_D \ , \tag{3}$$

where ω_D is the Debye angular frequency, viz., the maximum frequency of the phonons from which (in the Debye approximation) the electron can scatter. One knows that thermally excited electrons perturb the Fermi distribution in a range $\simeq \pm k_B T$ on each side of the Fermi surface, where k_B is Boltzmann's constant and

T is the absolute temperature in kelvins. But statistically single scattering is more probable than multiple scattering, i. e., it will be more probable for an electron on the surface to scatter than for an excited electron to scatter (the excited fraction at the melting point is of the order of T_m/T_F , where T_F is the Fermi temperature, and this ratio is small). Nonetheless, the fact that the electron being scattered by a phonon is not guaranteed to be precisely on the Fermi surface vitiates the rigorous nature of Eq. (3) as an inequality, as does the use of the Debye approximation. Thus, our results should be interpreted as estimates. The basic assumption of the previous articles is now invoked, namely, that the UP inequality becomes an equality at the melting point.

From Eqs. (2) and (3), this assumption takes the form

$$\frac{1}{\tau_{ep}(T_m)} = 2\omega_D \ . \tag{4}$$

The physical interpretation proposed here is the same as that advanced in Ref. 1; namely, that the maximum frequency phonons lose their validity at T_m, providing single-particle ion motion on the time scale $(2\omega_D)^{-1}$. As will be demonstrated below, this is the same time scale as that of the experimental free electron relaxation time $\tau = m\sigma/ne^2$, where σ is the experimental electrical conductivity, and n, e, and m are the electronic concentration, charge, and mass, respectively. Thus, on the average, an electron will make one collision during the time period over which the ion is moving as a free particle. This collision will not be subject to the UP in the form stated above since it will not involve a phonon, but will be determined by the dynamics of the electron-ion scattering process. Application of the UP to the electron-phonon system can only be made on the solid side of the melting transition where the phonon is still a valid excitation. Therefore, the inequalities asserted above must become invalid at T_m , and we expect an increased scattering rate, or decreased relaxation time in the liquid phase. In terms of Eq. (1), a larger value of *d* becomes available on the liquid side. This is confirmed for eight alkali and noble metals in Table I of Armstrong (1988b). This table gives a comparison of experimental values of τ_{el}, the electronic relaxation time in the liquid at the melting point with $1/(2\omega_D)$, the estimate asserted above of the relaxation time on the solid side of the melting point. The ratio of these two quantities is confirmed to be less than unity in all cases; the average for all cases is 0.26. From data given by Faber (1972), it can be seen that the average of experimental values of ρ_s/ρ_l, the ratio of electrical resistivities of the solid and liquid states, is 0.56 for these eight cases. Since this resistivity ratio is equal to τ_{el}/τ_{ep} on the classical kinetic model, the comparison of Table I in the reference given above indicates that the UP estimate of τ_{ep} at the melting point is within a factor 2, on the average, of experiment. A direct comparison with experiment as well as other theory will be given below.

It is expected that, for describing the maximum lattice vibrational frequencies the most appropriate Debye temperatures will be elastic-constant values. But values are needed at the melting point, and these are not available. Melting-point values may be approximated by room-temperature values because it is generally considered that Debye temperatures for most ordinary solids do not vary substantially above room temperature (e. g., Meaden, 1965, p. 101). For example, Blackman (1955, p. 372) notes that his type *a* Debye temperature is the most common and is found in the cubic metals. For this type, T_D approaches a high-temperature asymptote at or below room temperature. Unfortunately, a consistent, accurate set of room-temperature elastic-constant Debye temperatures is not available for the alkali metals. The problems associated with available values are discussed in Armstrong (1988b). As an alternative, we approximate the alkali metal melting-temperature Debye temperatures by the specific heat (entropy) values given in the careful assessment of Martin (1965). Martin's results go up to 300 K, where they are seen to be slowly decreasing due to anharmonicity. The accuracy of the present approach does not warrant an extrapolation to T_m. To maintain consistency, Kelly's (1954) specific heat values are used for T_D of Cu, Ag, and Au, taken from Figs. 4, 7, and 10, respectively, of that reference. The first column of Table I lists this selection of Debye temperatures.

TABLE I

Comparison of electrical resistivities at the melting point. Units are $10^{-6}\,\Omega$ cm. The Debye temperatures and the Debye resistivity temperatures used are shown in the second and third columns.

Species	T_D(K)	T_R(K)	ρ_U	ρ_B	ρ(exp)
Li	373	440	9.3	5.7	15.5
Na	149	195	7.5	5.8	6.6
K	86.9	110	8.0	8.0	8.32
Cu	310	333	4.1	3.9	10
Ag	217	223	4.0	4.1	8.2
Au	175	175	3.2	4.0	13.7

When we come to the evaluation of electrical resistivities from the Bloch high-temperature formula (Ziman, 1963) the so-called "electrical resistivity" values of Debye temperature, usually labelled T_R, are generally used. These are typically calculated either by fitting the Bloch formula or by fitting the ratio of values of the Bloch formula at two different temperatures, and have usually only been of interest at low temperatures. As a result, there is an even greater paucity of data on these parameters towards high temperature than for T_D . Their computation is reviewed at length by Meaden (1965) who also tabulates values of T_R. Such resistivity values of the Debye temperature are effectively adjustable parameters which compensate to some extent for the approximations of Bloch theory such as spherical Fermi surface, free-electron approximation, neglect of U processes, and simplified electron-phonon interaction. Here again, as in the case of T_D, there is no clearly appropriate choice for our purposes as discussed in Armstrong (1988b). Therefore, the somewhat arbitrary choice is made to use, for the alkali metals, the values given by Meaden (1965) for the temperature range $T_R/3$ to T_R. These values have the advantage of being corrected to a constant density and the disadvantage that this is the 0 K density. For Cu, Ag, and Au, Grüneisen's (1933) original values are used because he included resistivity data in their determination taken over temperature ranges that approach a significant fraction of the melting temperature for these metals. This selection of T_R values is given in the third column of Table I. They were used to evaluate ρ_U and ρ_B as given in columns four and five of Table I. The Debye temperatures listed in the second column of Table I were used in the comparison of solid-liquid electronic relaxation times mentioned in the preceding paragraph, and in results yet to be described below.

The electron-phonon scattering rate, as measured by the electrical resistivity, increases as T towards high temperature (Ziman, 1963; Pines, 1964, p. 52) like the three-phonon transition rate (Roufosse and Klemens, 1973). Hence, it should reach its maximum at the melting point. One can test this assertion by use of $1/(2\omega_D)$ for τ in the classical kinetic formula for the electrical conductivity σ:

$$\sigma = ne^2\tau/m \ . \tag{5}$$

With τ taken to be $\tau_{ep} = 1/(2\omega_D)$ as derived above, the "Uncertainty Principle" resistivity ρ_U at the melting point becomes

$$\rho_U = = 9.31x10^{14}\frac{T_D}{n} \quad \Omega\ cm\ . \tag{6}$$

It is interesting now to compare the result of Eq. (6) with experiment and with prediction of the high-temperature Bloch theory. The Bloch electron-phonon transition rate, which we denote τ_{eB}^{-1} can be obtained through use of Eq. (5) from the Bloch resistivity formula given by Ziman (1963) for the range $T/T_D \gg 1$. The result is

$$\tau_{eB}^{-1} \equiv \frac{\pi^3\hbar^2 v_F N T}{4Mk_B T_D^2} \ . \tag{7}$$

In this equation, N, M, and v_F, are the number of unit cells per unit volume, the unit cell mass, and the Fermi velocity, respectively. The Bloch resistivity ρ_B from which Eq. (7) was derived can be evaluated as

$$\rho_B(T_m) = 4.78x10^{-10}\frac{(n^{\frac{1}{3}}\ T_m)}{AT_D^2} \quad \Omega\ cm\ , \tag{8}$$

where A is atomic weight. Table I shows, for six metals, in addition to the Debye temperatures discussed above, a comparison between ρ_U, ρ_B, and $\rho(\exp)$, where the latter is the experimental result given by Cusack (1963). The electron/ion concentrations employed for this calculation are melting point values given by Ubbelohde (1978). The UP result clearly provides the proper order of magnitude, coming within about a factor 2 of experiment for all cases but gold. The results shown in Table I are typical of agreement between free-electron theory results and experiment (cf. MacDonald, 1956). The relatively closer agreement between ρ_U and ρ_B lends substantiation to our fundamental assumption $1/\tau_{ep} = 2\omega_D$ at T_m. This is, of course, the same as the fundamental assumption made earlier for the Debye zone boundary transition rate for 3-phonon processes, namely, $1/\tau(\omega_D)_{pp} = 2\omega_D$ at T_m, where $1/\tau(\omega_D)_{pp}$ is the Debye zone boundary value of the three-phonon transition rate. Consequently, the fundamental assumption requires the total electron-phonon scattering rate to be equal to an average frequency-maximum three-phonon scattering rate at the melting point. This latter rate is approximated by the Debye zone boundary rate herein. Originally it was proposed to take the average only over longitudinal modes (Armstrong, 1988a) A more general formulation of the average required was proposed in Armstrong (1988b) and is summarized in the Appendix.

The approximate agreement shown in Table I between the resistivity given by the Bloch formula and the UP formula also substantiates agreement between the electron-phonon scattering rate and the frequency-maximum three-phonon scattering rate at the melting point. There appears to be no *a priori* reason why any direct relationship should exist between the electron-phonon and three-phonon anharmonic transition rates, so the relationship may be connected with the melting process. It is suggested that such a relationship is required in order for there to be a unique, sharply defined melting point. The reasoning is as follows, stated in the context of the Debye approximation for simplicity of presentation. The concepts are not limited by this approximation.

It can be assumed that $1/\tau(\omega_D)_{pp}$ reaches its maximum value as a function of frequency at ω_D , and that both $1/\tau_{ep}$ and $1/\tau_{pp}$ increase linearly with T towards high T. From the UP argument above given above, $2\omega_D$ is the maximum value of both these transition rates. We know that $1/\tau_{ep}$ reaches its maximum at T_m and that the total electron scattering rate (assumed equal to $1/\tau_{ep}$ below T_m) increases discontinuously across the solid-liquid transition. This discontinuous increase is due to the electron-ion scattering that sets in at T_m concomitantly with the onset of single-particle ion motion (Faber, 1972). Now if $1/\tau(\omega_D)_{pp}$ were to reach the value $2\omega_D$ before $1/\tau_{ep}$ reaches this value, single particle motion would have set in without affecting the electron scattering rate (because the highest frequency phonons will have lost their validity as collective excitations according to the fundamental hypothesis stated above). Thus, melting would occur without the requisite jump in the electron scattering rate. Conversely, if the electron scattering rate reaches $2\omega_D$ and the discontinuous jump before $1/\tau(\omega_D)_{pp}$ reaches $2\omega_D$, melting will have occurred according to the behavior of the electron-phonon scattering, but not according to $1/\tau(\omega_D)_{pp}$. According to the behavior of this latter quantity, all phonons would still be valid collective excitations and no single-particle motion would be possible. Thus, we have an inconsistency unless both transition rates reach their common maximum $2\omega_D$ at the same temperature. Furthermore, the relaxation time determined by these transition rates is equal to the ion-ion collision rate as shown in Armstrong (1986 and 1988a). This happens because the motion lost from the spectrum of phonon excitations as the maximum-frequency phonons lose validity is converted into single-particle motion of the ions.

In view of the above finding, it is appropriate to compare $\tau(\omega_D)_{pp}$, used previously to derive the Lindemann melting law from the assertion of its equality to $(2\omega_D)^{-1}$, with the Bloch electron-phonon relaxation time, as well as with the ion-ion relaxation time. Furthermore, if all is to be consistent, it must be possible to obtain Lindemann's law from the Bloch expression.

Comparison of Bloch, three-phonon, and ion-ion relaxation times

The three-phonon, Debye-zone-boundary transition rate expression referred to above and used in our earlier work is that given by Roufosse and Klemens (1973) evaluated at $\omega = \omega_D$:

$$\tau_{pp}(\omega_D, T)^{-1} = \frac{12\sqrt{2}\,\pi^3\gamma^2 k_B T}{M a^2 \omega_D} . \tag{9}$$

In this expression, a is the lattice constant used by Ziman (1963) and Roufosse and Klemens (1973), defined such that $a^3 = 1/N$, and γ is the Grüneisen parameter. The numerical coefficient is that of Eq. (20b) of Roufosse and Klemens, adjusted empirically by a factor 4/9 for bcc alkali metals. Roufosse and Klemens derived their formula for sc crystals after strong approximations on the form of surfaces in $\vec{q}$ space. Hence, the precise coefficient is not well-determined resulting in a *de facto* adjustable parameter, although in principle the theory is deterministic. As noted previously, if Eq. (9) is equated to $2\omega_D$, Lindemann's law is obtained.

TABLE II

Comparison at the melting point of relaxation times in units of $10^{-14}\,s$.

Species	$\tau_{eB}(T_m)$	$\tau_{pp}(\omega_D, T_m)$	$(2\omega_D)^{-1}$	$\tau_I(\exp, T_m)$
Li	1.4	1.6	1.0	1.1
Na	2.5	2.5	2.5	3.1
K	3.5	4.2	4.4	5.2
Cu	1.2	1.5	1.3	2.2
Ag	1.6	1.7	1.8	2.7
Au	1.7	1.5	2.2	-

The ratio of the Roufosse-Klemens transition rate of Eq. (9) to the Bloch transition rate, Eq. (7), yields, with the same Debye temperature in each expression,

$$\frac{\tau(\omega_D)_{pp}}{\tau_{eB}} = \frac{v_F/v_D}{48\sqrt{2}\,(6\pi^2)^{\frac{1}{3}}\gamma^2}\,, \tag{10}$$

where v_D is the Debye mean velocity $a\omega_D/(6\pi^2)^{\frac{1}{3}}$. This ratio is easily seen to be of order of magnitude unity. If one uses thermal expansion gammas to approximate the large wavevector modal gamma averages required and uses melting point values of a and v_F, its value is 1.6, 1.7, and 1.9 for the Li, Na, and K, respectively, while for Cu, Ag, and Au, it is 1.4, 1.1, and 0.9, respectively. The gammas, discussed in Armstrong (1988b), were taken as 0.93, 1.15, 1.15, 1.98, 2.38, and 2.98 for these six metals in the above order (Vaks, *et al.*, 1978; Barron, Collins, and White, 1980). In evaluating the above ratios, the numerical coefficient of Eq. (9) was adjusted downward by a factor $(1.55)^2$ for Cu, Ag, and Au, to account for a difference between the fcc and bcc crystal structures (Armstrong, 1988b) that is not included in the Roufosse-Klemens formula. This same factor is also used in obtaining the relaxation times for the three fcc metals shown in Table II. The ratios of $\tau_{eB}(T_R)$ and $\tau_{pp}(T_D)$ as given in Table II are somewhat closer to unity.

Setting Eq. (10) equal to unity (by assumption) has the interesting consequence that the product of the Debye mean velocity and squared Grüneisen parameter is proportional to the Fermi velocity. This is reminiscent of the Bohm-Staver (1952) result, which yields a proportionality between the longitudinal sound velocity and the Fermi velocity. Equality of the two relaxation times of Eq. (10) also implies that the total phonon scattering rate and the three-phonon, Debye zone boundary scattering rate are equal not only at the melting point, but also over the asymptotic temperature range where both these quantities are linearly proportional to T. Furthermore, the ratio of Eq. (10) can be used to evaluate the lattice thermal conductivity at the melting point for good conductors separately from the electron thermal conductivity. Since the lattice component is poorly known for good conductors, this may prove to be a useful estimation procedure.

As indicated above, the Roufosse- Klemens formula depends upon the crystal structure (this is discussed from the standpoint of large crystals by those authors) and will have different coefficients for different lattices. In the Bloch result, on the other hand, error due to omission of U processes, to the precise Fermi surface shape, and to approximation of the electron-phonon interaction has been at least partially absorbed into the choice of the Debye temperature. Thus, Eq. (10) is not necessarily the best way to compare the two expressions. In Table II, we compare the explicit relaxation times using the set of T_R values (Table I) to evaluate $\tau_{eB}(T_m)$ of Eq. (7), which is used to approximate $\tau_{ep}(T_m)$. The set of specific-heat Debye temperature values (Table I) is used for $\tau_{pp}(\omega_D, T_m)$ and for $(2\omega_D)^{-1}$. The Grüneisen gammas used are those quoted above in the paragraph immediately preceding Table II.

Previously (Armstrong, 1988a), it was assumed that, because of their generally higher maximum frequency, only longitudinally polarized modes take part in the "mode failure", or loss of validity process leading to melting. It was then argued that $(2\omega_D)^{-1}$ comprised an approximate lower bound to the ion-ion mean collision time τ_M at the melting point; i. e.,

$$\tau_M(T_m) \gtrsim (2\omega_D)^{-1} \ . \tag{11}$$

This limitation to longitudinal polarization is lifted in the Appendix. From the results obtained in the Appendix, Inequality (11) is assumed to be true for the conventionally defined Debye frequency including the transversely polarized branches.

Now the experimental melting point ion-ion collision time can be estimated for five of the metals of Table II from the methods discussed in Armstrong (1986, 1988a). Therefore, it is of interest to compare these estimates with the prediction of Inequality (11) as well as with the other relaxation times discussed above. It was noted in the above references that ion-ion collision times are sufficiently short at the melting point for the perfect gas diffusion law $D = k_B T\tau_M/M$ to apply, where D is the self-diffusion coefficient. Thus, we can estimate $\tau(\exp)_l$, the experimentally determined value of τ_M, according to

$$\tau(\exp)_l = \frac{MD(\exp)}{k_B T_m} \ , \tag{12}$$

where D(exp) is the experimental self-diffusion coefficient at the melting point. Values of D(exp) obtained from Faber (1972) and from Nachtrieb (1967) were used to compute ion collision times according to Eq. (12) for the available cases and these are shown in Table II along with the theoretical mean times. For all five cases, $\tau(\exp)_l > (2\omega_D)^{-1}$ in agreement with Inequality (11). Considering the severity of the approximations employed in all cases (spherical Fermi surface, spherical surfaces in wave vector space, perfect gas law, etc.), the agreement among the various collision, or relaxation, times is quite satisfactory. The different relaxation times are all remarkably near equality for each species. The greatest departure from equality comes from the ion-ion times. This is hardly surprising, since the proposed equality of this parameter involves the additional perfect-gas behavior hypothesis which is independent of the hypotheses connecting the other relaxation times. In addition, the ion-ion relaxation time estimate is effectively evaluating the Debye temperature at the melting point from the self-diffusion coefficient, while the other relaxation times all use Debye temperatures evaluated in a different way from room or lower-temperature data.

ELECTRON-PHONON SCATTERING AND LINDEMANN'S LAW

Lindemann's Law from the Bloch Transition Rate

The foregoing considerations suggest, as was noted above, that $\tau_{ep} = (2\omega_D)^{-1}$ defines T_m in terms of the electron-phonon transition rate, just as $\tau_{pp} = (2\omega_D)^{-1}$ was found to define T_m in terms of the three-phonon transition rate by yielding Lindemann's law. Therefore, the high-temperature Bloch transition rate of Eq.

(7) is equated to $2\omega_D$ at $T = T_m$. The result of this assertion can be readily reduced to the Lindemann form

$$k_B T_m = \frac{T_D^2 V_0^{\frac{2}{3}} A}{C^2} , \tag{13}$$

where A, again, is atomic weight, V_0 the atomic volume (a^3), and C is the collection of constants and parameters defined by

$$C^2 \equiv \frac{\pi(6\pi^2)^{\frac{2}{3}} L v_F \hbar^2}{48 v_D k_B^2} . \tag{14}$$

Thus, as anticipated, we have yet another source of Lindemann's law. Numerical evaluation yields:

$$C = 5.91\left(\frac{v_F}{v_D}\right)^{\frac{1}{2}} \quad s \times K . \tag{15}$$

It should be noted that the factor $\hbar^2$ that appears in Eq. (14) is an artifact of the conventional definition, Eq. (13), of Lindemann's law. This factor, along with k_B^2 cancels against the Debye temperature in the numerator of Eq. (13). However, the Fermi velocity remains. Hence, the Lindemann melting law for metals, derived above from the Bloch formula, reflects a quantum-mechanical influence of the conduction electrons on the melting process. As was the case with the three-phonon transition rate Lindemann law, the parameter C will not be the same for different species even of the same crystal class. The Fermi and Debye velocities will always differ from metal to metal. However, the variation will be relatively slight again for some cases because the magnitude of these parameters does not change much between species in some metal groups.

Table III presents values of the Lindemann constants C for the six metals of Tables I and II, plus Al. These constants, labelled C_{ep} , have been calculated from Eq. (15) with v_D determined from the specific heat Debye temperatures of Table I. Predicted melting temperatures are also shown in the table. These are labelled T_m(th), and have been computed from Eq. (13), with T_D replaced by T_R, and the listed C_{pp} as the Lindemann constant. Observed melting temperatures T(obs) are also given in Table III for comparison. Melting point values of the Fermi velocity were used, and the Debye velocity was computed from the melting-point lattice constant and room-temperature Debye frequency. The resistivity Debye frequency was not used to evaluate the Debye velocity since this velocity does not arise from the Bloch transition rate (a function of T_R) but from the UP, and is independent of Bloch theory.

The results demonstrated in Table III are comparable to those of Ida (1969) who developed a classical "vibrational catastrophe" theory that predicts melting temperatures for these metals. The individual predictions in Table III all differ substantially from those of Ida, but the average absolute error of our results is about equal to his. This comparison between experiment and theory is reasonably favorable considering the crudeness of the free-electron approximation and the quadratic dependence on the Debye temperature, which is an uncertain quantity at best. It should be possible to improve upon the present approach by use of the theory reviewed by Grimvall (1981). This is discussed in Armstrong (1988b).

TABLE III

Theoretical melting temperatures T_m(th) predicted by the free-electron Bloch transition rate/Uncertainty principle. The observed values T_m(obs), and Ida's (1969) values, T_m(Ida) , are shown for comparison. The second column gives the Lindemann constants C_{ep}in sec × K .

Species	C_{ep}	T_m(th)	T_m(obs)	T_m(Ida)
Li	112	627	453	475
Na	160	295	371	393
K	153	268	336	464
Cu	147	1325	1358	1730
Ag	155	1170	1235	1220
Au	173	1050	1338	1070
Al	139	1113	934	1220

If one chooses v_D in Eqs. (14) and (15) to be determined by the same Debye temperature as used in the Bloch transition rate, the melting law, Eq. (13), can be reduced further to a form which is slightly different from Lindemann's law and in which the coefficient depends only on fundamental constants. It is not of basic significance as a melting law because of its dependence on the strong approximations of Bloch theory. But its degree of validity for the metals that are generally good candidates for the free-electron theory comprises another measure of confirmation of our fundamental hypothesis, which is the sole assumption leading to this equation. This equation also has the virtue of having no poorly known parameters except for the Debye temperature. This reduced melting law is used in Armstrong (1988b) to solve for T_D using observed melting temperatures, in order see if the results lie within the range of generally accepted values of this parameter for free-electron-like metals. They are seen to be in agreement in all cases with the range of high-temperature T_D values encountered in evaluations from specific heats, elastic constants, electrical resistivity, etc. One can conclude that this reduced "free electron" melting law is qualitatively sound. Since Debye temperatures are not known at the melting point, values computed this way may turn out to be useful for some of the good free-electron metals. The values for K , Cu and Ag, e. g., are essentially the same as the Meaden/Grüneisen values used above. It is also the case that values for Zn, Cd, and In are essentially the same as certain values for these metals given by Gschneidner (1964). The magnitude of most of the Debye temperatures calculated this way indicates that they cannot generally be "longitudinal" Debye temperatures along the lines of Meaden's (1965, p 102) discussion. Consequently, as in Meaden's analysis of the experimental values of T_R, one is led to conclude that transverse lattice waves are contributing to the electron scattering in most, if not all, cases. This is particularly interesting in the present context because the three-phonon anharmonic transition rate approach to the melting problem (Armstrong, 1986), depending as it does on the Debye approximation, does not offer any direct insight into the role of transverse phonons in the transition from maximum-frequency phonon breakdown to partially decoupled single-particle ion motion. The additional dependence of the "free-electron" Debye temperature on the electron-phonon interaction provides further clues.

CONCLUSION

It has been demonstrated that the Uncertainty Principle approach to melting via transition probabilities can be extended to the electron-phonon interaction. This extension provides additional confirmation of the fundamental hypotheses, including the nature of the onset of single-particle ion motion at the melting point. Application of the theory to "free electron" metals through the electron-phonon interaction provides an advantage over the three-phonon anharmonic interaction approach used earlier. The approximations underlying the Bloch resistivity formula are better understood than the approximations used by Roufosse and Klemens in deriving their high-temperature three-phonon expression. No adjustable parameters appear in the Bloch approach other than the Debye temperature. However, knowledge of this parameter, particularly toward the melting point is very limited. So even though more confidence can be placed in the electron-phonon scattering approach, its quantitative results are no better than those of the earlier theory. The connection between the two approaches is interesting, since both must apply to metals. The equality of the three-phonon Debye zone boundary transition rate and the electron-phonon transition rate in the asymptotic, T-proportional region suggests that the three-phonon scattering rate may be more than implicitly coupled to conduction electrons. This merits a more detailed calculation of the three-phonon transition rate, taking into account effects of zone structure on the dispersion relations, which was neglected by Roufosse and Klemens (1973).

It is hoped that the simple theory presented herein will serve as guide and motivation to elicit the more theoretically and computationally complex efforts required to extend and improve the theory. Large-scale numerical computations on crystal models may be able to provide accurate anharmonic transition rates, dispensing with the numerical uncertainty of the current analytic approximations and possibly leading the way to accurate *ab initio* calculations of melting points of insulators. Directional and polarization averages of the maximum Brillouin zone phonon frequencies as discussed in the Appendix, also requiring large-scale computation on crystal models, are also of interest to the prediction of accurate melting point self-diffusion coefficients and electrical conductivities.

APPENDIX

The Debye theory, unfortunately, hides much of the physics involved in the approach to the melting process presented above. We attempt to compensate for this as follows. In the Debye approximation, there is a unique maximum frequency to which we can apply the UP. In a real crystal this is, of course, not the case. In each direction in reciprocal space and for each polarization there will, in general, be a different maximum frequency. We could hypothesize that the anharmonic three-phonon transition rate behaved such that for each direction and polarization, the UP inequality (such as Inequality (2) of the text) becomes an equality at T_m for the maximum frequency mode in that direction and polarization. Although this would guarantee a sharp melting point, it seems unrealistic; in particular it would imply that the anharmonic transition rate depends linearly on frequency in the region near each such maximum. A more realistic hypothesis is to require that Inequality (2) becomes an equality at T_m only on average, where the average is taken over the maximum frequencies which occur in each direction for each branch. In this way, the melting temperature is defined by the equation

$$<<\frac{1}{\tau(\Omega_j(\vec{q}_P), T_m)}>>_j = 2<<\Omega_j(\vec{q}_P)>>_j, \qquad (A1)$$

where the inner brackets signify an average over solid angle and the outer brackets with subscript j, an average over polarizations. The wavevector $\vec{q}_P$ is that for which $\omega(\vec{q},j)$ has its maximum, or "peak" value $\Omega_j(\vec{q}_P)$ in the range $0 \leq q_P \leq q_{ZB}$ in the direction of $\vec{q}$. From the UP, the mean free time averaged over direction and polarization, which we term τ_M, obeys

$$\tau_M \geq <<\frac{1}{2\Omega_j(\vec{q}_P)}>>_j \geq \frac{1}{2<<\Omega_j(\vec{q}_P)>>_j}, \qquad (A2)$$

where the second step follows from Schwartz's inequality. Reciprocals of the inner-bracketed quantities on both sides of Eq. (A1) could also be used to define T_m, but the same final inequality on τ_M still holds. The precise value of T_m, however, would differ between the two cases. Numerical computation of the averages over peak frequencies and their reciprocals, as well as the three-phonon transition rate might shed additional light on this non-uniqueness in the definition of T_m.

REFERENCES

Armstrong, B. H., 1986, Three-Phonon Zone-Boundary Processes and Melting of Solids. In: A. C. Anderson and J. P. Wolfe (Editors), *Phonon Scattering in Condensed Matter V*. Springer-Verlag, Berlin, pp. 341-343.

Armstrong, B. H. 1988a. Electrical Conductivity, Self-Diffusion, and Volume Expansion of Alkali Halides at the Melting Point. *International Journal of Thermophysics*, 9: 825-838.

Armstrong, B. H. 1988b. The Electron-Phonon Interaction and the Melting of Metals. *IBM Palo Alto Scientific Center Report G320-3518,* Nov. 1988, unpublished.

Armstrong, B. H. 1988c. Self Diffusion at the Melting Point and Theory of Melting. *IBM Palo Alto Scientific Center Report G320-3519*, Nov. 1988, unpublished.

Barron, H. K., J. G. Collins, and G. K. White, 1980. Thermal expansion of solids at low temperatures. *Advances in Physics* , 29: 609-730.

Blackman, M., 1955. The Specific Heat of Solids. In S. Flügge (Editor), *Encyclopedia of Physics,* Vol. VII Part 1, Crystal Physics I, Springer-Verlag, Berlin, pp. 325-382.

Bohm, D., and T. Staver, 1951. Application of Collective Treatment of Electron and Ion Vibrations to Theories of Conductivity and Superconductivity. *Physical Review*, 84: 836.

Cusack, N. E., 1963. The Electronic Properties of Liquid Metals. *Reports on Progress in Physics*, 26: 361- 371.

Faber, T. E., 1972. *Introduction to the Theory of Liquid Metals.* Cambridge Univ. Press, London, 587 pp.

G. Grimvall, 1981. *The Electron-Phonon Interaction in Metals.* North Holland, Amsterdam, 304 pp.

Grüneisen, E., 1933. Die Abhängigkeit des elektrischen Widerstandes reiner Metalle von der Temperatur. *Annalen der Physik*, 16: 530-540. (5), 530.

Gschneidner, Jr., K. A., 1964. Physical Properties and Interrelationships of Metallic and Semimetallic Elements. In F. Seitz and D. Turnbull (Editors) *Solid State Physics*, Vol. 16, Academic Press, New York, pp. 275-385.

Ida, Y., 1969. Theory of Melting Based on Lattice Instability. *Physical Review*, 187: 951-958.

Iida, T., and R. I. L. Guthrie, 1988. *The Physical Properties of Liquid Metals.* Clarendon Press, Oxford, 288 pp.

Kelly, F. M., 1954. On Θ Values in Metals. II. *Canadian Journal of Physics*, 32: 81-89.

Kittel, C., 1956. *Introduction to Solid State Physics, 2nd ed.*, Wiley, New York, 615 pp.

Kramers, H. A., 1958: *Quantum Mechanics*. North-Holland Publishing Co., Amsterdam, 496 pp.

MacDonald, D. K. C., 1956. Electrical Conductivity of Metals and Alloys at Low Temperatures. In S. Flügge (Editor), *Encyclopedia of Physics*, Vol. XIV, Low Temperature Physics I, Springer-Verlag, Berlin, pp. 137-197.

Martin, D. L., 1965. Analysis of Alkali-Metal Specific-Heat Data. *Physical Review*, 139A: 150-160.

Meaden, G. T., 1965. *Electrical Resistance of Metals*. Plenum Press, N. Y., 218 pp.

Moleko, L. K., and H. R. Glyde, 1983. Vibrational stability and melting. *Physical Review B*, 27: 6019-6030.

Moleko, L. K., and H. R. Glyde, 1984. Crystal stability, thermal vibration, and vacancies. *Physical Review B*, 30: 4215-4229.

Nachtrieb, N. H., 1967. Self-diffusion in Liquid Metals. *Advances in Physics*, 16: 309-323.

Papoulis, A., 1962. *The Fourier Integral and its Applications*. McGraw-Hill Book Co. Inc., New York, 318 pp.

Pines, D., 1964. *Elementary Excitations in Solids*. W. A. Benjamin, Inc., New York, 299 pp.

Roufosse, M., and P.G. Klemens, 1973. Thermal Conductivity of Complex Dielectric Crystals. *Physical Review*, 87: 5379-5386.

Ubbelohde, A. R., 1978. *The Molten State of Matter*. John Wiley and Sons, Inc., New York. 454 pp.

Vaks, V. G., E. V. Zarochentsev, S. P. Kravchuk, V. P. Safronov, and A. V. Trefilov, 1978. Thermal Expansion and Grüneisen Parameters in Alkali Metals. *Physica Status Solidi.*, (b) 85: 749-759.

Ziman, J. M., 1963. *Electrons and Phonons*. Oxford University Press, 554 pp.