V. I. Antropov, V. G. Vaks, M. I. Katsnel'son, V. G. Koreshkov, A. I. Likhtenshteĭn, and A. V. Trefilov. *Effect of proximity of the Fermi level to singular points in the band structure on the kinetic and lattice properties of metals and alloys.* Systems in which the Fermi level ε_F lies near singular points in the state density, e.g., near points (ε_c) of electronic topological transitions, are interesting in connection with the structural features and instability of their properties, since even a small change in an external parameter—the concentration of an alloy, the pressure p, etc.—can lead to sharp changes in these properties. For example, there may be sharp changes in the thermal emf, shear moduli, and thermal expansion coefficients.[1-3]

In anisotropic metals, e.g., hcp metals, large anomalies, opposite in sign, should appear in the low-temperature longitudinal and transverse thermal expansion coefficients, $\alpha_{\parallel}$ and $\alpha_{\perp}$. If we denote by u_1 and u_2 the strains corresponding to a change in the volume Ω and the tetragonality c/a [$du_1 = d \ln \Omega$, $du_2 = d \ln(c/a)$], and if we denote by B_{ik} the corresponding moduli in the elastic energy E_{el}, we can write thermodynamic expressions for $\alpha_{\parallel}$ and $\alpha_{\perp}$ as follows:

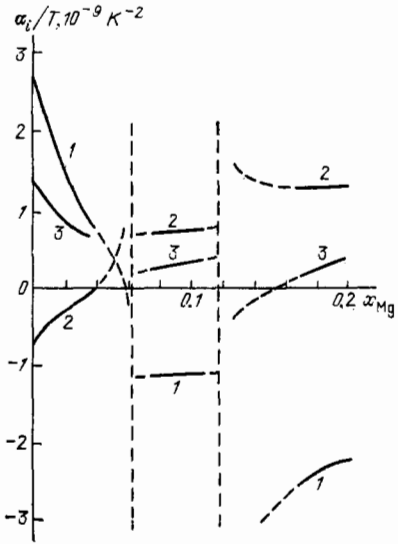

FIG. 1. Electronic components of the thermal expansion coefficients in $Cd_{1-x}Mg_x$. 1—$\alpha^e_{\parallel}/T$; 2—$\alpha^e_{\perp}/T$; 3—$\beta_e/T = (\alpha^e_{\parallel} + 2\alpha^e_{\perp})/T$.

TABLE I. Results of band-structure calculations of the shear modulus (in kb) $C' = (C_{11} - C_{12})/2$ as a function of the compression $u = (\Omega_0 - \Omega)\Omega_0$ in bcc metals.

	$u = 0$	0.1	0.2	0.3	0.4	0.5
Na	7.9 (7.7)	9.1	10.6			19.3
Li	9.2 (11)	9.15	6.3	1.15	−6.2	−27
Ba	20 (23±1)	24	25	15	−299	

Experimental values are shown in parentheses.

$$\alpha_{\parallel} = \frac{1}{3}(B_{11}B_{22} - B_{12}^2)^{-1}\left[(B_{22} - 2B_{12})\frac{\partial S}{\partial u_1} + (2B_{11} - B_{12})\frac{\partial S}{\partial u_2}\right], \quad (1a)$$

$$\alpha_{\perp} = \frac{1}{3}(B_{11}B_{22} - B_{12}^2)^{-1}\left[(B_{22} + B_{12})\frac{\partial S}{\partial u_1} - (B_{11} + B_{12})\frac{\partial S}{\partial u_2}\right]. \quad (1b)$$

Here S is the entropy, which consists of the electronic component $S_e = \pi^2 N(E_F)T/3$ and the phonon component $S_{ph} = 4\pi^4 T^3/5T_D^3$, where T_D is the Debye temperature. Near electronic topological transitions, i.e., at small values of $\eta = (\varepsilon_F - \varepsilon_c)/\varepsilon_c$, the derivatives of $N(E_F)$ and T_D with respect to u_i are proportional to $\eta^{-1/2}$, and at the usual small values of the pseudopotential of the electron-ion interaction, $V(\mathbf{g})$, where $\mathbf{g}$ is a reciprocal-lattice vector, i.e., at $v = |V(\mathbf{g})/\varepsilon_F| \ll 1$, we have $\partial S/\partial u_1 \sim v\eta^{-1/2} \ll \partial S/\partial u_2 \sim \eta^{-1/2}$ (Ref. 2). Since the relation $|B_{12}| < B_{11}$ holds in all known crystals, the most singular terms in (1a) and (1b) have opposite signs. In other words, near an electronic topological transition one of the coefficients $\alpha_{\parallel}$, $\alpha_{\perp}$ should be negative. Anomalies of this sort ($\alpha_{\parallel} > 0$, $\alpha_{\perp} < 0$) have been observed at low T in Zn and Cd, for which band-structure calculations[5,6] indicate small values of $\varepsilon_F - \varepsilon_c$.

Figure 1 shows the results of first-principles calculations by the semirelativistic KKR-ASA method[7] of the electronic components α^e corresponding to S_e in (2) for $Cd_{1-x}Mg_x$ alloys. These calculations were carried out in the "rigid-band" model; i.e., the effect of Mg was taken into account only through a change in the lattice parameters in accordance with the data of Ref. 8. This approximation appears to be sufficient for describing the electronic topological transition in Cd-Mg alloys,[6] as is confirmed by both our calculations of $N(\varepsilon)$ for an isolated Mg impurity in Cd and the good agreement between the calculated positions of the electronic topological transition, $x_{1c} = 0.063$, and

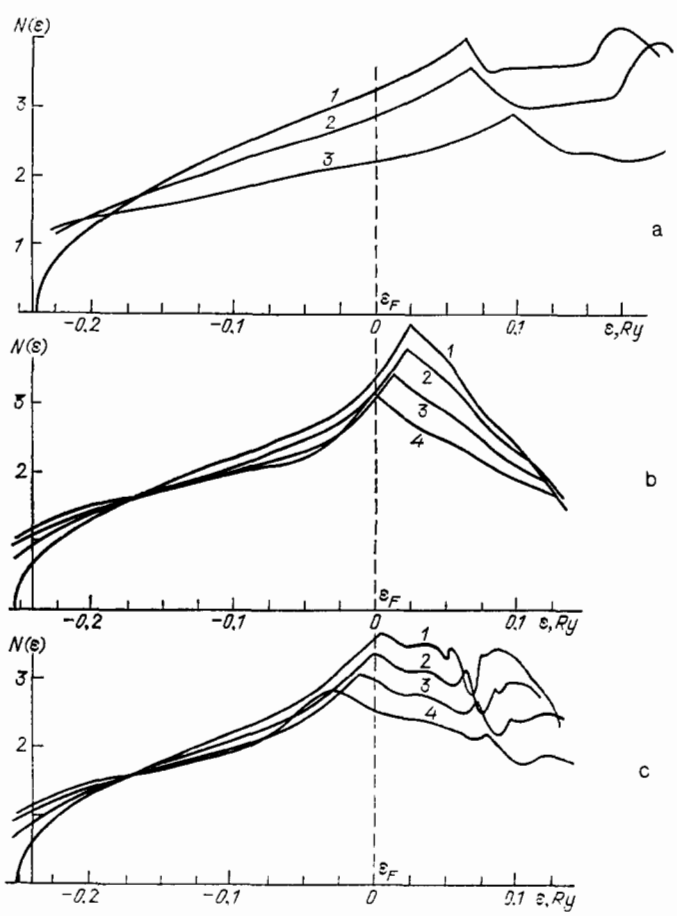

FIG. 2. The state density $N(\varepsilon)$ for various compressions u. a: Body-centered cubic Na. 1—$u = 0$; 2—$u = 0.2$; 3—$u = 0.5$. b, c: Li, bcc and R9 phases. 1—$u = 0$, 2—$u = 0.2$, 3—$u = 0.4$, 4—$u = 0.6$. Here $N(\varepsilon)$ is given in units of 1/(Ry·atom·spin).

$x_{2c} = 0.118$, with experimental data.[9] Figure 1 shows the sharp anomalies in the behavior of $\alpha_{\parallel}$ and $\alpha_{\perp}$ as functions of x. For pure Cd we have $\alpha_{\parallel} > 0 > \alpha_{\perp}$ according to experimental data, while at $x > x_{1c}$ we predict an inversion of the anomaly ($\alpha_{\parallel} < 0$, $\alpha_{\perp} > 0$). At $x > x_{2c}$, it should intensify. The dashed lines in Fig. 1 show the suggested behavior of the singular contributions. These lines could not be pursued further because of the lack of precision of the numerical calculations. The sign of the singular component of α_{ph} is the same as that in α^e (Ref. 2), so the anomalies should be observed over fairly wide intervals of T. This conclusion agrees with data on pure Cd and Zn (Ref. 4).

For the band-structure calculations of the shear moduli C_{ij} we used the relation

$$C_{ij} = \frac{\partial^2 E}{\partial u_i \, \partial u_j} = \frac{\partial^2}{\partial u_i \, \partial u_j} (E_{es} + E_b) = C_{ij}^{es} + C_{ij}^{b}; \qquad (2)$$

where u_i is a strain, and the energy E is the sum of the single-particle band energy E_b and the "electrostatic" component E_{es} (Ref. 10). The nonsingular component E_{es} was approximated by the expression yE_M, where E_M is the Madelung energy, and the constant y was estimated on the basis of the "jellium" model, from the condition for the cancellation of the electron-electron-interaction terms which are taken into account twice in E_b: $y = 5/3$. In the metals under consideration here, this estimate leads to good agreement between the calculated and measured values of the moduli C' (the measured values are shown in parentheses in Table I). The calculated dependence of C' on the compression u in Table I demonstrates the softening of the shear modulus as ε_F "crawls" toward the state-density peak,[2] as it does, according to the calculations, with increasing value of u in the bcc Li crystal (Fig. 2, b and c) and in Ba. The softening of C' under pressure in Li and Ba agrees qualitatively with the experiments of Ref. 11 and reflects the decrease in the stability of the bcc phase, which leads to martensitic transitions to close-packed structures, R9 or fcc in Li and hcp in Ba (Ref. 11). The existence of these band effects, which were not considered in the pseudopotential calculation of the phase diagrams in Li and Na (Ref. 12), explains the discrepancies between these calculations and experimental data in the case of Li (Ref. 12), while in Na, where effects of this sort do not occur (Fig. 2a), the phase diagram predicted in Ref. 12 agrees with the observed phase diagram.[13] Our first-principles calculations of the energies of bcc, fcc, and hcp phases confirm the increase in the stability of the bcc phase in Na with increasing p, while in Li there is a sequence of transitions, bcc-R9-fcc phase, according to the calculations.

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