COMMENTS AND ADDENDA

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Grüneisen Parameter for Born–von Kármán Lattices*

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The Grüneisen parameter of some fcc and bcc metals has been recently calculated by Shapiro and Knopoff[1] (SK). In the lattice-dynamical model used by them, only nearest- and next-nearest-neighbor central forces were included. The Grüneisen parameter, which is an average of the form

$$\gamma = \sum C_i \gamma_i / \sum C_i , \tag{1}$$

where

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \tag{2}$$

are the mode γ's of the individual modes, was evaluated only in the high-temperature limit, i.e., when all the C_i's (the Einstein specific-heat functions) are equal. SK have not calculated individual-mode γ's, but gave instead an expression of γ in terms of a complicated integral over the Brillouin zone, which was evaluated numerically. Their high-temperature results γ_H are given in Table I. They compared these results with thermodynamic values γ_{th} of the Grüneisen parameter, which were obtained from room-temperature thermal-expansion and specific-heat data. Also given in Table I is the quantity $U_L = h\omega_L/kT$, where ω_L is the maximum frequency and $T = 300\,^\circ$K. SK pointed out that there exists a strong correlation between U_L and the magnitude of the difference between the calculated and the thermodynamic Grüneisen parameters. They argued that for materials with a high U_L value, 300 °K is not sufficiently high for γ_{th} to correspond to the limit γ_H which they calculated.

We have calculated the Grüneisen parameter at 300 °K employing the same lattice dynamical model that SK have used. This was done directly from (1) without resorting to a high-temperature approximation. The individual-mode γ's were derived from

$$\gamma_i = B_T \frac{\partial \ln \omega_i}{\partial P} , \tag{3}$$

which is equivalent to (2). Here, B_T is the isothermal bulk modulus. Pressure derivatives of individual frequencies were obtained numerically by solving the lattice-dynamical problem at some closely spaced pressures. This was done for 1000 points in the Brillouin zone. The input data for the elastic constants and their pressure derivatives were taken from the same sources[2,3] which SK used. (We have also performed the calculation for Fe, which SK did not include in their paper.) Our room-temperature results γ are given in Table I, and it can be seen that they are practically the same as the high-temperature results of SK even for materials for which U_L is large. This suggests that the asserted correlation between U_L and $|\gamma_H - \gamma_{th}|$ is accidental and that any discrepancies between calculated and experimental values of the Grüneisen parameter arise from the deficiencies of the lattice-dynamical model. Furthermore, by observing the behavior of the calculated individual-mode γ's over

TABLE I. Comparison of thermal and theoretical Grüneisen parameters.

Element	U_L	γ_H	γ_{th}	γ (300 °K)	$\frac{1}{3}(\gamma_l + 2\gamma_t)$
K	0.29	1.13	1.13	1.13	1.13
Na	0.51	1.04	1.15	1.04	1.04
Fe	1.36	(1.73)	1.66	1.73	1.72
Pb	0.33	2.59	2.69	2.60	2.59
Au	0.52	3.22	2.96	3.22	3.21
Ag	0.74	2.35	2.35	2.35	2.35
Cu	1.15	1.87	1.99	1.87	1.87
Al	1.15	2.72	2.13	2.72	2.73

the Brillouin zone, we can point out the following unrealistic features of the lattice-dynamical model. The γ's of all modes are rather closely spaced, and the solid tends towards the limit of a pure Grüneisen solid (i.e., one for which all the γ_i are equal). This explains, of course, the negligible temperature dependence of the calculated Grüneisen parameter. The mode γ's which are most severely distorted in this model are those corresponding to longitudinal modes. Thus, for long-wave LA phonons propagating in the [100] direction, the model gives

$$\gamma_l = -\tfrac{1}{6} + B_T (C'_{11} - C'_{12} + C'_{44})/2(C_{11} - C_{12} + C_{44}) , \tag{4}$$

whereas the correct value (derived from acoustic-continuum theory) is $-\frac{1}{6} + B_T C'_{11}/2C_{11}$, which in general is significantly different from (4). For potassium, for example, γ_l, as calculated from (4), is equal to 1.11, and the correct value of the γ of these longitudinal modes is 1.59.

For the corresponding [100] transverse modes the model yields the correct γ,

$$\gamma_t = -\tfrac{1}{6} + B_T C'_{44}/2C_{44} . \tag{5}$$

We note, finally, that because of the extremely small amount of dispersion and anisotropy which the γ's of this model exhibit, a simple expression of the form

$$\bar{\gamma} = \tfrac{1}{3}(\gamma_l + 2\gamma_t) \tag{6}$$

already gives a very good estimate of the Grüneisen parameter (as shown in the last column of Table I).

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Valley-Orbit Splitting of Excitons – A Comment*

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It is shown that when an indirect exciton is created during an optical absorption, the matrix elements of the exciton Hamiltonian calculated between different degenerate final states of the system are not necessarily zero. This implies that valley-orbit splitting of the states assigned to the indirect exciton creation may exist.

In a recent paper Shaklee and Nahory[1] point out that on the basis of the translational invariance of the exciton wave function there is no possibility of any valley-orbit splitting of the exciton in the way proposed by Ascarelli.[2] They correctly point out that the existence of a mixing of excitons related to each one of the valleys of a multivalley insulator requires some mechanism to provide the necessary crystal momenta in order to compensate for the different crystal momenta of the individual excitons.

A mechanism that provides the crystal momentum exists in the indirect optical absorption, since not only is an exciton created, but a phonon of the appropriate wave vector is exchanged as well. The wave function describing the system therefore has zero wave vector for the creation of an exciton with zero kinetic energy.

Following Ref. 1, H_1 is defined as the perturbation Hamiltonian describing both the electron-hole interaction and the interaction of the exciton with the appropriate phonon. Then $H_{ij} = \langle \psi_i^* | H_1 | \psi_j \rangle$, where ψ_i and ψ_j are wave functions describing the existence of an exciton and a phonon, respectively, with momenta $(\vec{k}_i, -\vec{k}_i)$ and $(\vec{k}_j, -\vec{k}_j)$. Applying the translation operator T to H_1, we obtain

$$H_{ij} = \langle \psi_i^* | \; T^{-1} T H_1 | \psi_j \rangle = e^{i(\vec{K}_i - \vec{K}_j)\cdot \vec{a}} H_{ij} .$$

H_{ij} is therefore not necessarily zero, since the wave vectors $\vec{K}_i$ and $\vec{K}_j$ of both ψ_i and ψ_j are zero.

The emission of electromagnetic radiation during the annihilation of an exciton may give rise to valley-orbit splitting in the same way as absorption does, since the same arguments used above remain valid.

The magnitude of the valley-orbit splitting will