Anharmonic damping of phonon modes in the fcc metals

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For the fcc metals Cu, Ag, Au, and Al, a theoretical analysis has been made of the one-phonon linewidth due to cubic anharmonic interactions. Third-order central and angular force constants have been obtained by using the symmetry properties of the lattice to relate the force constants with the experimental third-order elastic moduli. The convergence of the value of the nearest-neighbor third-order force constant has been studied as a function of the range of the cubic interactions. We have found that for metals for which the third-order Cauchy relations are violated it is necessary to introduce cubic angular forces to obtain a convergent value of the nearest-neighbor force constant. For Al and Cu the evaluated linewidths are compared with experimental data.

I. INTRODUCTION

The effects of anharmonic interactions among the normal modes of vibration of crystals have been studied experimentally starting from the nineteen sixties, by using the techniques of coherent inelastic scattering of slow neutrons.[1]

Particular attention has been paid to one-phonon scattering processes from which one can determine the linewidth, which shows up experimentally in the broadening of the peaks in the cross section. In addition to the broadening, there is a shift in the center of the peak. Both features are temperature dependent. The theory of these phenomena was worked out in the same period by Van Hove,[2] Glauber,[3] and Maradudin and Fein.[4] However, refined calculations, which involve double sums in the Brillouin zone, were not possible because of the lack of suitable computing facilities, which are now available. In this paper we present calculations of the linewidth associated with one-phonon processes, which are the dominant contributions in the scattering experiments. We will consider fcc metals, in particular, the noble metals and aluminum. To determine the linewidth, one has to know the harmonic phonon frequencies and polarization vectors. For the simple metals the lattice-dynamical problem can be conveniently solved by using a pseudopotential approach.[5] The phonon frequencies obtained with this method[6] reproduce the experimental ones to within a few percent. However, for the noble metals, the presence of the sp-d hybridization makes the construction of a pseudopotential[7] less accurate and the theoretical phonon frequencies do not reproduce the experimental values with satisfactory precision. For this reason in the present paper we prefer to use a force-constant parametrization scheme to solve the dynamical problem with the same degree of accuracy for both noble and simple metals.[8,9] Another advantage of this method is that one can perform calculations of the linewidth for both bulk phonons and surface phonons. The latter possibility is of current interest in connection with the rapid growth of surface science. With atom-surface scattering it is now possible[10] to perform such measurements (for a wide range of temperatures) with an accuracy of 0.2–0.3 meV. We will treat the surface problem in a separate paper.

In our approach we will retain only terms up to cubic in the crystal Hamiltonian, which has proven to be a good approximation up to room temperature in the range of the available experimental data for Cu (Ref. 11) and Al.[12] The harmonic part of the potential includes central interactions up to sixth neighbors, with both the first and second derivatives of the potential for each neighbor, and angular interactions involving triplets of nearest neighbors. The range used for the central interactions and the determination of the parameters is described in Sec. II. The anharmonic part of our model contains central interactions up to third neighbors and angular interactions involving triplets of nearest neighbors. The determination of the cubic force constants is carried out by expanding the total energy of the crystal both in terms of homogeneous deformations, as given by the elastic continuum approach,[13] and in terms of the normal coordinates of the lattice vibrational energy as discussed in Sec. III. The two expansions[14] give relationships between the experimentally known third-order elastic moduli (TOE) and the unknown third-order force constants. In Sec. IV we consider models with different ranges of cubic central interactions in order to study the variation of the value of the nearest-neighbor force constant as a function of the range of the central interactions. A realistic value for this quantity is essential because the calculated linewidth depends critically on the value of this force constant. In Sec. V numerical results for the linewidth are presented and discussed in connection with the available experimental data. The conclusions are drawn in Sec. VI.

II. HARMONIC AND ANHARMONIC POTENTIALS

The harmonic part of the potential is based on the force-constant parametrization scheme developed earlier.[8,9] In this model are included central forces and nearest-neighbor three-body angular forces to avoid the fulfillment of the second-order Cauchy relations (SOCR). The force constants are determined through a least-squares procedure by using the experimentally observed phonon frequencies along the principal symmetry directions and the elastic moduli. With this procedure the range of the central interaction, for a given element, is chosen as the one that gives the minimum χ^2 between the experimental and the theoretical dispersion relations. In the case of the noble metals we take central interactions up to fourth nearest neighbors,[15] while for Al, in order to account for the large Friedel oscillations of the potential, the range of the interaction was extended up to sixth-neighbor shells.[15] In this way the experimental phonon frequencies for all the noble metals and Al are reproduced to within 5%. The values of the force constants are given in Ref. 15.

The force constants are defined as follows. The first-order tangential force constants α_i are defined by

$$\alpha_i = \frac{1}{r}\frac{\partial\phi(r)}{\partial r}\bigg|_{r=r_i} , \tag{1}$$

where r_i is the equilibrium distance of the ith atom with respect to the reference atom and ϕ is the central two-body potential. The second-order radial force constants β_i are defined by

$$\beta_i = \frac{\partial^2\phi}{\partial r^2}\bigg|_{r=r_i} . \tag{2}$$

The second-order nearest-neighbor angular force constant δ_1 is defined by

$$\delta_1 = \frac{1}{3a^2}\frac{\partial^2\phi_\theta(\cos\theta_{ijk})}{\partial(\cos\theta_{ijk})^2}\bigg|_{\theta_{ijk}=\theta^0_{ijk}} , \tag{3}$$

where ϕ_θ is the angular part of the potential, a is the lattice spacing, and θ^0_{ijk} is the angle formed by the vectors $\mathbf{R}(i)-\mathbf{R}(j)$ and $\mathbf{R}(i)-\mathbf{R}(k)$, where $\mathbf{R}(i)$ is the equilibrium position vector of the ith atom with respect to the reference atom. In the case of nearest neighbors the atoms i,j,k are located at the corners of an equilateral triangle. These force constants are determined by the previously outlined procedure and are reported in Table I.

The harmonic potential that we are using can be easily generalized to include cubic anharmonic terms. In this case we can define the third-order central force constants by

$$\gamma_i = r\frac{\partial\phi^3}{\partial r^3}\bigg|_{r=r_i} \tag{4}$$

and the third-order nearest-neighbor angular force constant τ_1 by

$$\tau_1 = \frac{1}{3a^2}\frac{\partial^3\phi_\theta}{\partial(\cos\theta_{ijk})^3}\bigg|_{\theta_{ijk}=\theta^0_{ijk}} , \tag{5}$$

TABLE I. First- and second-order force constants in units of 10^{12} dyn. These values are obtained by fitting the second-order elastic constants and the measured phonon frequencies as discussed in Ref. 15.

	Cu	Ag	Au	Al
$(\beta_1-\alpha_1)/a$	0.859 05	0.665 47	1.165 60	0.594 43
$(\beta_2-\alpha_2)/a$	−0.030 48	−0.002 70	0.071 77	0.067 42
$(\beta_3-\alpha_3)/a$	0.030 38	0.026 73	0.024 99	−0.018 31
$(\beta_4-\alpha_4)/a$	0.006 86	−0.000 90	−0.007 33	0.006 08
$(\beta_5-\alpha_5)/a$	0.0	0.0	0.0	0.003 00
$(\beta_6-\alpha_6)/a$	0.0	0.0	0.0	−0.000 99
δ_1/a	−0.025 92	−0.026 16	−0.069 63	−0.017 05

where i,j,k designate nearest-neighbor atoms.

The cubic anharmonic force constants that we have introduced must be determined by fitting experimental values such as third-order elastic moduli, thermal expansion, mode Grüneisen parameters, etc.

III. RELATIONSHIP BETWEEN FORCE CONSTANTS AND ELASTIC CONSTANTS

We start by considering how the anharmonic force constants can be determined from the TOE that are available for the noble metals and Al. This can be done by equating the elastic and lattice vibrational energy densities. In the elastic continuum[13] theory the energy density U related to a homogeneous deformation can be expanded in terms of the strain tensor ϵ_{ik}. The third-order contribution which we need is given by

$$U_3^e = \frac{1}{6}\sum_{i,k}\sum_{j,l}\sum_{r,s}(C_{ik,jl,rs}+C_{ik,ls}\delta_{jr}+C_{ks,jl}\delta_{ir}$$
$$+C_{kl,rs}\delta_{ij})\epsilon_{ik}\epsilon_{jl}\epsilon_{rs} , \tag{6}$$

where $C_{ik,jl,rs}$ are the TOE. For a given choice of the strain tensor one obtains a particular form for U_3. We have employed six different forms of homogeneous deformations,[16] since, in our case, the six independent TOE are available.[17,18] The strain tensors related to the six independent deformations are given by

$$\epsilon_{\alpha\beta}=\epsilon\delta_{\alpha\beta}(\delta_{\alpha1}+\delta_{\alpha2}+\delta_{\alpha3}) , \tag{7a}$$

$$\epsilon_{\alpha\beta}=\epsilon\delta_{\alpha\beta}(\delta_{\alpha1}+\delta_{\alpha2}) , \tag{7b}$$

$$\epsilon_{\alpha\beta}=\epsilon\delta_{\alpha\beta}\delta_{\alpha1} , \tag{7c}$$

$$\epsilon_{\alpha\beta}=\epsilon(\delta_{\alpha1}\delta_{\beta1}+\delta_{\alpha2}\delta_{\beta3}+\delta_{\alpha3}\delta_{\beta2}) , \tag{7d}$$

$$\epsilon_{\alpha\beta}=\epsilon(\delta_{\alpha1}\delta_{\beta1}-\delta_{\alpha1}\delta_{\beta2}-\delta_{\alpha2}\delta_{\beta1}) , \tag{7e}$$

$$\epsilon_{\alpha\beta}=\epsilon(\delta_{\alpha1}\delta_{\beta2}+\delta_{\alpha2}\delta_{\beta1}+\delta_{\alpha1}\delta_{\beta3}+\delta_{\alpha3}\delta_{\beta1}$$
$$+\delta_{\alpha2}\delta_{\beta3}+\delta_{\alpha3}\delta_{\beta2}) . \tag{7f}$$

The first one corresponds to a uniform dilatation of the crystal. The others are related to more complicated deformations. The corresponding expressions for the cubic term U_3 can be written as

$$U_3^e(a) = (\tfrac{1}{2}C_{111} + 3C_{112} + C_{123} + \tfrac{3}{2}C_{11} + 3C_{12})\epsilon^3 , \quad (8a)$$

$$U_3^e(b) = (\tfrac{1}{3}C_{111} + C_{112} + C_{11} + C_{12})\epsilon^3 , \quad (8b)$$

$$U_3^e(c) = (\tfrac{1}{6}C_{111} + \tfrac{1}{2}C_{11})\epsilon^3 , \quad (8c)$$

$$U_3^e(d) = (\tfrac{1}{6}C_{111} + 2C_{144} + \tfrac{1}{2}C_{11} + C_{12})\epsilon^3 , \quad (8d)$$

$$U_3^e(e) = (\tfrac{1}{6}C_{111} + 2C_{166} + C_{11} + \tfrac{1}{2}C_{12} + 2C_{44})\epsilon^3 , \quad (8e)$$

$$U_3^e(f) = (8C_{456} + 6C_{44})\epsilon^3 , \quad (8f)$$

where the Voigt notation has been used for the elastic moduli.

To compare these expressions of the energy with those related to the force constants we start by considering the case of central anharmonic forces. The cubic term ϕ_3 in the potential energy is given by

$$\phi_3 = \tfrac{1}{12} \sum_i \sum_{l,l'} \sum_{\alpha,\beta,\gamma} \phi_{\alpha\beta\gamma}^{(i)}(l|l') u_\alpha(l|l') u_\beta(l|l') u_\gamma(l|l') , \quad (9)$$

where i labels the shell of neighbors, l, l' are unit cells indices, α, β, γ are Cartesian components,

$$u_\alpha(l|l') = u_\alpha(l) - u_\alpha(l') ,$$

and $u_\alpha(l)$ is the atomic displacement component related to the atomic position vector component $R_\alpha(l)$ by the relation

$$u_\alpha(l) = \sum_{\alpha'} \epsilon_{\alpha\alpha'} R_\alpha(l) . \quad (10)$$

Finally, $\phi_{\alpha\beta\gamma}^{(i)}(l|l')$ is given in terms of the force constants by

$$\phi_{\alpha\beta\gamma}^{(i)}(l,l') = \frac{1}{r_i^4}(\gamma_i - 3\beta_i + 3\alpha_i) R_\alpha(l|l') R_\beta(l|l') R_\gamma(l|l') + \frac{1}{r_i^2}(\beta_i - \alpha_i)[R_\alpha(l|l')\delta_{\beta\gamma} + R_\beta(l|l')\delta_{\alpha\gamma} + R_\gamma(l|l')\delta_{\alpha\beta}] , \quad (11)$$

where r_i is the distance of the ith shell from the origin and

$$R_\alpha(l|l') = R_\alpha(l) - R_\alpha(l') . \quad (11a)$$

By inserting the six strain tensors of Eq. (7) into Eq. (10) we can evaluate the cubic anharmonic energy ϕ_3 of Eq. (9) in terms of the various ϵ_{ij}. However, for a pairwise central potential, the Cauchy relations (SOCR) and (TOCR) are satisfied, so that one obtains only three independent relations. For the moment we assume that both harmonic and anharmonic central interactions extend up to sixth neighbors, so that for the vibrational anharmonic energies we obtain

$$U_3^V(a) = \frac{1}{a}(2\gamma_1 + 2\gamma_2 + 12\gamma_3 + 8\gamma_4 + 20\gamma_5 + 8\gamma_6) , \quad (12a)$$

$$U_3^V(b) = \frac{1}{a}[\tfrac{5}{6}\gamma_1 + \tfrac{4}{3}\gamma_2 + \tfrac{43}{9}\gamma_3 + \tfrac{10}{3}\gamma_4 + \tfrac{173}{15}\gamma_5 + \tfrac{64}{27}\gamma_6$$
$$+ \tfrac{1}{2}(\beta_1 - \alpha_1) + \tfrac{11}{3}(\beta_3 - \alpha_3) + 2(\beta_4 - \alpha_4)$$
$$+ \tfrac{9}{5}(\beta_5 - \alpha_5) + \tfrac{32}{9}(\beta_6 - \alpha_6)] , \quad (12b)$$

$$U_3^V(c) = \frac{1}{a}[\tfrac{1}{6}\gamma_1 + \tfrac{2}{3}\gamma_2 + \tfrac{11}{9}\gamma_3 + \tfrac{2}{3}\gamma_4 + \tfrac{73}{15}\gamma_5 + \tfrac{8}{27}\gamma_6$$
$$+ \tfrac{1}{2}(\beta_1 - \alpha_1) + \tfrac{7}{3}(\beta_3 - \alpha_3) + 2(\beta_4 - \alpha_4)$$
$$+ \tfrac{9}{5}(\beta_5 - \alpha_5) + \tfrac{16}{9}(\beta_6 - \alpha_6)] , \quad (12c)$$

$$U_3^V(d) = \frac{1}{a}[\tfrac{1}{6}\gamma_1 + \tfrac{2}{3}\gamma_2 + \tfrac{35}{9}\gamma_3 + \tfrac{2}{3}\gamma_4 + \tfrac{73}{15}\gamma_5 + \tfrac{104}{27}\gamma_6$$
$$+ \tfrac{3}{2}(\beta_1 - \alpha_1) + \tfrac{1}{3}(\beta_3 - \alpha_3) + 6(\beta_4 - \alpha_4)$$
$$+ \tfrac{27}{5}(\beta_5 - \alpha_5) - \tfrac{32}{9}(\beta_6 - \alpha_6)] , \quad (12d)$$

$$U_3^V(e) = \frac{1}{a}[\tfrac{7}{6}\gamma_1 + \tfrac{2}{3}\gamma_2 + \tfrac{53}{9}\gamma_3 + \tfrac{14}{3}\gamma_4 + \tfrac{127}{15}\gamma_5 + \tfrac{104}{27}\gamma_6$$
$$+ (\beta_1 - \alpha_1) + 2(\beta_2 - \alpha_2) + \tfrac{28}{3}(\beta_3 - \alpha_3)$$
$$+ 4(\beta_4 - \alpha_4) + \tfrac{82}{5}(\beta_5 - \alpha_5) + \tfrac{64}{9}(\beta_6 - \alpha_6)] , \quad (12e)$$

$$U_3^V(f) = \frac{1}{a}[\tfrac{32}{3}\gamma_3 + \tfrac{128}{9}\gamma_6 + 6(\beta_1 - \alpha_1) + 4(\beta_3 - \alpha_3)$$
$$+ 24(\beta_4 - \alpha_4) + \tfrac{108}{5}(\beta_5 - \alpha_5) - \tfrac{32}{3}(\beta_6 - \alpha_6)] . \quad (12f)$$

By equating the elastic U_3^e and the corresponding vibrational U_3^V energies one obtains explicit expressions connecting the TOE with the force constants. By suitable manipulations, one can see that these equations fulfill the TOCR, namely,

$$C_{166} = C_{112} , \quad (13)$$

$$C_{144} = C_{456} = C_{123} . \quad (14)$$

From this analysis, it follows that one can determine, as a maximum, three anharmonic force constants, so that it is possible to use anharmonic models with the range of the

TABLE II. Room-temperature-measured third-order elastic constants of Cu, Ag, Au (Ref. 17), and Al (Ref. 18). Units: 10^{12} dyn cm^{-2}.

	Cu	Ag	Au	Al
C_{111}	−12.71	−8.43	−17.29	−12.24
C_{112}	−9.14	−5.29	−9.22	−3.73
C_{166}	−7.90	−6.37	−6.48	−3.68
C_{123}	−0.50	+1.89	−2.33	+0.25
C_{144}	−0.03	+0.56	−0.13	−0.64
C_{456}	−0.95	+0.83	−0.12	−0.27

central forces extending from the first to the third shell of the neighbors. We want to remark that the choice of a central anharmonic model is reasonable for Cu and Al, since in this case the experimental values of the TOE do satisfy the TOCR given by Eqs. (13) and (14). This can be seen from Table II, where the experimental TOE are re-

ported.

We pass now to the discussion of the role of the nearest-neighbor second- and third-order angular interactions. Similar to Eq. (3), we define the third-order angular force constant in Eq. (5). The third-order angular force-constant tensor can be easily written as

$$\phi_{\alpha\beta\gamma}^{(a)}(m,n,p)=\frac{a^2}{2}\sum_{i,j,k}\left[\tau_1\frac{\partial\cos\theta_{ijk}}{\partial R_\alpha(m)}\frac{\partial\cos\theta_{ijk}}{\partial R_\beta(n)}\frac{\partial\cos\theta_{ijk}}{\partial R_\gamma(p)}+\delta_1\left|\frac{\partial\cos\theta_{ijk}}{\partial R_\alpha(m)}\frac{\partial^2\cos\theta_{ijk}}{\partial R_\beta(n)\partial R_\gamma(p)}+\frac{\partial\cos\theta_{ijk}}{\partial R_\beta(n)}\frac{\partial^2\cos\theta_{ijk}}{\partial R_\alpha(m)\partial R_\gamma(p)}\right.\right.$$

$$\left.\left.+\frac{\partial\cos\theta_{ijk}}{\partial R_\gamma(p)}\frac{\partial^2\cos\theta_{ijk}}{\partial R_\alpha(m)\partial R_\beta(n)}\right|\right]. \tag{15}$$

The third-order angular force constant is the new parameter that should be determined by fitting the TOE. The contribution of the angular forces to the vibrational energies results are found to be

$$U_3^{VA}(a)=0 , \tag{16a}$$

$$U_3^{VA}(b)=\frac{1}{a}(-\tfrac{1}{2}\tau_1-7\delta_1) , \tag{16b}$$

$$U_3^{VA}(c)=\frac{1}{a}(\tfrac{1}{2}\tau_1-5\delta_1) , \tag{16c}$$

$$U_3^{VA}(d)=\frac{1}{a}(\tfrac{13}{2}\tau_1-47\delta_1) , \tag{16d}$$

$$U_3^{Va}(e)=\frac{1}{a}(-\tfrac{5}{2}\tau_1-8\delta_1) , \tag{16e}$$

$$U_3^{VA}(f)=\frac{1}{a}(24\tau_1-168\delta_1) . \tag{16f}$$

By equating the elastic and vibrational energy densities one obtains elastic moduli that violate the Cauchy relations.

The angular contribution to the elastic moduli after a lengthy calculation turns out to be

$$C_{111}=\frac{1}{a}(3\tau_1-66\delta_1) , \tag{17}$$

$$C_{112}=\frac{1}{a}(-\tfrac{3}{2}\tau_1+9\delta_1) , \tag{18}$$

$$C_{166}=\frac{1}{a}(-\tfrac{3}{2}\tau_1-15\delta_1) , \tag{19}$$

$$C_{123}=\frac{1}{a}(3\tau_1+6\delta_1) , \tag{20}$$

$$C_{144}=\tfrac{1}{4}(3\tau_1-18\delta_1) , \tag{21}$$

$$C_{456}=\frac{1}{a}(3\tau_1-30\delta_1) . \tag{22}$$

From Eqs. (17)–(22) it is clear that the violation of the TOCR occurs because of the presence of the harmonic angular force δ_1. The third-order angular force constant τ_1 appears with the same coefficients both in Eqs. (18) and (19) and in Eqs. (20)–(22). Only by going beyond nearest neighbors do the third-order angular forces produce a violation of the TOCR. For these reasons, with our model containing central and first-nearest-neighbor angular forces it is possible to determine only three independent parameters.

IV. NUMERICAL DETERMINATION OF THE FORCE CONSTANTS

Using the harmonic force constants tabulated in Table I, we present the calculations of the third-order force constants as determined from the experimentally known TOE,[17,18] reported in Table II. Within these models we can determine up to three force constants. To investigate the importance of the range of the central interactions and of the angular force on the determination of the anharmonic coefficient γ_1, which gives the leading contribution to the linewidth, as discussed in the next section, we have performed calculations for the nearest-neighbor central cubic anharmonic model (1CM) by equating $U_3^e(a)$ to $U_3^V(a)$, Eqs. (8a) and (12a), with

$$\gamma_2=\gamma_3=\gamma_4=\gamma_5=\gamma_6=0 .$$

The results are reported in Table III for Cu, Ag, Au, and Al. No significant changes in the value of γ_1 are obtained by employing Eqs. (8b) and (12b). In Table IV are reported the values of the force constants for the second-neighbor central cubic anharmonic model (2CM) obtained by equating $U_3^e(a),U_3^e(b)$ to $U_3^V(a),U_3^V(b)$, respectively, with $\gamma_3=\gamma_4=\gamma_5=\gamma_6=0$. In Table V are given the parameters for the 3CM, obtained by using Eqs. (8a)–(8c) together with Eqs. (12a)–(12c). As expected for

TABLE III. Third-order force constant in the 1CM (see text); a is the lattice constant. Units: 10^{12} dyn cm^{-2}.

	Cu	Ag	Au	Al
γ_1/a	−12.59	−6.82	−15.41	−6.81

TABLE IV. First- and second-neighbor cubic force constants in 2 CM (see text). Units: see Table II.

	Cu	Ag	Au	Al
γ_1/a	−13.69	−5.58	−17.11	−5.30
γ_2/a	1.09	−1.24	1.69	−1.51

TABLE V. First-, second-, and third-neighbor cubic force constants in 3CM (see text). Units: see Table II.

	Cu	Ag	Au	Al
γ_1/a	-11.62	-15.00	-6.14	-6.29
γ_2/a	0.75	-0.77	0.80	-1.34
γ_3/a	-0.29	1.49	-1.68	0.14

TABLE VI. First-, and second-neighbor central and first-neighbor angular force constants in the 2C1AM (see text). Units: see Table II.

	Cu	Ag	Au	Al
γ_1/a	-13.20	-6.05	-15.52	-5.02
γ_2/a	0.61	$-.077$	0.11	-1.79
τ_1/a	0.11	0.52	-0.63	0.14

those metals that practically fulfill the TOCR there is a substantial convergence to the value of γ_1 by increasing the range of the central interaction forces whereas for Ag and Au there are substantial discrepancies. By introducing the angular forces that are very important for Ag and Au, and using the second-neighbor, central, *single* angular model (2C1AM), equating Eqs. (8a)–(8c) to the sum of the corresponding Eqs. (12a)–(12c) and Eqs. (16a)–(16c), we get the results presented in Table VI for the relative force constants. The introduction of the angular forces has the effect of stabilizing the leading force constant γ_1. For this reason in the evaluation of the phonon linewidth we will use the 2C1AM model.

V. NUMERICAL CALCULATIONS OF THE LINEWIDTH

The linewidth that enters in the one-phonon anharmonic cross section is given by[4]

$$\Gamma(q,j;\omega)=\frac{18\pi}{\hbar^2}\sum_{q_1,j_1}\sum_{q_2,j_2}|V^{(3)}(-q,j;q_1,j_1;q_2,j_2)|^2\{(n_1+n_2+1)[\delta(\omega-\omega_1-\omega_2)-\delta(\omega+\omega_1+\omega_2)]$$

$$+(n_1-n_2)[\delta(\omega+\omega_1-\omega_2)-\delta(\omega-\omega_1+\omega_2)]\}\ , \qquad (23)$$

where (q,j) labels the harmonic mode of momentum $\hbar q$ corresponding to branch j, $\omega=\omega(q,j)$, $\omega_i=\omega(q_i,j_i)$ $(i=1,2)$, and $n_i=n(\omega_i)$ are the Bose factors. The $V^{(3)}$ coefficient is the Fourier transform of the third-order term $\phi^{(i)}_{\alpha\beta\gamma}$ in the potential energy which is given by (with the replacements $q_1 j_1 \rightarrow q'j'$, $q_2 j_2 \rightarrow q''j''$)

$$V^{(3)}(q,j;q',j';q'',j'')=\frac{1}{12}\sum_i\sum_{l,l'}\sum_{\alpha,\beta,\gamma}\left[\frac{\hbar}{2NM}\right]^{3/2}\phi^{(i)}_{\alpha\beta\gamma}(l;l')(\omega\omega_1\omega_2)^{-1/2}e_\alpha(q,j)(e^{iq\cdot R(l)}-e^{iq\cdot R(l')})e_\beta(q',j')$$

$$\times(e^{iq'\cdot R(l)}-e^{iq'\cdot R(l')})e_\gamma(q'',j'')(e^{iq''\cdot R(l)}-e^{iq''\cdot R(l')})\Delta(q+q'+q'') \ , \qquad (24)$$

where $e(q,j)$ are the harmonic eigenvectors of the mode (q,j), N is the number of atoms, and M is the atomic mass. The $\phi^{(i)}_{\alpha\beta\gamma}$ are the sum of the anharmonic term of Eq. (9) plus the anharmonic contribution of Eq. (15). The function $\Delta(q)$ is unity if q is a reciprocal-lattice vector and zero otherwise. Its presence is a consequence of periodicity.

By taking into account the Δ function, the sums over the Brillouin zone (BZ) are reduced to a simple sum over q' with $q''=-q-q'$. If q'' lies in the first BZ, the process is called normal; otherwise, if a reciprocal-lattice vector G is required to return q'' to the first BZ, the process is classified as umklapp. As a consequence of the form of q'', the sum over q' in Eq. (23) cannot be carried out over any irreducible part of the BZ, but should be performed over the whole BZ. In this summation we found that the best convergence was obtained by taking, for the δ function, the representation

$$\delta(f(x))=\sum_n\frac{\delta(x-x_n)}{|f'(x_n)|} \ , \qquad (25)$$

where $f(x)$ is any of the arguments of the δ function of Eq. (23) and x is one Cartesian component of q', say $x=q'_z$. The sum in Eq. (25) runs over the zeros of the function $f(x)$.

To use the property of the one-dimensional δ function, Eq. (25), the q' sum is transformed as follows:

$$\frac{1}{N}\sum_{q'}\rightarrow\frac{1}{N_xN_y}\sum_{q_x,q_y}\frac{L_z}{N_z}\int\frac{dq'_z}{2\pi} \ , \qquad (26)$$

where N_i $(i=1,2,3)$ is the number of atoms along the Cartesian component i, N_xN_y is the number of atoms over which the summation is carried out, and $L_z/N_z=a/3\sqrt{4}$ is the cubic root of the volume of the primitive unit cell of the fcc structure.

For a fixed pair (q'_x,q'_y) the argument of the δ function depends on the one-dimensional variable $q'_z=x$ and the integration of Eq. (26) is easily done. We find that the derivatives of $f(x)$ never vanish at the zeros $f(x_n)$ so that we have no bulk focusing effects. In the actual calculation we use the harmonic phonon frequencies $\omega(q,j)$ and eigenvectors $e(q,j)$ of Sec. II and the anharmonic force constants of the 2C1AM model. In the evaluation of the linewidth 2Γ we find a convergence in the second decimal figure by taking $N_xN_y=3109$. The sum over n in Eq. (25) ranges from 1 to 4 for a given $q'_x q'_y$ so that we are sampling roughly 10 000 points of the BZ. The number of umklapp processes, which depends on the value of (q'_x,q'_y) is generally comparable to the number of normal
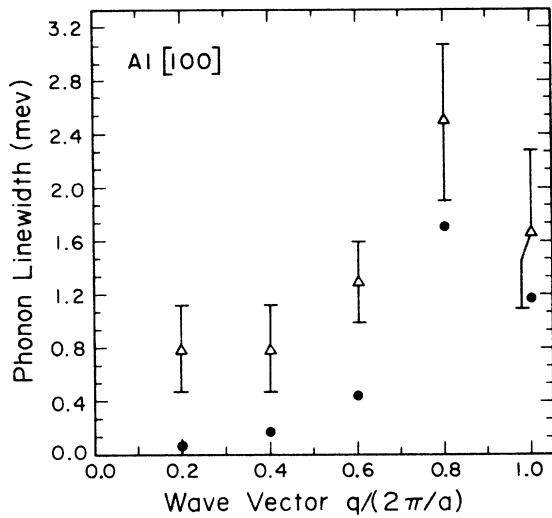
FIG. 1. Phonon linewidths 2Γ for Al at 300 K. Solid circles: calculated values for longitudinal modes with q along the [100] direction.
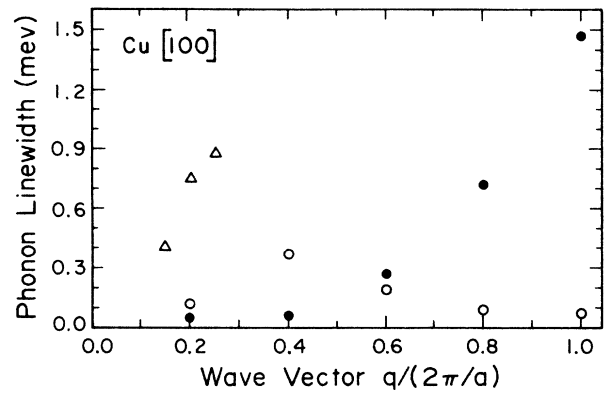

FIG. 3. Phonon linewidths for Cu at 300 K with q in the [100] direction. Solid circles: longitudinal modes. Open circles: transverse modes. The triangles refer to the transverse experimental points of Ref. 11 without the error bars.
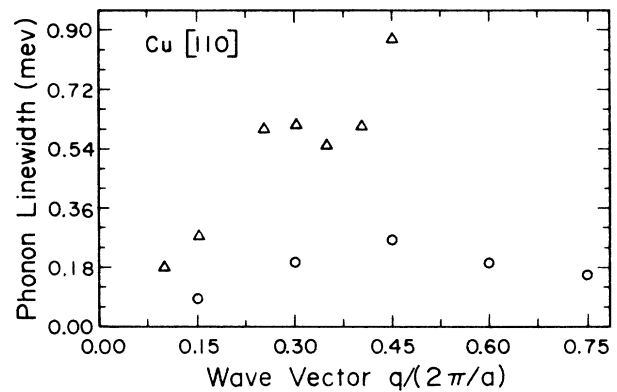
processes. This proves that umklapp processes play a very important role in the determination of 2Γ.

We begin by discussing Al for which there are available extensive experimental measurements by Stedman and Nilsson.[12] In Figs. 1 and 2 are depicted our calculations of the phonon widths at $T = 300$ K for selected q values, for longitudinal phonons in the [100] and [111] directions, respectively. The margins of error in the experimental values prevent any accurate comparison, even if our results seem to be too low. However, some general conclusions can be drawn. Around the zone boundary in

FIG. 4. Same as Fig. 3, but for q along the [110] direction.

FIG. 2. As in Fig. 1, but for longitudinal phonons in the [111] direction.
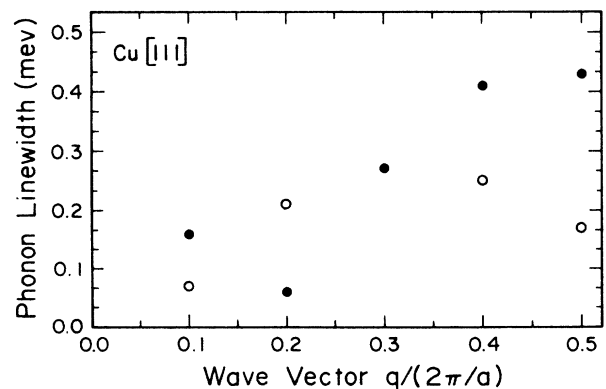

FIG. 5. Same as Fig. 3, but for q along the [111] direction. Only the transverse (T_1) branch is drawn.
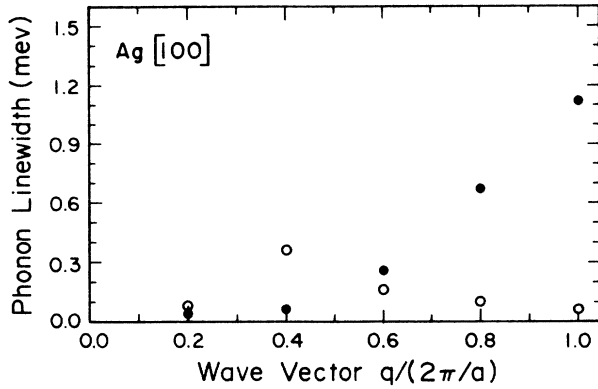
FIG. 6. Calculated linewidths for Ag at 300 K with q along the [100] direction. Solid circles: longitudinal modes. Open circles: transverse modes.

FIG. 8. Same as Fig. 6, but for Au.

both directions, the calculated widths are very large in agreement with the corresponding experimental widths. In the [100] direction we find the maximum at $q=0.8$ $(2\pi/a)$ (1,0,0), in agreement with the experimental values. We want to point out that in the phonon width, in addition to the evaluated anharmonic contribution, there is a contribution arising from the electron-phonon interaction. This contribution around the zone boundary is rather small compared to the anharmonic contribution, so that from our calculations one can deduce that the observed maximum in the [100] direction is related to phonon-phonon interactions more than to the electron-phonon interaction as was argued in the past.[19] We have also evaluated the width of the transverse phonons. In all the symmetry directions the experimental transverse widths are 2–4 times smaller than the longitudinal one. Our results underestimate, by roughly an order of magnitude, the experimental ones. For instance, at the X point we obtain 0.02 meV while the experimental value is 0.6 ± 0.5 meV. In the case of transverse phonons the linewidths both theoretically and experimentally are
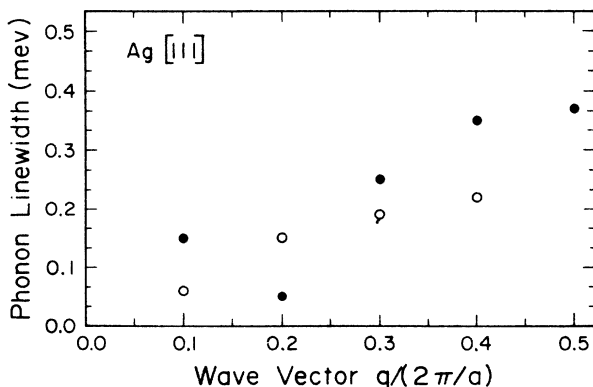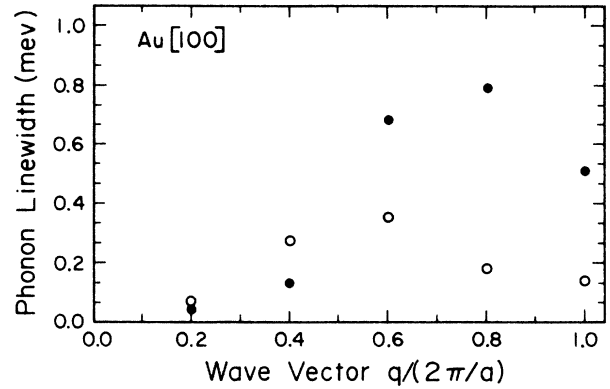
monotonically increasing functions of q. We want to point out that for the simple metal Al the pseudopotential approach has been used to determine the third-order force constants. The linewidths evaluated by Koehler et al.[20] and by Högberg and Sandström[21] that are based on different potentials are in overall agreement with our results.

We now turn to discuss our results for Cu. For this element there are a limited number of experimental data obtained at 300 K by Larose and Brockhouse.[11] Again, the experimental errors are about 25% due to the experimental difficulties of such measurements. We display in Figs. 3–5 our results for the [100], [110], and [111] directions. In Figs. 3 and 4 we present the calculated linewidths for transverse phonons together with the experimental results. The comparison shows that we strongly underestimate the experimental values for transverse phonons, as for Al, but in this case we reproduce the experimentally observed maximum at $q=0.45$ $(2\pi/a)$ (1,0,0). A maximum inside the BZ is also found for the transverse phonons in the other two directions. Concerning the longitudinal phonons, Figs. 3 and 5 show that the maximum linewidth is strongly peaked around the zone boundary, especially in the [100] direction. In Figs. 6 and

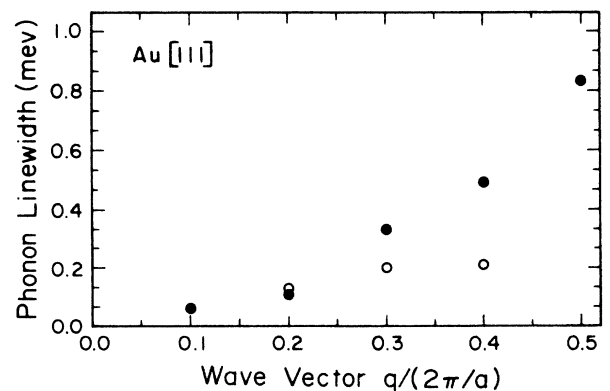FIG. 7. Same as Fig. 6, but for q along the [111] direction.

FIG. 9. Same as Fig. 7, but for Au.

7 we show the linewidths of Ag in the two directions [100] and [111], and in Figs. 8 and 9 those of Au. These results show the same trends obtained for Cu and Al. The only exception is Au. In this case the longitudinal mode widths are not peaked at the zone boundary, but at $q = 0.8$ $(2\pi/a)$. Unfortunately, for these metals (Ag and Au) there are no experimental data available with which to compare our results.

VI. CONCLUSIONS

In this paper we have shown that the major contribution to the evaluation of the phonon linewidth arises from the nearest-neighbor cubic central force constant entering $V^{(3)}$ [Eq. (24)]. This proves the necessity of a reliable estimate of the anharmonic force constants. The method that we have presented of determining the time of flight from the third-order elastic moduli fulfill this requirement. By increasing the range of the anharmonic potential we have determined a convergent value of γ_1. In particular, we have shown that for those metals for which the experimental TOE do violate the third-order Cauchy relations, Eqs. (13) and (14), it is necessary to introduce three-body forces in order to obtain an appropriate value of γ_1. Furthermore, an accurate evaluation of the phonon frequencies and eigenvectors is required to evaluate $V^{(3)}$. This is provided by our new central harmonic potential. For Al, which has been studied in the past, our evaluated linewidths compare rather well with pseudopo-

tential calculations[20,21] and reproduce the experimental behavior as a function of the momentum transfer, indicating the presence of a maximum in the proximity of the BZ boundary. Our calculations, however, do underestimate the experimental values especially in the small-q region. We think that this discrepancy is mainly due to the role played by the higher-order anharmonic interactions which are very important[22] in the region of small momenta. For large momentum transfers, where the one-phonon theory is more adequate, our results present an overall agreement with the available experiments. In view of the present capability to perform accurate calculations of the phonon linewidths for metals we hope that the present work will stimulate new experimental research in this field in order to obtain a microscopic description of the phonon-phonon interactions.

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