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"Anharmonic Effects in Surface Phonons"

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These are preliminary lecture notes, intended only for distribution to participants.

ANHARMONIC EFFECTS IN SURFACE PHONONS

by

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CRYSTAL POTENTIAL

$$\Phi = \Phi^{(0)} + \vec{\Phi}^{(1)} \cdot \vec{u} + \vec{u} \cdot \vec{\Phi}^{(2)} \cdot \vec{u} + \vec{u} \cdot (\vec{u} \cdot \vec{\Phi}^{(3)} \cdot \vec{u}) + \vec{u} \cdot (\vec{u} \cdot \vec{\Phi}^{(4)} \cdot \vec{u}) \cdot \vec{u} + \cdots$$

At the surface the reflection coefficient is given by:

$$\frac{d^2R(\vec{k}_f, \vec{k}_i)}{d\Omega_f dE_f} = \frac{m^2}{2\hbar^4 NMk_{iz}} \sum_j \frac{|\vec{k}_f|}{\omega(\vec{Q}, j)} \left| \langle k_{fz} | \vec{\nabla} \cdot \vec{U}(\vec{Q}, z) | k_{iz} \rangle \right|^2 \times$$

$$\{[1 + n(\omega(\vec{Q}, j))] \frac{\Gamma(\vec{Q}, j; \omega)}{[\omega - \omega(\vec{Q}, j) - \Delta(\vec{Q}, j; \omega(\vec{Q}, j))]^2 + \Gamma^2(\vec{Q}, j; \omega(\vec{Q}, j))} +$$

$$n(\omega(\vec{Q}, j)) \frac{\Gamma(\vec{Q}, j; \omega)}{[\omega + \omega(\vec{Q}, j) + \Delta(\vec{Q}, j; \omega(\vec{Q}, j))]^2 + \Gamma^2(\vec{Q}, j; \omega(\vec{Q}, j))} \}$$

where 2Γ is the phonon linewidth, Δ is the phonon energy shift and $\vec{U}$ is the dynamical interaction.

The first term related to [1+n] corresponds to processes in which the atom gives up energy $\hbar\omega(\vec{Q},j)$ to the crystal.

The second term related to n corresponds to processes in which the atom adsorbs energy $\hbar\omega(\vec{Q},j)$ from the crystal.

In the present calculations we are interested in the frequency and momentum dependence of the phonon linewidth 2Γ for the Rayleigh mode given by:

$$\Gamma(\vec{Q},j;\omega(\vec{Q},j)) = \frac{18}{\hbar^2}\sum_{\vec{G}}\sum_{\vec{Q}_1\in BZ}\sum_{j_1,j_2}\left|V^{(2)}(-\vec{Q},j;\vec{Q}_1,j_1;\vec{Q}-\vec{Q}_1+\vec{G},j_2)\right|^2 \times$$
$$\{(n_1+n_2+1)[\delta(\omega-\omega_1-\omega_2)-\delta(\omega+\omega_1+\omega_2)]+$$
$$(n_1-n_2)[\delta(\omega+\omega_1-\omega_2)-\delta(\omega-\omega_1+\omega_2)]\}$$

with j=R.

$\vec{Q},j$ labels the harmonic mode of momentum $\vec{Q}$ corresponding to the j-th branch and:

$$\omega = \omega(\vec{Q},j)$$
$$\omega_1 = \omega(\vec{Q}_1,j_1)$$
$$\omega_2 = \omega(\vec{Q}_2,j_2)$$

LATTICE DYNAMICS IN THE HARMONIC APPROXIMATION

Born Von Karman model:

$$\Phi^{(2)} = \Phi_C{}^{(2)} + \Phi_A{}^{(2)}$$

where $\Phi_C{}^{(2)}$ is related to two-body central forces and $\Phi_A{}^{(2)}$ is related to three body angular forces.

The force constants related to $\Phi_C{}^{(2)}$ are:

$$\alpha_i = \frac{1}{r}\frac{\partial \Phi_C{}^{(2)}}{\partial r}\bigg|_{r=r_i} \qquad \text{tangential force constants}$$

$$\beta_i = \frac{\partial^2 \Phi_C{}^{(2)}}{\partial r^2}\bigg|_{r=r_i} \qquad \text{radial force constants}$$

The force constants related to $\Phi_A{}^{(2)}$ are:

$$\delta_i = \frac{1}{3a^2}\frac{\partial^2 \Phi_A{}^{(2)}}{\partial \cos^2 \vartheta_{ijk}}\bigg|_{\vartheta_{ijk}=\vartheta_{ijk}{}^{(0)}} \qquad \text{angular force constants}$$

The α's, the β's and the δ's are determined with a weighted least square fitting procedure, that takes into account of the experimental errors, to the:

- available experimental bulk phonon frequencies at low temperature.
- second order elastic constants.

To determine the range of the interactions we evaluate the mean square deviation:

$$\chi^2 = \frac{1}{N} \sum_{\vec{Q},j} \frac{\left[\omega^2{}_{exp}(\vec{Q},j) - \omega^2{}_{th}(\vec{Q},j)\right]^2}{\omega^2{}_{exp}(\vec{Q},j)}$$

The minimum of the χ^2 is achieved for:

- central interactions extending up to:

  10 *n.n.*

- angular interactions extending up to:

  2 *n.n.*

- Radial force constants β for Al in dyne/cm

Neighbor	Non perturbative	Perturbative	Born Von Karman
1	20900	21700	24600
2	2140	2600	2680
3	-680	-860	-640
4	650	240	250
5	310	580	30
6	-430	-310	-360
7	160	90	120
8	230	160	200
9	-100	-120	120
10	-60	-96	-380

FOURIER TRANSFORMED ANHARMONIC COEFFICIENTS

The cubic anharmonic potential can be written as:

$$\Phi^{(3)} = \frac{1}{12}\sum_{L,l}\sum_{L',l'}\sum_{\alpha,\beta,\gamma}\Phi_{\alpha\beta\gamma}{}^{(i)}(L-L';l,l')\times$$
$$u_\alpha(L,l;L',l')\,u_\beta(L,l;L',l')\,u_\gamma(L,l;L',l')$$

For central forces:

$$\Phi^{(i)}{}_{\alpha\beta\gamma}(L-L';l,l') = \left[\frac{r_\alpha r_\beta r_\gamma}{r^4}(\gamma_i - 3\beta_i + 3\alpha_i) + \frac{r_\alpha\delta_{\beta\gamma} + r_\beta\delta_{\alpha\gamma} + r_\gamma\delta_{\alpha\beta}}{r^2}(\beta_i - \alpha_i)\right]_{\vec{r}=\vec{R}(L,L';l,l')}$$

where $\vec{R}(L-L';l,l') = \vec{R}(L;l) - \vec{R}(L';l')$.

The Fourier coefficients of the cubic potential are determined by using the normal coordinate representation:

$$\vec{u}(L,l) = \sum_{\vec{Q},j}\sqrt{\frac{\hbar}{2NM}}\,\vec{e}(\vec{Q},j;l)\,e^{i\vec{Q}\cdot\vec{R}(L)}\,A_{\vec{Q},j}$$

where $A_{\vec{Q},j}$ are the normal coordinates.

The Fourier transform of the potential becomes:

$$V(\vec{Q},j;\vec{Q}_1,j_1;\vec{Q}_2,j_2)=\Delta(\vec{Q}+\vec{Q}_1+\vec{Q}_2)\frac{1}{6N}\left(\frac{\hbar}{M}\right)^{\frac{3}{2}}\left[\omega(\vec{Q},j)\omega(\vec{Q}_1,j_1)\omega(\vec{Q}_2,j_2)\right]^{-\frac{1}{2}}\times$$

$$\sum_i\sum_{l,l'}\sum_{\alpha,\beta,\gamma}\{\Phi_{\alpha\beta\gamma}{}^{(i)}(\vec{Q},l,l')e_\alpha(\vec{Q},j;l)e_\beta(\vec{Q}_1,j_1;l')e_\gamma(\vec{Q}_2,j_2;l')+$$

$$\Phi_{\alpha\beta\gamma}{}^{(i)}(\vec{Q}_1,l,l')e_\alpha(\vec{Q},j;l')e_\beta(\vec{Q}_1,j_1;l)e_\gamma(\vec{Q}_2,j_2;l')+$$

$$\Phi_{\alpha\beta\gamma}{}^{(i)}(\vec{Q}_2,l,l')e_\alpha(\vec{Q},j;l')e_\beta(\vec{Q}_1,j_1;l')e_\gamma(\vec{Q}_2,j_2;l)\}$$

Peierls approximation

$$V\propto\left[\omega(\vec{Q},j)\ \omega(\vec{Q}_1,j_1)\ \omega(\vec{Q}_2,j_2)\right]^{\frac{1}{2}}$$

$$V_{\vec{Q}\to 0}=0$$

while for V:

$V_{\vec{Q}\to 0}$ = finite value which depends on $\vec{Q}_1$

ANHARMONIC PART

The third order central force constants are:

$$\gamma_i = r \left. \frac{\partial^3 \Phi^{(3)}}{\partial r^3} \right|_{r=r_i}$$

The cubic force constants are determined by a proper fit of the experimentally measured third order elastic moduli $c_{111}, c_{112}, c_{166}, c_{123}, c_{144}$ and c_{456} . This is done by equating the third order contribution of the elastic and lattice vibrational energy.

The third order central force constants which best fit the experimental third order elastic moduli extend up to third shells of neighbors.

The introduction of the second and third neighbors interactions is important to obtain numerical convergence in the value of γ_1 which is the most important ingredient in the evaluation of the linewidth.

USING THE THEORY OF ELASTICITY AND THE METHOD OF HOMOGENEOUS DEFORMATIONS WE HAVE OBTAINED THE RELATIONS BETWEEN THE ANHARMONIC FORCE CONSTANTS AND THE ELASTIC THIRD ORDER CONSTANTS:

$$\frac{1}{a}\left[2\gamma_1+2\gamma_2+12\gamma_3\right]=\frac{1}{2}C_{111}+3C_{112}+C_{123}+\frac{3}{2}C_{11}+3C_{12}$$

$$\frac{1}{a}\left[\frac{5}{6}\gamma_1+\frac{4}{3}\gamma_2+\frac{43}{9}\gamma_3+\frac{1}{2}(\beta_1-\alpha_1)+\frac{11}{3}(\beta_3-\alpha_3)\right]=\frac{1}{3}C_{111}+C_{112}+C_{11}+C_{12}$$

$$\frac{1}{a}\left[\frac{1}{6}\gamma_1+\frac{2}{3}\gamma_2+\frac{11}{9}\gamma_3+\frac{1}{2}(\beta_1-\alpha_1)+\frac{7}{3}(\beta_3-\alpha_3)\right]=\frac{1}{6}C_{111}+\frac{1}{2}C_{11}$$

THESE RELATIONS ORIGINATE FROM AN EXPANSION TO THIRD ORDER IN THE ATOMIC DISPLACEMENTS OF THE INTERATOMIC POTENTIAL AND FROM AN EXPANSION TO THIRD ORDER IN THE DEFORMATIONS OF THE ELASTIC ENERGY.

THE EXPERIMENTAL VALUES FOR THE THIRD ORDER ELASTIC CONSTANTS ARE FROM THE LANDOLTD-BURSTEIN TABLES, THE SECOND ORDER ELASTIC CONSTANTS ARE FROM THOMAS JR. ET AL.

Third order force constants γ for Al in dyne/cm

Neighbor	Born Von Karman	Wallace	Ruggerone
1	$-2.566\ 10^5$	$-4.423\ 10^5$	$-2.757\ 10^5$ [Al(001)] $-2.852\ 10^5$ [Al(111)]
2	$-5.367\ 10^4$	$-0.411\ 10^4$	
3	$5.650\ 10^3$	$-1.679\ 10^3$	

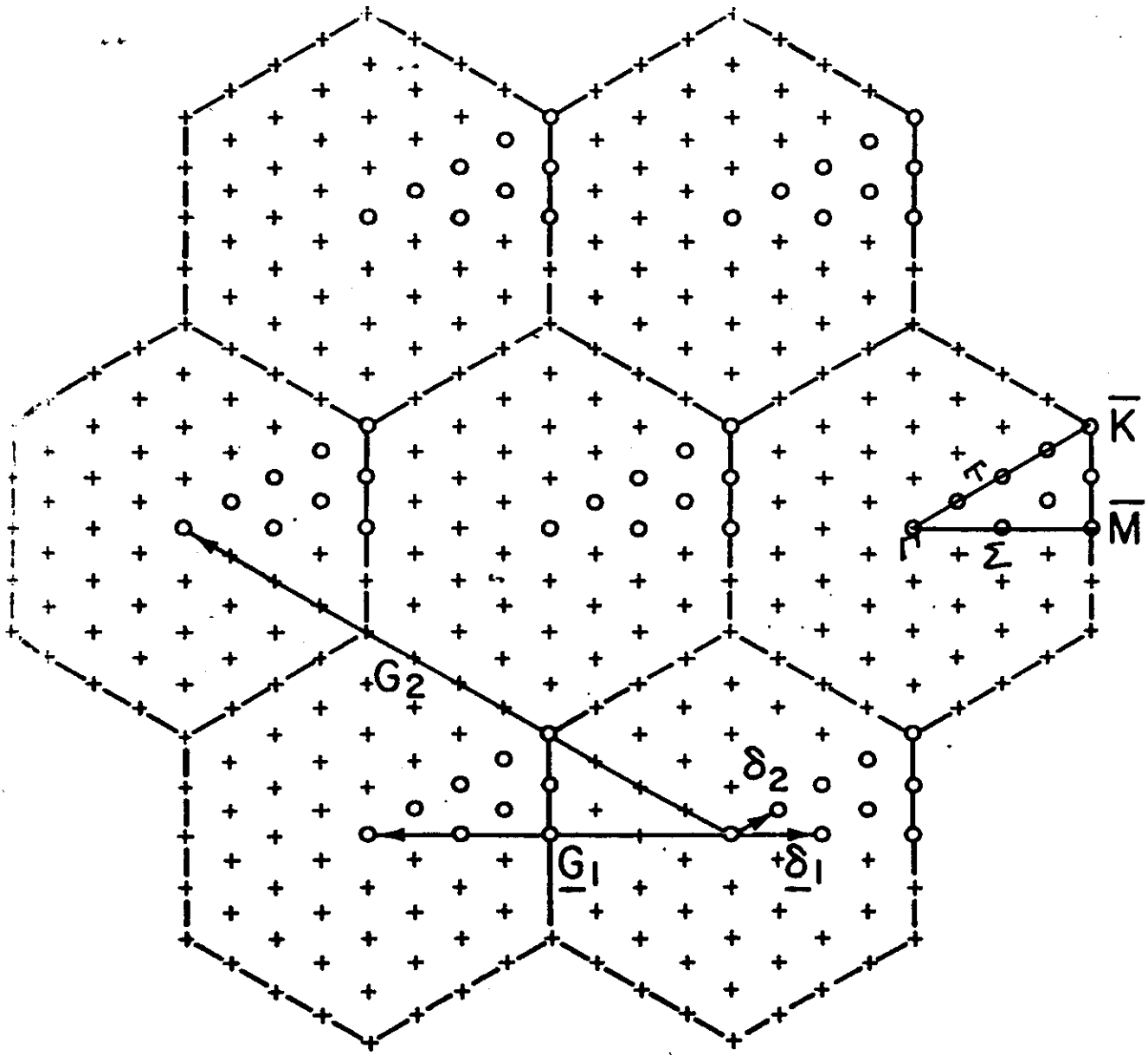
Fourth order force constants η for Al in dyne/cm

Neighbor	Born Von Karman	Wallace	Ruggerone
1	$1.458 10^6$	$6.590\ 10^6$	$3.310\ 10^6$ [Al(001)] $3.215\ 10^6$ [Al(111)]

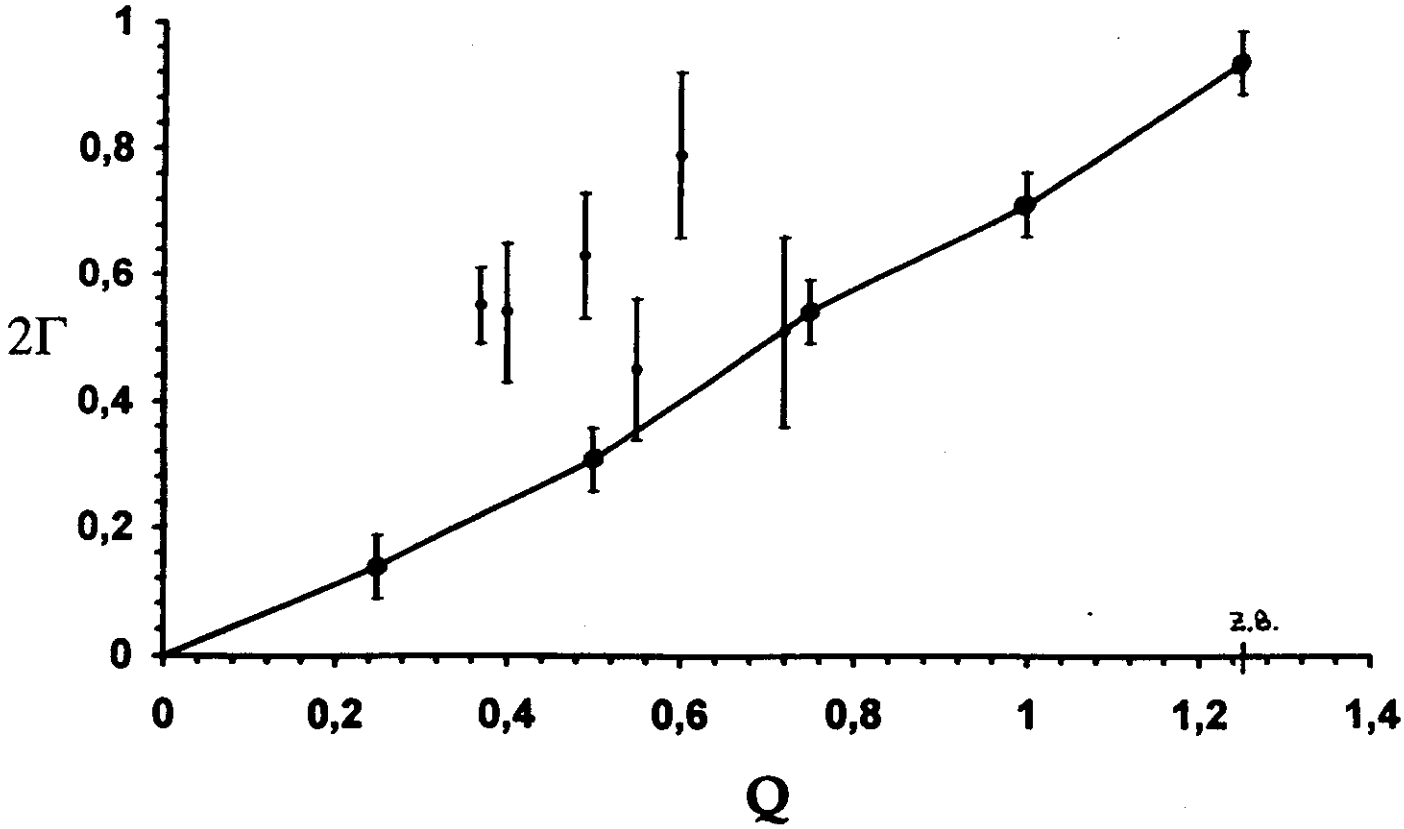
BULK PHONON LINEWIDTH of Al
(from ZOLI M. P.H.D. Thesis)

	WAVE VECTOR	LONGITUDINAL LINEWIDTH (meV)	TRASVERSAL LINEWIDTH (meV)
	0.2 0.0 0.0	0.06	0.122
	0.4 0.0 0.0	0.17	0.635
Δ	0.6 0.0 0.0	0.44	0.378
	0.8 0.0 0.0	1.71	0.268
	1.0 0.0 0.0	1.18	0.165
	0.1 0.1 0.1	0.09	0.059
	0.2 0.2 0.2	0.13	0.163
Λ	0.3 0.3 0.3	0.43	0.305
	0.4 0.4 0.4	0.72	0.306
	0.5 0.5 0.5	1.41	0.268
	0.15 0.15 0.0		0.055
	0.30 0.30 0.0		0.265
Σ	0.45 0.45 0.0		0.303
	0.60 0.60 0.0		0.290
	0.75 0.75 0.0		0.277

Al (111)

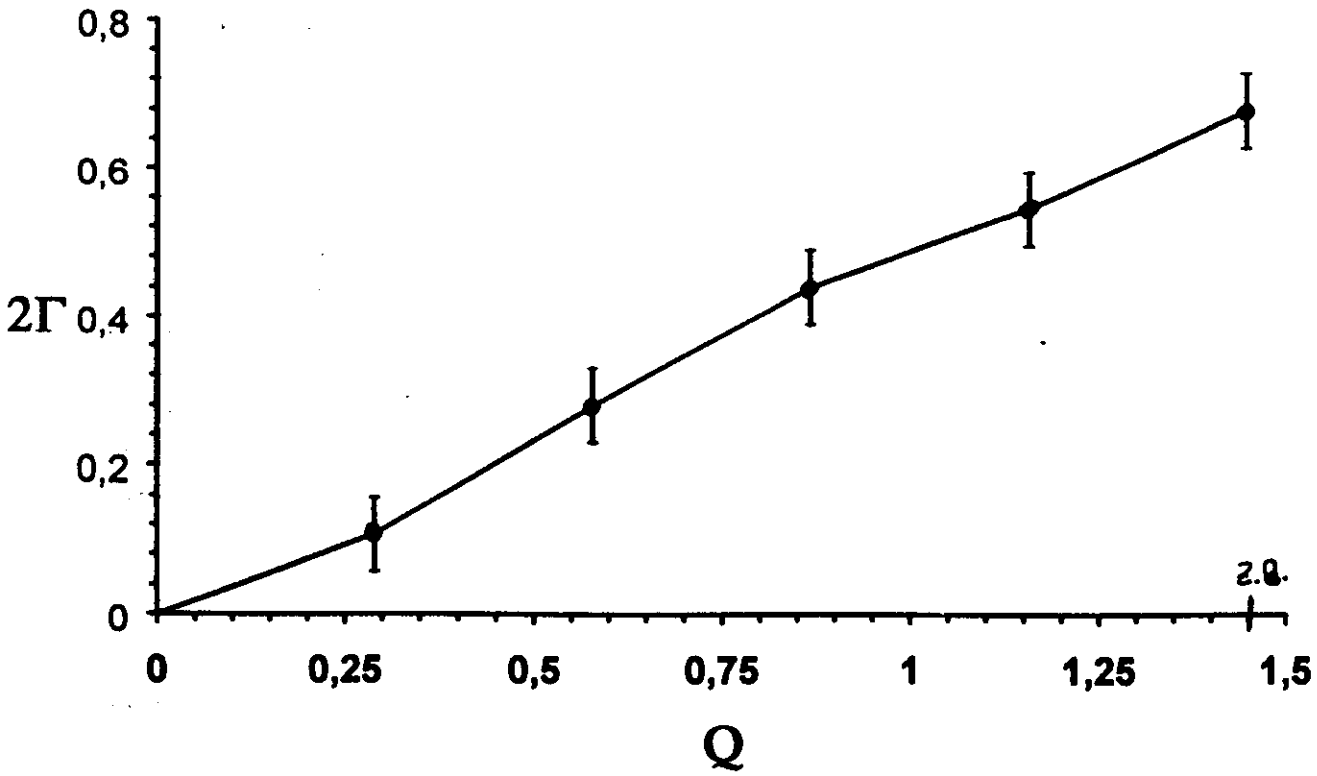


Phonon linewith 2Γ (in meV) of the Rayleigh mode for Q (in A^{-1}) along the $\bar{\Sigma}[11\bar{2}]$ direction

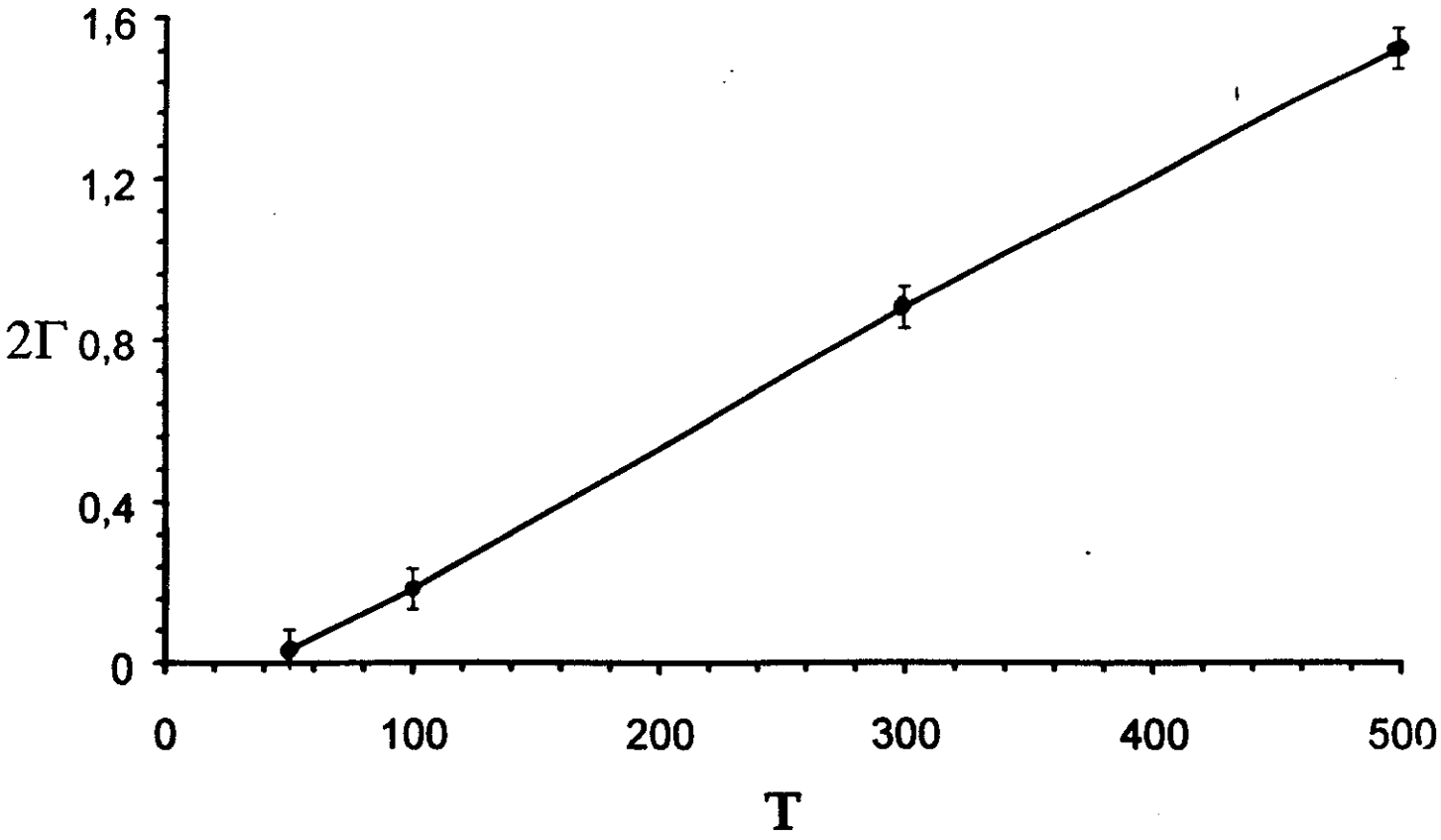


$\lim_{Q\to 0} 2\Gamma(\vec{Q}) = Q^{11/3}$ Mayer et al

Phonon linewith 2Γ (in meV) of the Rayleigh mode for Q (in A^{-1}) along the T [110]direction



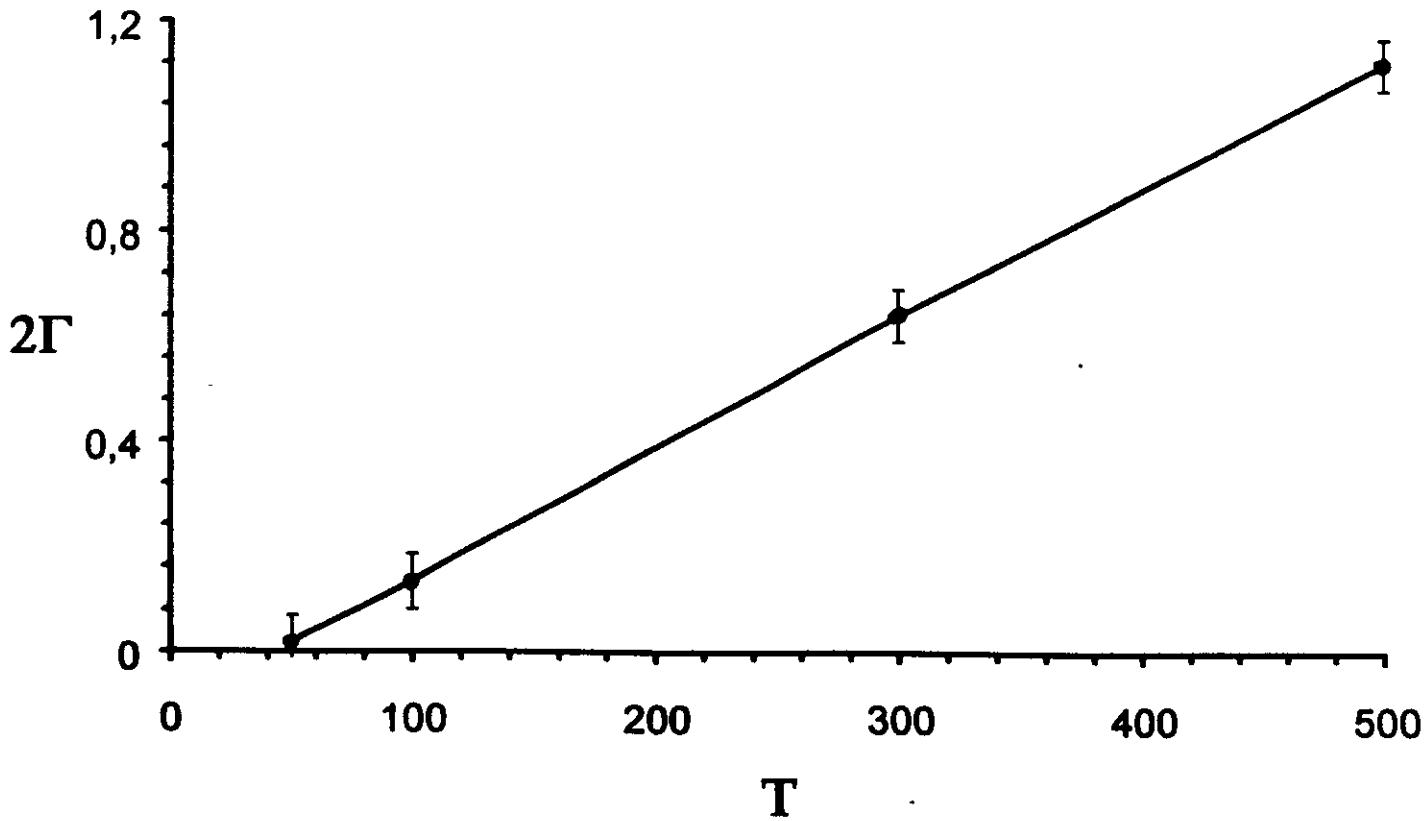
Phonon linewith 2Γ (in meV) of the Rayleigh mode at the $\overline{M}$ point vs. T (in K)



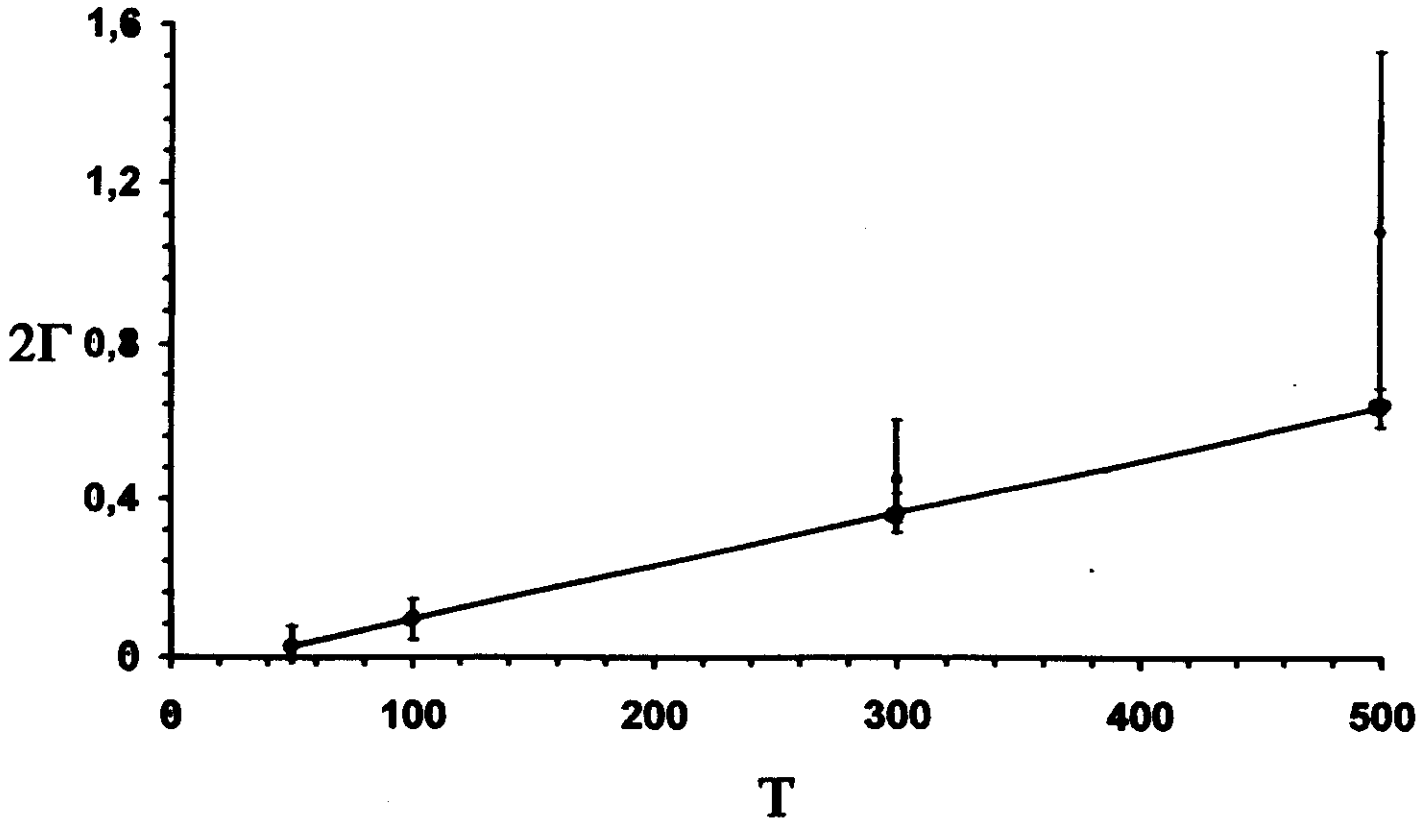
$$\lim_{T\to 0} 2\Gamma(\vec{Q}) \propto e^{-\hbar\omega/k_B T} + C$$

C = zero point motion contribution

Phonon linewith 2Γ (in meV) of the Rayleigh mode at the $\overline{K}$point vs. T (in K)



Phonon linewith 2Γ (in meV) of the Rayleugh mode at $Q=0.54\ A^{-1}$ vs. T (in K)



Phonon linewith 2Γ (in meV) of the Rayleugh mode at the $\overline{M}$ point vs. T (in K)