

Thermodynamic properties of metals when the Fermi surface is close to Brillouin zone surfaces

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The pseudopotential-theory formulas for the energy of a metal are generalized to the case in which the Fermi surface lies a short distance z from Brillouin zone surfaces. The anomalous features in the shear modulus, the heat capacity, and the coefficient of thermal expansion as functions of z may be very sharp in this region, while those in the bulk modulus are much weaker.

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How the proximity of the Fermi surface to Brillouin zone surfaces affects the properties of metals and alloys (the “surface effect”) has been discussed extensively in the literature.^{1–10} The question which has received the most attention, however, is that of the comparative energy advantages of various structures,^{1–3} in which the surface effect is manifested indirectly and, frequently, ambiguously. Working in a theory of phase transitions of order 2.5, Lifshitz *et al.*⁴ have also discussed the electron contributions to the thermodynamics which arise when the parameter z - a measure of the

proximity of the Fermi surface to the third-zone surface approaches zero. However, they considered only the immediate vicinity of the point $z = 0$ and discussed the matter at a phenomenological level, with any attempt at quantitative or elementary-level calculations. Furthermore, the effects on the thermodynamics which have been discussed have usually been assumed to be small,^{1,4} and they have apparently not yet been observed experimentally (in contrast with surface effects in kinetics and in electronic properties⁵⁻⁸). Exceptional cases are the qualitative discussion by Naumov *et al.*⁹ of the possibility of significant manifestations of the surface effect in the shear modulus and the general comments offered by Kagan *et al.*¹⁰ regarding the importance of "zone-structure effects" in the elastic moduli (but there was no detailed discussion).

In this letter we examine surface effects in thermodynamics by the methods of pseudopotential theory. We show that these effects should be large and easily observable in several properties, in particular, the shear modulus, the heat capacity, and the thermal expansion coefficient.

To simplify the equations we assume that the pseudopotential \hat{V} is local: $\hat{V} = V(q)$. As usual, we assume that for vectors \mathbf{q} which are equal to reciprocal-lattice vectors \mathbf{g} the potential $V(\mathbf{g})$ is small in comparison with the Fermi energy ϵ_F . We assume that the center of the third-zone surface, in which we are interested, corresponds to a momentum $\mathbf{p}_c = \mathbf{g}/2$ and that the energy of a free electron is $\epsilon_c^0 = p_c^2/2$ (in atomic units). For electrons with $\mathbf{p} \approx \mathbf{p}_c$ the customary perturbation theory cannot be used, even at small values of $v \approx V(\mathbf{g})/\epsilon_F$, because of the pronounced mixing of the states $|\mathbf{p}\rangle$ and $|\mathbf{p} - \mathbf{g}\rangle$ (Refs. 1 and 3). Correspondingly, the perturbation-theory expansion of the total energy of the metal, E , for small values of $\alpha = (\epsilon_F - \epsilon_c^0)/\epsilon_c^0$ contains terms of the type $(v/\alpha)^n$, so that the perturbation-theory formulas must be generalized to arbitrary v/α .

This problem—without screening effects and without the electron-electron interaction—was essentially solved by Vul' and Krivoglaz,³ and these other effects can be taken into account by the methods of quantum field theory.¹¹ As a result, we find the following generalization of the standard formulas^{1,12} of the pseudopotential theory for E :

$$E = E_i + E^{(0)} + E^{(1)} + \sum_{\mathbf{g}} [E^{(2)}(\mathbf{g}) + E_s(\mathbf{g})]. \quad (1)$$

Here E_i is the energy of the ions (the Madelung term), $E^{(n)}$ is the ordinary contribution of n th order in V , and the term E_s , which is nonanalytic in v , is

$$E_s(\mathbf{g}) = Cv^3 F_s(\alpha/v); \quad (2a)$$

$$C = \frac{\Omega p_c^5}{32\pi^3}; \quad v = \frac{|V(\mathbf{g}) S(\mathbf{g})|}{\epsilon_c^0} m^* Z_0 \frac{\Gamma(\mathbf{g})}{\epsilon(\mathbf{g})}; \quad S(\mathbf{g}) = \frac{1}{\nu} \sum_{j=1}^{\nu} e^{i\mathbf{g}\cdot\vec{r}_j}. \quad (2b)$$

Here Ω is the atomic volume; m^* , Z_0 , and $\Gamma(\mathbf{g})$ are the effective mass, the renormalization of the Fermi-filling jump, and the vertex part at the Fermi surface in the electron Fermi liquid; $\epsilon(\mathbf{g})$ is the dielectric function; $S(\mathbf{g})$ is the structure factor of the elementary cell, and ν is the number of atoms in the cell. The function $F_s(x)$ in (2a) is equal to $\phi_0(x)$ at $|x| < 1$ or $\phi_0(x) + \phi_s(x)$ at $|x| > 1$, where ϕ_0 and ϕ_s are given by

$$\phi_0(x) = \frac{x}{2} + \frac{x^3}{3} - x \ln|2x|; \quad \phi_s(x) = x \ln(|x| + \sqrt{x^2 - 1}) - \frac{\operatorname{sgn} x}{3} (2 + x^2) \sqrt{x^2 - 1}. \quad (3)$$

In the limit $z = x \pm 1 \rightarrow 0$, the function $\phi_s(x)$ has known singularities of the type $(\pm z)^{5/2}$, which correspond to a phase transition of order 2.5 (Refs. 4 and 3). The Kohn singularities, $\sim x \ln|x|$ in $E^{(2)}(g)$ and $E_s(g)$, on the other hand, cancel out, so that E is regular in the limit $\alpha \rightarrow 0$. When α is not small, $\alpha \gtrsim 1$, we have $E_s \sim v^4$, while at $|\alpha| \lesssim v$, i.e., when the Fermi surface lies near the third-zone surface, we have $E_s \sim v^3$. As α is varied over this range, however, E_s changes $1/v$ times as rapidly as the other terms in (1), so that the contribution of E_s to the thermodynamic derivatives (in particular, the elastic moduli) is intensified. This intensification does not occur for the bulk modulus $B = -\Omega \partial^2 E / \partial \Omega^2$, since the quantity $\alpha = (\epsilon_F - \epsilon_c^0) / \epsilon_c^0$ does not change in the lowest order in v in the case of hydrostatic compression. In the calculations of the shear moduli $c_{ij} = \partial^2 E / \partial u_i \partial u_j$, however, we find derivatives $\partial \alpha / \partial u_i \sim \ln \epsilon_c^0 / \partial g \partial g / \partial u_i \sim 1$, and the contribution of E_s to c_{ij} is on the order of v , i.e., "literally" greater than the contribution of $E^{(2)}$ and not small. In the calculations of the shear moduli (and of several other properties), therefore, when the Fermi surface is near the third-zone surfaces (in polyvalent metals, in particular), the surface effect must be taken into account.

For quantitative estimates of the effects we have used (1) to calculate the concentration dependence of several characteristics of the disordered alloys $\text{Li}_{1-x}\text{Mg}_x$ in three structures: bcc, hcp, and fcc (the latter structure does not actually occur in these alloys). The properties of the alloys [their valence, volume, and effective pseudopotential $\bar{V} = m^* Z_0 V$ in (2b)] and the nonsingular contributions to the moduli [from the first three terms in (1) and from surfaces not close to the Fermi surface] are described in the average-crystal approximation.⁵ The function $\Gamma(q)/\epsilon(q) = 1/\bar{\epsilon}(q)$ and the pseudopotentials $V(q)$ in Li and Mg were taken to be the same as in Ref. 5; for Mg we assumed $\bar{V}(g) = V(g)$, while for Li we used the two values $\bar{V}(g) = V(g)$ and $\bar{V}(g) = 2V(g)$. The latter agrees better with data on the Fermi surface of Li, so that the results with $\bar{V}_{\text{Li}} = V_{\text{Li}}$ are shown only by curve 4 in Fig. 1 to illustrate the sensitivity to \bar{V} . The model used by us seems adequate for evaluating the nature and scale of the surface effects, although it of course does not give an adequate description of the quantitative details (the positions $x = x_c$ of the points of the phase transition of order 2.5; the contributions of the electron states near points K and L in the hcp phase, where the three- and four-wave approximations, respectively, should be used in place of the two-wave approximation; etc.).

Figures 1-3 show the results calculated for the shear modulus $c' = (1/2)(c_{11} - c_{12})$, the low-temperature phonon heat capacity C_V , and the low-temperature thermal expansion coefficient $\beta_T = (\partial \ln \Omega / \partial T)_p$. The singularities in these figures ($\sim z^{1/2}$ in c' and D_V and $\sim z^{-1/2}$ in β_T) correspond to phase transitions of order 2.5, i.e., to a succession of points where the Fermi surface touches the third-zone surfaces⁵ or spills across them. These points are $L(110)$ in the bcc phase, $L(111)$ and $X(200)$ in the fcc phase, and $M(010)$, $A'(002)$, and $L(011)$ in the hcp phase. We see that these surface effects depend strongly on the configuration of the Fermi surface and of the third-zone surfaces and can be extremely large. The anomalous features in the other shear moduli

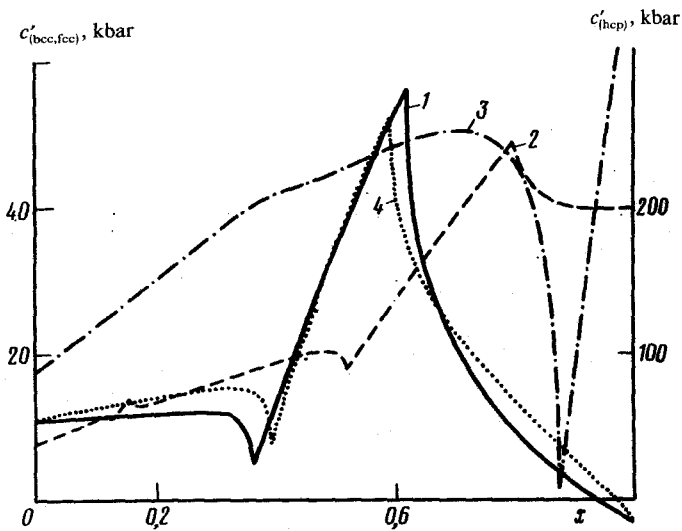


FIG. 1. Concentration dependence of the shear modulus, $c'(x) = 1/2(c_{11} - c_{12})$, in $\text{Li}_{1-x}\text{Mg}_x$ alloys. Curves 1, 2, and 3 (here and below) correspond to the bcc, hcp, and fcc phases; curve 4 corresponds to the bcc phase and $\bar{V}_{\text{Li}} = V_{\text{Li}}$ (see the text proper for an explanation).

and in the electron contributions to C_V and β_T are of the same order of magnitude. In the bulk modulus (and in the optical-phonon frequencies in the hcp phase at $\mathbf{k} = 0$), on the other hand, these anomalies are extremely small, in accordance with the discussion

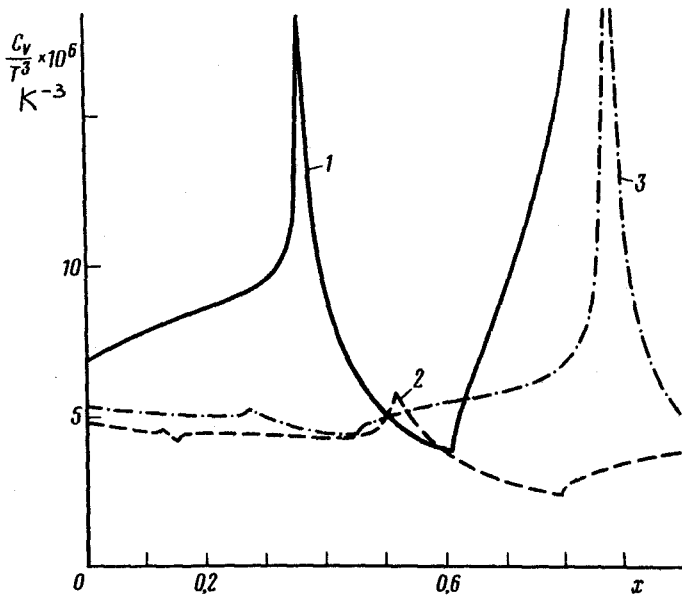


FIG. 2. Low-temperature lattice heat capacity $C_V(x)$ in $\text{Li}_{1-x}\text{Mg}_x$ alloys.

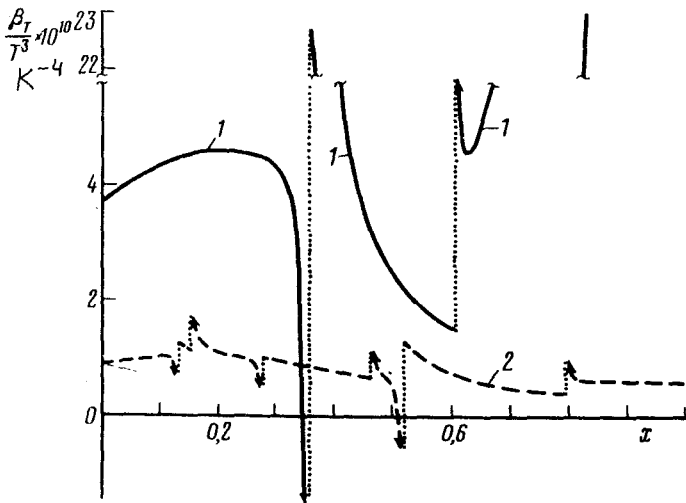


FIG. 3. Lattice contribution to the low-temperature thermal expansion coefficient $\beta_T(x)$ in $\text{Li}_{1-x}\text{Mg}_x$ alloys. Dotted lines—positions of the points of the phase transition of order 2.5, $x = x_c$; arrows— $|\beta_T|$ goes off to infinity in accordance with $|x - x_c|^{-1/2}$. The curve for the fcc phase has been omitted for clarity.

above, although the “literally” have the same form, $\sim z^{1/2}$, as the shear modulus in the limit $z \rightarrow 0$.

An experimental study of these anomalous features, particularly near the phase transitions of order 2.5 in the strain or the density, can yield important direct information about the role played by the surface effect in the properties of metals and alloys and also on how this effect is influenced by various factors which we have not considered here, in particular, the temperature-induced and concentration-induced blurring of the Fermi surface and of the third-zone surfaces.^{5,7}

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