V. G. Vaks, S. P. Kravchuk, and A. V. Trefilov. *Microscopic theory of anharmonic effects in alkali and bcc alkaline earth metals.* Anharmonic effects in the dynamics and thermodynamics of metals are important to their high-temperature properties, in the physics of soft modes, and in other phenomena. So far, we have little in the way of quantitative data on anharmonic effects, and the theoretical predictions are frequently uncertain and contradictory.[1,2] Alkali metals are some of the most convenient objects for a study of anharmonic effects, and there are several indications that the nature and relative scale of the anharmonic effects (e.g., near the melting point T_m), are identical in these and other metals. This suggestion is supported, in particular, by our calculations for alkaline earth metals. Consequently, the calculations of Refs. 1–5 and the experiments of Refs. 6–9 for alkali metals may also be regarded as sources of information on the general features of anharmonic effects in metals.

The following anharmonic effects have been studied in detail in Refs. 1–5 on the basis of the pseudopotential model developed previously, which permits an extremely accurate description of the properties of alkali metals (see, for example, Ref. 10 and the bibliography there):

1. anharmonic frequency shifts $\Delta\omega_i(T) = \omega_i(T) - \omega_i(0)$ and an anharmonic phonon damping[1] $\Gamma_i(T)$;

2. the effect of pressure on anharmonic effects and the temperature dependence of the Grüneisen parameters,[3] $\gamma i(T) = -\partial \ln \omega_i(T)/\partial \ln V$;

3. The third-order elastic moduli[4] c_{ijk} and the temperature dependence of the second-order elastic moduli[5] $c_{ij}(T)$;

4. anharmonic effects in thermodynamics[2]—in the free energy, the heat capacity, the thermal expansion, etc.;

5. anomalies in anharmonic effects for "soft" phonons associated with martensitic phase transitions.[1,3]

The calculations of Refs. 1–5 showed that anharmonic effects are dominated by soft phonons (in the bcc metals under consideration here, near the transverse branch Σ_4, i.e., $TA_1[110]$). This seems to be a general property of anharmonic effects in crystals with soft modes.[11] The form and

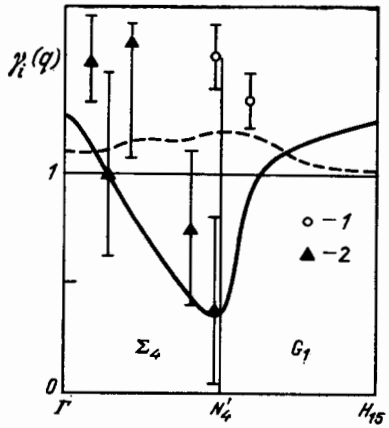

FIG. 1. The Grüneisen parameters γ_i for the Σ_4 and G_1 phonon branches in bcc alkali metals. The lines are theoretical.[3] Dashed line—Potassium, $T = 0$; solid line—$T = 299$ K. The points are experimental. 1—Potassium,[9] $T = 4.2$ K; 2—sodium,[6] $T = 295$ K.

TABLE I. Relative frequency shifts δ_i, the damping η_i, and the Grüneisen parameters γ_i of phonons at $T = T_m$

Phonon	$10^2\,\delta_i^{an}(T_m)$				$10^2\,\eta_i(T_m)$		$\gamma_i(T_m)$			
	K	Ba	Ca	Sr	K	Ca	K	Ba	Ca	Sr
H_{15}	−10	−7	−9	−11	6,2	5,1	1,3	1,5	1,6	1,7
P_4	−2,2	−0,8	0,3	1,7	5,8	5,7	1,3	1,5	1,5	1,4
N_1'	−1,8	−1,7	−1,8	−2,3	4,8	6,8	1,5	1,6	1,7	1,8
N_3'	−8,4	−6,2	−7,3	−9,7	7,7	5,5	0,9	1,1	1,4	1,8
N_4'	21	24	41	98	36	45	0,3	0,5	−0,6	−14

scale of the anharmonic effects are different in the cases of soft phonons and other ("normal") phonons. The frequencies ω_i of normal phonons fall off with increasing T, and the values of $\delta_i = \Delta\omega_i(T)/\omega_i(0)$, $\eta_i = \Gamma_i(T)/\omega_i(0)$ and $\Delta\gamma_i(T) = \gamma_i(T) - \gamma_i(0)$ are small. At $T = T_m$, for example, we have $\delta_i = -(0.1 - 0.15)$, $\eta_i = 0.05 - 0.1$ and $\Delta\gamma_i = 0.1 - 0.2$. For soft $TA_1(\xi,\xi,0)$ phonons with $\xi = qa/2\pi \geqslant 0.2$, on the other hand ($a$ is the lattice constant of the bcc lattice), we see the following: a) The frequencies $\omega(0,T)$ do not fall off with increasing T. They instead increase (as is typical of soft modes associated with a phase transition[11]; the transition here is from a bcc phase to a close-packed phase—hcp, fcc, or R9). b) The Grüneisen parameters γ_i fall off sharply with increasing T (Fig. 1). c) The relative damping η_i is significant at temperatures T which are not low. For example, we find $\eta_i(T_m) \sim 0.3$–0.4.

Prediction a) has been confirmed experimentally[6–8] for Na and Li. Some extremely small values of γ_i have also been observed for short-wavelength TA_L phonons at room temperatures T in Na; specifically, values smaller than those at low T in K by a factor of two or three have been observed (Fig. 1). Since all the phonon properties of Na and K are similar,[1–5,10] these data apparently also confirm prediction b), although it would of course be desirable to see some direct measurements of the $\gamma_i(T)$ dependences. We might add that the sharp dependence of the values of δ_i and η_i of soft modes on the volume V which was found in Ref. 3 (and which was also manifested at large values of $d\gamma_i/dT$) points out the importance of the electron-ion interactions, the contributions of the band-structure energy, and the properties of the soft modes. Specifically, in a purely ionic lattice we would have $\delta_i, \eta_i \sim V^{-1/3}$; i.e., these properties would vary very slowly with V.

The calculations of Ref. 4 of the moduli c_{ijk} (the coefficients of $u_i u_j u_k$ in an expansion of the free energy in the strains u_i) yield values of their ratio to the ordinary moduli c_{ij} in the range $c_{ijk}/c_{ij} = 2$–4. For a shear strain u corresponding to long-wavelength TA_1 phonons, however, the result $c_{uuu}/c_{uu} = -(20$–$30)$ is found. This result reflects the small size of the energy barrier along u and the tendency of the crystal toward a corresponding phase transition. The high-temperature asymptotic behavior for the shear moduli, $c_{ij}(T) \approx c_1 - Tc_2$, sets in even at very low temperatures, $T \leqslant 0.1\,T_D$, where T_D is the Debye temperature.[5] The reason is a governing contribution of soft phonons to these anharmonic effects. This result shows that the presence of a $c_{ij}(T)$ dependence of this sort, which is characteristic of many metals and alloys, may indicate the presence of soft modes.

The calculations in Ref. 2 of the contributions of anharmonic effects to the heat capacity C_p made it possible, in particular, to distinguish the contributions of equilibrium lattice defects from the observable values c_p^{exp} and to use this information to estimate the vacancy formation energy E_{1v} and entropy S_{1v}. Estimates carried out[2] under the assumption of small values $S_{1v} \lesssim 1$ have yielded small values $E_{1v} = 0.15$–0.2 eV. In microscopic calculations[12] carried out in the same model, however, values $E_{1v} = 0.25$–0.35 eV were found, and the values of S_{1v}, according to the estimates in Ref. 12, are again not small: $S_{1v} = 3$–4. These values of E_{1v} and S_{1v} (not small) agree both with estimates found from C_p^{exp} and with other experiments.[2]

Recent measurements[13–16] indicate similarities in the phonon spectra of bcc alkaline earth and alkali metals. In this connection, the model and methods of Refs. 1 and 3 have been used to calculate $\Delta\omega_i$, Γ_i, and γ_i in bcc, Ca, Sr, and Ba. The results are summarized in Table I, where $\delta_i^{an} = [\Delta_i^3(T) + \Delta_i^4(T)]/\omega_i(0)$; Δ_i^3 and Δ_i^4 are the contributions of three- and four-phonon processes to the frequency shift (found in Ref. 1); and the values of T_m for K, Ba, Ca, and Sr are 337, 998, 1112, and 1045 K. We see that the relative scale of the anharmonic effects is similar in K and Ba, while it increases in the series Ba-Ca-Sr, reflecting the decrease in the stability of the bcc phase in this series. We also see that the soft-mode anomalies in the anharmonic effects which we discussed above, a)–c), are expressed even more vividly here, and the Grüneisen parameters $\gamma(N_4')$ in Ca and Sr are negative at $T = T_m$. We might note in this connection that large negative values $\gamma_i = -(30$–$40)$ have been observed for soft acoustic phonons associated with martensitic phase transitions[17,18], in Nb_3Sn and In–Tl alloys, so a sharp anharmonic decrease in γ_i may be characteristic of a wide class of soft modes associated with phase transitions.

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