Density-Wave Instabilities and Thermoelectric Parameters in the Alkali Metals

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We use a first-principles pseudopotential approach to evaluate the thermoelectric parameters of the alkali metals. The values obtained for these parameters are extremely sensitive to the approximation used to describe the screening of the electron-ion interaction in these systems at wave vectors near $q=2k_F$. A criterion for the occurrence of charge-density-wave instabilities in the alkali metals is derived We argue that the measured values of the thermoelectric parameters are inconsistent with the proximity of a charge-density-wave instability.

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The alkali metals continue to be of interest because they are strongly correlated charged-fermion systems in which the complications coming from interactions of the electrons with positively charged ion cores can be treated simply and accurately. This situation results from the fact that the electron-ion interaction may be replaced by a weak pseudopotential. It is therefore surprising that fifty years after the beginnings of the quantum theory of metals, general agreement concerning the nature of the electronic ground state of these systems still does not exist. The controversy originated with a proof by Overhauser[1] that the degenerate electron gas is unstable, within the Hartree-Fock approximation, toward density-wave states with wave vectors near twice the Fermi momentum (k_F). This instability is a consequence of the long range of the Coulomb interaction and many workers have assumed that correlations, which screen the Coulomb interaction at large separations and are neglected by the Hartree-Fock approximation, eliminate the instability. Thus while most properties of the alkali metals seem consistent with a normal ground state, Overhauser and co-workers[2] have continued to point to some "anomalous" observations as evidence for a charge-density-wave (CDW) ground state. In this Letter we report calculations of the thermoelectric parameters of the alkali metals which are in quantitative agreement with experiment and are based on the assumption of a normal ground state. The thermopower is proportional to the voltage developed across a metal by a temperature gradient and is determined by differences between the scattering of electrons at energies a little below and a little above the Fermi level. We show that the thermoelectric parameters provide a measure of the tendency toward formation of a CDW ground state and argue that our results provide convincing evidence against the CDW hypothesis.

We employ pseudopotentials generated by the prescription of Dagens, Rasolt, and Taylor[3] which are intended for use in the leading order of perturbation theory and have been found to yield accurate values for phonon frequencies and transport coefficients.[4] If we assume a normal ground state, pseudopotential theory gives the phonon-scattering–limited electronic contribution to the thermoelectric power as[5]

$$S(T)=(-\pi^2k_B^2T/3eE_F)\xi(T), \tag{1}$$

where E_F is the Fermi energy of the noninteracting gas and $\xi(T)$, the thermoelectric parameter, is given by

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

In Eq. (2) the contribution $q(T)$ is proportional to the square of the scattering rate at wave vectors equal to $2k_F$ and, as we see below, will be very large if the system is close to a CDW instability:

$$2q(T)=\frac{k_F(2k_F)^3\,W^2(2k_F{:}k_F)\int_{k=2k_F}d\Omega_{\mathbf{k}}\,a(\mathbf{k})}{\int_{k\leq 2k_F}d^3k\,k\,a(\mathbf{k})\,W^2(k{:}k_F)}. \tag{3}$$

The contribution $r(T)$ to the thermoelectric parameter is proportional to the degree of nonlocality of the pseudopotential:

$$\tfrac{1}{2}r(T)=\frac{\int_{k\leq 2k_F}d^3k\,k\,a(\mathbf{k})\,W(k{:}k_F)\,dW(k{:}k_F)/d\ln k_F}{\int_{k\leq 2k_F}d^3k\,k\,a(\mathbf{k})\,W^2(k{:}k_F)}. \tag{4}$$

In Eqs. (3) and (4), $a(\mathbf{k})$ is a weighting factor related to the phonon frequencies

$$\{a(\mathbf{k})=\textstyle\sum_\lambda|\mathbf{k}\cdot\mathbf{e}_{\mathbf{k},\lambda}|^2 n(\omega_{\mathbf{k},\lambda})[1+n(\omega_{\mathbf{k},\lambda})]\},$$

and $W(k{:}k_F)$ is the screened form factor for the electron-ion scattering with wave-vector transfer k and both initial and final states on a Fermi sphere of radius k_F [see Ref. 4 and Eq. (10) below]. We have evaluated Eqs. (3) and (4) for all the alkali metals and our results for the thermoelectric parameters are compared with experiment[6–10] in Table I. The Na and K results are consistent with those of Leavens and Taylor[11] who used the same formalism. We emphasize that our calculations have no adjustable parameters and that the experimental thermopower has small contributions from electron-electron scattering,[8] lattice anharmonicities, and multiphonon effects which are not included in our calculation. Given the cancellation between $2k_F$ scattering and nonlocality contributions, then, the agreement between theory and experiment seems convincing even in Li and Cs where the weak-pseudopotential description is expected to be less accurate.

TABLE I. Thermoelectric parameters in the alkali metals. $\xi(T)=3-2q(T)-\frac{1}{2}r(T)$.

Metal	T (K)	$2q(T)$	$\frac{1}{2}r(T)$	$\xi(T)$ Theory	$\xi(T)$ Experiment
Li	424	9.76	−1.43	−5.33	−6.3[a]
Na	300	0.04	−0.09	3.05	2.9[b]
K	200	0.83	−1.87	4.04	4.0[c]
Rb	100	4.78	−4.49	2.71	2.8[d]
Cs	100	9.32	−7.15	0.83	0.0[e]

[a] Reference 6.
[b] Reference 7.
[c] Reference 8.
[d] Reference 9.
[e] Reference 10.

The calculations described above used the response functions calculated by Geldart and Taylor[4,12] to describe the screening of the electron-ion interaction by the electron gas. There is an intimate connection between these response functions and requirements for the stability of the normal state of the electron gas which is most clearly illustrated by our specializing to the case of a local pseudopotential. In this case leading-order perturbation theory for the electron-ion interaction gives the energy of the system as

$$E=E_0+(1/2\Omega)\sum_{\mathbf{q}}|N_I(\mathbf{q})|^2V_{\mathrm{II}}(\mathbf{q}), \tag{5a}$$

where E_0 is independent of the ionic positions Ω, and is a function of the system volume;

$$N_I(\mathbf{q})=\sum_i d^{-i\mathbf{q}\cdot\mathbf{R}_i}, \tag{5b}$$

$\mathbf{R}_i$ is the position of the ith ion, and[13]

$$V_{\mathrm{II}}(q)=V_c(q)-V_p^2(q)\chi(q). \tag{5c}$$

If we write $\mathbf{R}_i=\mathbf{L}_i+\mathbf{u}\cos(\mathbf{Q}\cdot\mathbf{L}_i)$, corresponding to a CDW disturbance with wave vector $\mathbf{Q}$, Eq. (5a) yields

$$\begin{aligned}\delta E(\mathbf{u})&=E(\mathbf{u})-E(\mathbf{u}=0)\\&=\frac{N^2}{2\Omega}\sum_{\mathbf{G}}\sum_{n=-\infty}^{\infty}\{V_{\mathrm{II}}(\mathbf{G}+n\mathbf{Q})J_{|n|}^2((\mathbf{G}+n\mathbf{Q})\cdot\mathbf{u})-V_{\mathrm{II}}(\mathbf{G})J_{|n|}^2(\mathbf{G}\cdot\mathbf{u})\},\end{aligned} \tag{6}$$

where the sum over $\mathbf{G}$ is over reciprocal lattice vectors and $J_n(X)$ is a Bessel function. If the lowest energy of the system were for a CDW state, Eq. (6) could be used to determine the magnitude and direction for both the CDW wave vector and the accompanying lattice distortion. In order to consider the stability of the normal state, however, it is sufficient to expand Eq. (6) to leading order in $\mathbf{u}$ which gives

$$\delta E(\mathbf{u})=\frac{N^2}{4\Omega}\left\{V_{\mathrm{II}}(\mathbf{Q})|\mathbf{Q}\cdot\mathbf{u}|^2+\sum_{\mathbf{G}\neq 0}[V_{\mathrm{II}}(\mathbf{G}+\mathbf{Q})|(\mathbf{G}+\mathbf{Q})\cdot\mathbf{u}|^2-V_{\mathrm{II}}(\mathbf{G})|\mathbf{G}\cdot\mathbf{u}|^2]\right\}+\dots. \tag{7}$$

In the first term of Eq. (7) we have isolated the contribution from the principal CDW harmonic. Assuming this contribution to be dominant gives $V_{\mathrm{II}}(\mathbf{Q})\geqslant 0$ as an approximate stability criterion for the normal state. (The effect of higher harmonics on the stability criterion will be discussed elsewhere[14] and is unimportant for the qualitative discussion below.)

We now follow a common notation in writing

$$\chi(q)=\Pi_0(q)/\{1+\Pi_0(q)[V_c(q)-\phi_{xc}(q)]\}, \tag{8}$$

where Π_0 is the density response function of the noninteracting system and $\phi_{xc}(q)$ is an exchange-correlation local field which can be used to specify the contributions to $\chi(q)$ omitted by the random-phase approximation. By use of Eq. (8) the stability requirement for the normal ground state becomes

$$\Pi_0^{-1}(q)-\phi_{xc}(q)+V_c(q)-V_p^2(q)/V_c(q)=0. \tag{9}$$

Equation (7) is similar to stability criteria discussed by Chan and Heine.[15] The four terms in Eq. (9) represent the contributions to the stiffness of the system toward the introduction of density waves from the kinetic energy $[\Pi_0^{-1}(q)>0]$, exchange and correlation $[\phi_{xc}(q)>0]$, the Coulomb energy of the electrons $[V_c(q)>0]$, and the screening of electron density oscillations by the ions $[-V_p^2(q)/V_c(q)<0]$. In the Hartree-Fock approximation[16,17] $\phi_{xc}(2k_F)\to\infty$ and the normal state is unstable at all densities. According to the calculations of Geldart and Taylor[4,12] the inclusion of correlation reduces the magnitude of

$\phi_{xc}(2k_F)$ sufficiently to satisfy Eq. (7) at $q=2k_F$.[18] However, the treatment of correlations is approximate and, although we believe it to be accurate, it cannot be *rigorously* justified. Instead we appeal to experiment by showing that the thermoelectric parameter becomes extremely large and negative if Eq. (9) is near to being violated.

For a local pseudopotential the relation between the screened electron-ion form factor and the bare pseudopotential is frequently[19] approximated by

$$W(q)=\frac{V_p(q)}{1+\Pi_0(q)[V_c(q)-\phi_{xc}(q)]}. \tag{10}$$

In Table II we have listed values of $V_p(2k_F)/V_c(2k_F)$ for the alkali metals[20] and the same ratio for the screened form factor corresponding to Geldart-Taylor screening, $W^{GT}(2k_F)/V_c(2k_F)$. When the rigidity of the system toward charge-density waves at $q=2k_F$ vanishes [i.e., when the left-hand side of Eq. (7) equals zero] the screened form factor becomes

$$W^{CDW}(2k_F)=\frac{V_c(2k_F)}{V_p(2k_F)\Pi_0(2k_F)} \gg V_c(2k_F). \tag{11}$$

As we see in Table II the screened form factors at $q=2k_F$ in the alkali metals would have to be many times larger than those used to produce Table I if the system were close to a CDW instability. According to Eq. (3) this would lead to large negative thermoelectric parameters in the alkali metals. We have listed estimates of these thermoelectric parameters in Table II by noting that the nonlocal contribution to the form factor is independent of screening considerations[4,21] and that the denominator of Eq. (3) is proportional to the electrical resistivity which we can regard as being given by experiment. The basic point that we are making in Table II is that the conditions required to generate a charge-density-wave instability necessarily imply that the high-temperature (T greater than the Debye temperature) thermoelectric parameter is very large and negative in all the alkali metals. This is in direct contradiction to the experimental data. By contrast, the use of response functions derived from uniform-electron-gas theory combined with first-principles pseudopotentials produces quantitatively good agreement with the data in all cases, with no parameters adjusted to fit any experimental quantity. We should point out, at this juncture, that the possibility that the temperatures at which the experimental data were measured are higher than the possible critical temperature (T_c) for charge-density-wave formation does not in any way invalidate our argument. The conditions necessary to obtain a CDW instability would still be present above T_c and these conditions imply major disagreement with the measured $\xi(T)$.

There are several objections which can be raised against association of ξ^{CDW} with the thermoelectric parameter for a CDW ground state. For example, the transition to a CDW state may well be weakly first order so that the normal-state stability criterion could be satisfied even if it were not the ground state. Also, if the ground state were a CDW Eqs. (2)-(4) would no longer be valid and the thermoelectric parameter would depend on the detailed nature of the ground state. Nevertheless we believe that the qualitative conclusion from the above argument, namely that the thermoelectric parameter would be very different from that of the normal state, is valid. On the other hand detailed *a priori* calculations based on the assumption of a normal ground state agree extremely well with experiment. Given the sensitivity of the thermoelectric parameter to the screening of scattering form factors at $q=2k_F$ it seems inconceivable to us that this agreement could result from a fortuitous combination of circumstances. We believe that our results provide overwhelming evidence that all the alkali metals have normal ground states and, consequently, equally overwhelming evidence against the CDW ground-state hypothesis. Explanations for "anomalous" phenome-

TABLE II. Screened form factors at $q=2k_F$ in units of $V_c(2k_F)$ for the Geldart-Taylor $\phi_{xc}(q)$ [$W^{GT}/(2k_F)$] and for a $\phi_{xc}(q)$ which puts the system at the edge of CDW instability [$W^{CDW}(2k_F)$]. The corresponding thermoelectric parameters, $\xi(T)$ and $\xi^{CDW}(T)$, are also listed. For each metal we use the same temperature as in Table I. Recall that $\xi(T)=3-2q(T)-\frac{1}{2}r(T)$ and that $q(T)\propto W^2(2k_F)$.

Metal	$\frac{V_p(2k_F)}{V_c(2k_F)}$	$\frac{W^{GT}(2k_F)}{V_c(2k_F)}$	$\frac{W^{CDW}(2k_F)}{V_c(2k_F)}$	ξ^{GT}	ξ^{CDW}
Li	0.4796	0.4686	3.82	−5.33	−614
Na	0.0208	0.0201	72.6	3.05	-4.9×10^5
K	0.0800	0.0759	15.3	4.04	-3.0×10^4
Rb	0.2115	0.1993	5.46	2.71	-3.2×10^3
Cs	0.2995	0.2792	3.55	0.83	−1300

na in these systems must be sought elsewhere.

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