Zn and Cd, as done by Brindley & Ridley (1939). In Table 4 the mean of the results No. 17 and 21 of Table 5 in R-77 for the root-mean-square displacements of the atoms in Zn is used to calculate the u_c/u_a ratio of Zn. The ratio is compared with the Cd ratio of the present work and with that of Brindley & Ridley (1939).

Table 4. u_c/u_a *ratio for* Zn *and* Cd

	Zn (R-77)	Cd (present work)	Cd (Brindley & Ridley, 1939)
u_c/u_a	1·63 (2)	1·62 (2)	1·54

Zn and Cd have similar electronic structures (Zn: $3d^{10}4s^2$; Cd: $4d^{10}5s^2$) and are both built up of an h.c.p. lattice with an anomalously large c/a ratio (ideal h.c.p.: $c/a = 1{\cdot}633$; Zn: 1·853, Cd: 1·885). If we therefore assume a similar vibrational behaviour for Zn and Cd, the ratio u_c/u_a obtained in the present work suggests a more satisfactory result.

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Anharmonic Contributions to Bragg Diffraction.
I. Copper and Aluminium

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Anharmonic contributions to the atomic motion in copper and aluminium single crystals have been determined from measurements of the elastic scattering of recoil-less γ-rays at temperatures up to 1200 K for copper and 900 K for aluminium. The results are compared with theoretical predictions.

Introduction

The thermal motion of the atoms in a crystal lattice reduces the intensity of the elastically diffracted Bragg X-ray peaks while increasing the intensity of thermal diffuse scattering (TDS). If the magnitude of a particular Bragg reflection is recorded as a function of temperature, information about the amplitudes of the atomic vibrations can be found and estimates can, in principle, be made of their anharmonicity. However, in the regions where the anharmonic effects are most significant, namely for the higher-order Bragg reflections at elevated temperatures, the TDS makes a substantial contribution to the total scattered intensity. The TDS results from interactions between the incident

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photons and phonons present in the lattice, but the relative energy change (10^{-2} eV) is so small that it is impossible with standard X-ray techniques to distinguish this from the elastically scattered Bragg component. However, a separation of the two components can be achieved by using the high-energy resolution (10^{-8} eV) of the Mössbauer effect (O'Connor & Butt, 1963; Ghezzi, Merlini & Pace, 1969), and this was employed in the present work to study the angle and temperature dependences of the elastic-scattering intensity from single crystals of copper and aluminium.

Experimental method

A 90 mCi ^{57}Co source in rhodium foil was used for the experiments. ^{57}Co decays to the 14·4 keV level of ^{57}Fe which gives a Mössbauer γ-ray of wavelength 0·8602 Å. To utilize as large a fraction of the radiation as possible, large single crystals were employed in a Bragg reflection geometry. The source was a 3 mm diameter spot at a distance of 100 mm from the crystal and the detector was an Ortec lithium-drifted silicon counter having a detection window measuring 20 × 3 mm, also placed 100 mm from the crystal. To separate the elastic and inelastic components, a resonant absorber containing ^{57}Fe nuclei in ammonium lithium fluoroferrate was placed between the crystal and detector. This absorber has an absorption line width of about 10^{-8} eV. A measure of the fraction of the radiation absorbed resonantly $R(\theta)$ can then be derived from measurements of the intensity with the absorber at rest, $I_0(\theta)$, and vibrated at a speed sufficient to destroy the resonance, $I_\infty(\theta)$, $R(\theta) = [I_\infty(\theta) - I_0(\theta)]/I_\infty(\theta)$. If a similar quantity $R(0)$ is determined for the incident beam by placing the absorber between the source and crystal, the fraction of the radiation scattered without energy change is given by $fc(\theta) = R(\theta)/R(0)$. Then $I_\infty(\theta)fc(\theta)$ gives a measure of the elastically scattered radiation and $I_\infty(0)[1 - fc(\theta)]$ of the inelastic component.

To obtain a uniform temperature over the large crystals the specimens were clamped to plates of a similar metal to reduce thermal strains, and mounted centrally within an electrically heated oven equipped with windows for the γ-rays. A nitrogen atmosphere maintained at slightly above atmospheric pressure prevented oxidation of the samples. For the experiments aluminium crystals 1 mm thick set on the (111) and (100) planes were spark cut from a 99·99% pure, single-crystal rod, diameter 25 mm, and copper crystals of dimensions 25 × 12 × 0·4 mm set on similar planes were employed. These were first annealed for several hours near the upper limit of the temperature range over which measurements were to be taken until a constant state of perfection was attained. The scattering was then recorded at intervals of 50 to 80 K as the temperature was raised.

Theory

The reduction in the Bragg-peak intensity produced by thermal vibrations is described by the Debye–Waller factor which has the form:

$$\exp(-2W_Q) = \exp - \langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle \qquad (1)$$

if the displacements are small and follow a Gaussian distribution, where $\mathbf{Q}$ is the scattering vector equal to the difference between the wave vectors of the incident and scattered γ-rays, $\mathbf{u}$ is the vector displacement of the atom from its equilibrium position and the angle brackets denote a thermal average.

The magnitude of the displacements in the harmonic approximation is given, in the high-temperature limit by:

$$W(T) = \frac{Q^2KT}{2m}\left[\overline{\omega^{-2}} + \frac{1}{12}\left(\frac{\hbar}{KT}\right)^2\right] \qquad (2)$$

where m is the atomic mass, $\hbar$ is Planck's constant divided by 2π, K is Boltzmann's constant and $\overline{\omega^{-2}}$ is a moment of the phonon frequency distribution $G(\omega)$ defined as

$$\overline{\omega^{-2}} = \tfrac{1}{3}N \int_0^{\omega_{\max}} \omega^{-2}\,G(\omega)\,\mathrm{d}\omega$$

(Barron, Leadbetter, Morrison & Salter, 1966), or in terms of the X-ray Debye temperature Θ, $\omega^{-2} = 3(h/K\Theta)^2$. Additional corrections have to be applied to allow for the effect of thermal expansion upon ω^{-2} and Q so that

$$W(T) = \frac{KT}{2m}\left\{\overline{\omega^{-2}}\,[1 + 6\gamma(-2)\,\alpha(T - T_0)] + \frac{1}{12}\left(\frac{\hbar}{KT}\right)^2\right\} Q^2[1 - 2\alpha(T - T_0)], \qquad (3)$$

where α is the coefficient of thermal expansion, $\gamma(-2)$ is the Grüneisen constant describing the volume dependence of ω^{-2} and the values of ω^{-2} are taken at room temperature T_0.

At high temperatures the distribution of the atomic displacements is no longer Gaussian and the Debye–Waller factor takes the form:

$$\exp - 2W = \exp\left\{- \langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle + \frac{1}{12}\,[\langle(\mathbf{Q}\,.\,\mathbf{u})^4\rangle - 3\langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle^2] + O(Q^6)\right\}. \qquad (4)$$

Detailed analyses of these anharmonic effects carried out by a number of authors including Maradudin & Flin (1963) and Wolfe & Goodman (1969) show that

$$\frac{1}{2}\,\langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle = W_0 + (m_e + m_{12})(Qd)^2\left(\frac{T}{\Theta}\right)^3 \qquad (5)$$

and

$$\frac{1}{24}\,[\langle(\mathbf{Q}\,.\,\mathbf{u})^4\rangle-3\langle(\mathbf{Q}\,.\,\mathbf{u})^2\rangle^2]=m_{34}(Qd)^4\left(\frac{T}{\Theta}\right)^3, \quad (6)$$

where W_0 is the harmonic factor in (2), m_e describes the thermal expansion correction in (3), m_{12} and m_{34} are factors derived from sums over the lattice displacements and d is the nearest-neighbour atomic distance.

Results and discussion

The use of a large single crystal in diverging the incident beam gives an effective integrated intensity similar to that obtained by rotating a small crystal through the Bragg angle, provided that the incident beam intensity is spread over an angular divergence greater than the mosaic spread of the crystal. Measurements with a narrow counter slit showed that the TDS was peaked under the elastic scattering intensity, but for the lower-order planes in aluminium there appeared to be a slight dip in this peak. As measurements were carried out with the absorber placed between the source and crystal to eliminate systematic errors in $R(0)$, it is thought that the effect resulted from reduced γ-ray penetration at the centre of the crystal caused by extinction (O'Connor, 1967). The integrated intensities were taken to be proportional to the peak values.

From the variation of the scattering intensities with temperature, Figs. 1 and 2, values for the Debye temperature at 293 K were found from fits to the quasi-harmonic model described in (3), with the macroscopic Grüneisen parameter instead of the second moment $\gamma(-2)$ for which we know of no reported calculations. But, because of anharmonicity in the higher-temperature regions these estimates tend to be lower than those made from measurements of the integrated intensities of a number of reflections at one temperature (Table 1).

An examination of (4) shows that a measure of the non-Gaussian U_Q^4 term can be found by comparing the Debye–Waller factors for two sets of parallel planes described by Q_1 and Q_2 at two temperatures T and T_0 with the expression derived by Butt & Solt (1971):

$$\frac{1}{(Q_1d_1)^2-(Q_2d_2)^2}\left\{\frac{2W_{Q_1}(T)-2W_{Q_1}(T_0)}{(Q_1d)^2}-\frac{2W_{Q_2}(T)-2W_{Q_2}(T_0)}{(Q_2d)^2}\right\}=D(T)-D(T_0) \quad (7)$$

where $D(T)=(\langle U_Q^4\rangle-3\langle U_Q^2\rangle^2)_T/d^4$. This, written in terms of the measured intensities, has the form

$$D(T)-D(T_0)=\frac{1}{(Q_1d)^2-(Q_2d)^2}\left[\frac{1}{(Q_1d)^2}\ln\left(\frac{I_{Q_1}T_0}{I_{Q_1}T}\right)-\frac{1}{(Q_2d)^2}\ln\left(\frac{I_{Q_2}(T_0)}{I_{Q_2}(T)}\right)\right], \quad (8)$$

where $I_Q(T)$ is the elastic intensity corrected for

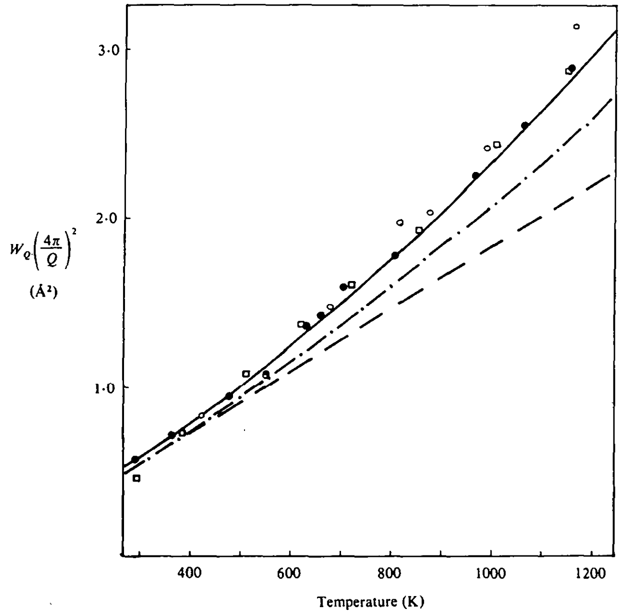

Fig. 1. The temperature dependence of the Debye–Waller factor for copper: ● (400) plane results, ○ (600) plane results, □ (333) plane results; — — harmonic theory, Θ = 315 K (Wolfe & Goodman, 1969), —·— quasi-harmonic theory, —— curve with T^2 term derived by Wolfe & Goodman (1969) added to the quasi-harmonic curve.

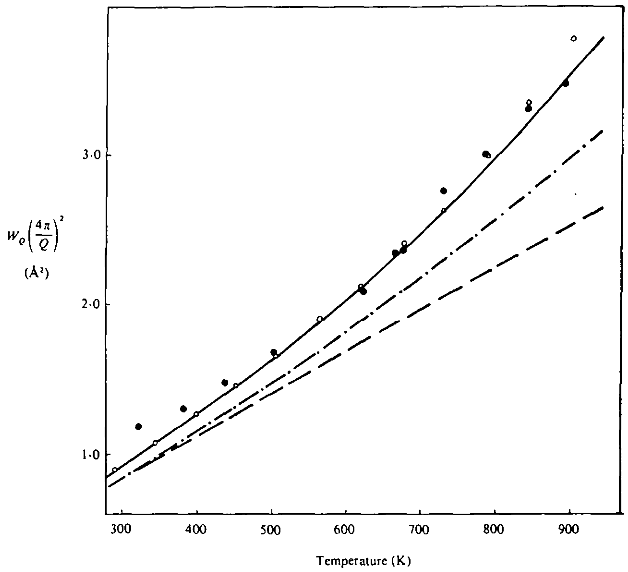

Fig. 2. The temperature dependence of the Debye–Waller factor for aluminium: ● (222) plane results, ○ (333) plane results; — — harmonic theory, Θ = 390 K (value calculated by Gilat & Nicklow, 1966), —·— quasi-harmonic theory, —— fit with T^2 term included.

Table 1. *Values of the X-ray Debye temperature*

The symbols used to indicate the methods have the following meaning: X X-ray, γ γ-ray, N neutron, P powder, SC single crystal, T temperature dependence, I integrated intensity measurements, B anomalous X-ray transmission (Borrmann effect).

Other experimental measurements			Present results		
Reference	Method	Θ (K)	Method	Θ (K)	
Copper			γSC I	320 ± 15	
			T below 900 K Plane		With T^3 term
Owen & Williams (1947)	X P T	314	(600)	293 ± 6	307 ± 6
Chipman & Paskin (1959)	X P T	307	(400)	296 ± 6	306 ± 6
Flinn *et al.* (1961)	X SC T	320	(200)	295 ± 8	300 ± 8
Webb (1962)	X P I	311	(333)	288 ± 8	295 ± 8
Baldwin (1968)	X SC T B	306 ± 4	(222)	299 ± 8	303 ± 8
Linkoaho (1971)	X P I	307 ± 3	Mean	296 ± 4	304 ± 4
Aluminium			γSC I	393 ± 6	
			T below 800 K Plane		
Chipman (1960)	X P T	407 ± 10	(333)	379 ± 8	
Nicklow & Young (1966)	X SC T	393	(222)	385 ± 6	
Butt & O'Connor (1967)	γ SC T	387 ± 14	(111)	390 ± 15	
De Marco (1967)	X SC I	387 ± 2	(600)	390 ± 6	
McDonald (1967)	N SC T	386 ± 10	(400)	382 ± 15	
Dingle & Medlin (1972)	X SC I	393 ± 1	Mean	385 ± 2	

Table 2. *Anharmonic parameters for copper and aluminium*

	Present determination	Experimental determinations	Quasi-harmonic theory	Theoretical calculations
Copper				
$m_e + m_{12}$	$(2{\cdot}78 \pm 0{\cdot}2) \times 10^{-5}$		$1{\cdot}54 \times 10^{-5}$	$2{\cdot}1 \times 10^{-6\,a}$ $2{\cdot}3 \times 10^{-6\,b}$ $1{\cdot}5 \times 10^{-5\,c}$
m_{12}	$(1{\cdot}24 \pm 0{\cdot}2) \times 10^{-5}$			$-5{\cdot}3 \times 10^{-6\,a}$ $+1{\cdot}7 \times 10^{-5\,b}$ $-5{\cdot}6 \times 10^{-6\,c}$
$m_{34}(n00)$	$(8 \pm 3) \times 10^{-10}$ (200)/(400) $(9 \pm 3) \times 10^{-10}$ (400)/(600) $(8 \pm 3) \times 10^{-10}$ (200)/(600)			$-4{\cdot}2 \times 10^{-10\,a}$ $-7{\cdot}9 \times 10^{-10\,b}$ $4{\cdot}2 \times 10^{-12\,c}$
$m_{34}(nnn)$	$(4 \pm 3) \times 10^{-10}$ (222)/(333)			$0{\cdot}9 \times 10^{-10\,a}$ $-1{\cdot}3 \times 10^{-10\,b}$ $5{\cdot}6 \times 10^{-12\,c}$
Aluminium				
$m_e + m_{12}$	$(8{\cdot}8 \pm 0{\cdot}5) \times 10^{-5}$	$9{\cdot}3 \times 10^{-5\,d}$ $9{\cdot}3 \times 10^{-5\,e}$	$5{\cdot}7 \times 10^{-5}$	$4{\cdot}9 \times 10^{-5\,c}$
m_{12}	$(3{\cdot}1 \pm 0{\cdot}5) \times 10^{-5}$			$-1{\cdot}8 \times 10^{-5\,c}$
$m_{34}(n00)$		$3{\cdot}0 \times 10^{-8\,f}$		$9{\cdot}2 \times 10^{-12\,c}$

References: (*a*) and (*b*) Wolfe & Goodman (1969) models I and III. (*c*) Maradudin & Flinn (1963). (*d*) Chipman (1960). (*e*) McDonald (1967). (*f*) Albanese & Ghezzi (1973).

changes in the atomic scattering factor, the Lorentz–polarization factor and other expansion-sensitive terms. The analysis at T_0 was taken as the reference temperature and the term $D(T) - D(T_0)$ evaluated from differences in the curves depicting the temperature dependences of $\{\ln[I_Q(T_0)/I_Q(T)]\}(Qd)^2$ for different reflections (Fig. 3) and the non-Gaussian term m_{34} in (6) calculated from a plot against $(T/\Theta)^3$.

The results for copper derived in this way confirmed a T^3 form of temperature dependence (Fig. 4), although below 700 K the graphs involving the lower-order planes exhibited a sharp fall resulting from extinction.

But, no U_Q^4 term was detectable in the data taken from aluminium crystals up to the (333) set of planes. Measurements of a similar type have, however, been made by Albanese & Ghezzi (1973) who found a significant difference between their higher-order (333) and (444) plane results (Table 2). Theoretical evaluations of the anharmonic terms in the Debye–Waller factor have been computed by Wolfe & Goodman (1969) for copper, and by Maradudin & Flinn (1963), who derived general expressions from which the coefficients could be evaluated for any face-centred cubic metal (Table 2). The present measurements yield an m_{34} term for copper which is an order of magnitude greater than that found by Maradudin & Flinn (1963), but agrees roughly with the calculations of Wolfe & Goodman (1969), although the result for the n00 set of planes differs in sign.

The anharmonic term, m_{12}, appearing in the magnitude of (5) is more difficult to measure for it makes a similar contribution to the Debye–Waller factors for each plane. An estimate can, however, be made by assuming a theoretical value for the harmonic factor, and using that derived for copper by Wolfe & Goodman (1969), the term in T^2 $(m_e + m_{12})$ required to fit the experimental data is an order of magnitude larger than that derived from their theory (Table 2). The difference between their thermal expansion term, $m_e = 0{\cdot}23 \times 10^{-5}$, and that given by the quasi-harmonic relation, $m_e = 1{\cdot}9 \times 10^{-5}$, would bring the values of m_{12} derived here, $m_{12} = 1{\cdot}24 \times 10^{-5}$, into agreement with the value given by Wolfe & Goodman's (1969) model III, $m_{12} = 1{\cdot}7 \times 10^{-5}$.

The results for aluminium were fitted in a similar manner with a value of 390 K for the Debye temperature derived theoretically by Gilat & Nicklow (1966), which agreed with fits of the data below 600 K where anharmonic effects were small. The values for $(m_e + m_{12})$ agreed with other experimental measurements made with X-rays and neutrons (Table 2), and showed, as with copper, that the term in T^2 is over $1\frac{1}{2}$ times that expected from thermal expansion. Neither of these results agree with the calculations of Maradudin & Flinn (1963) which suggests that the T^2 anharmonic term should have a negative sign, but their method

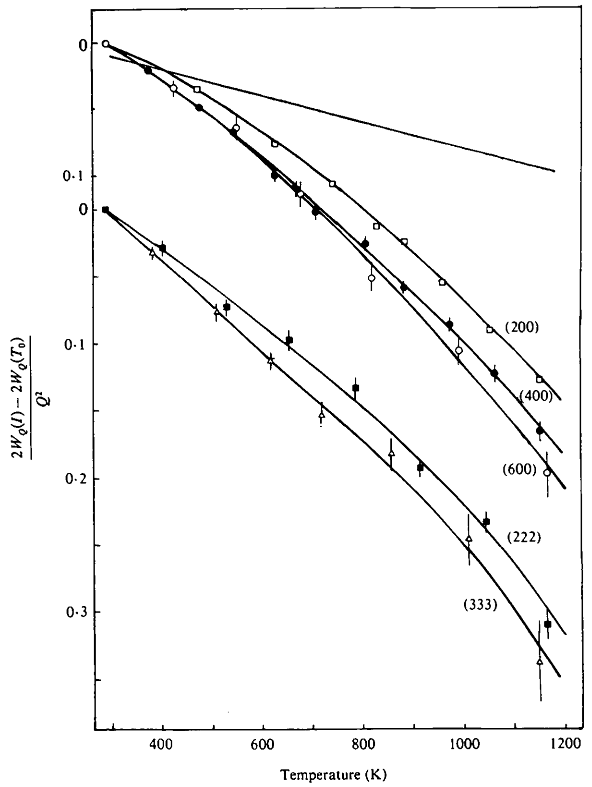

Fig. 3. Differences in the Debye–Waller factors from different planes in copper. The origin for the top three curves has been shifted for clarity.

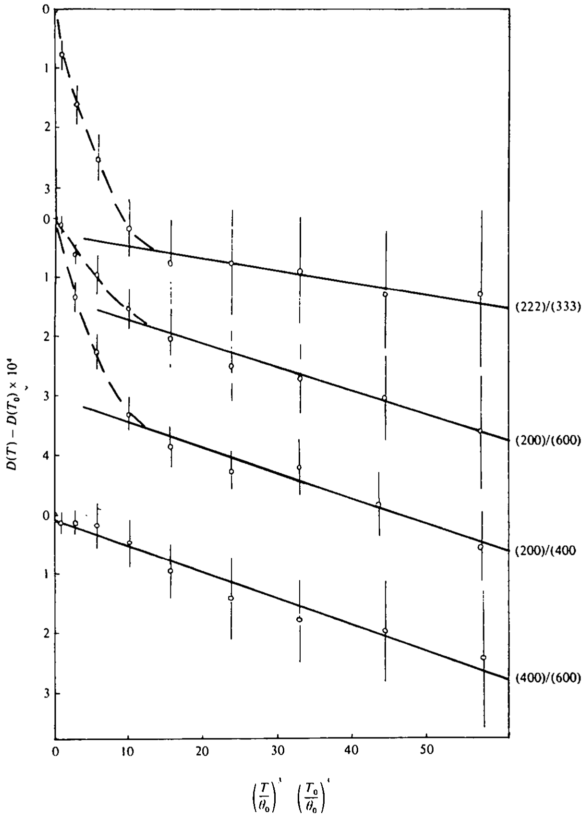

Fig. 4. Plot of the non-Gaussian contribution to the Debye–Waller factor for copper.

involved several assumptions in the evaluation of complicated lattice sums in reciprocal space, and, as the parameters are derived from the difference of terms in the potential energy, such discrepancies could easily arise. Detailed calculations in the manner of those made by Wolfe & Goodman (1969) would probably be required for each metal to give better agreement. Finally, it must be emphasized that the values obtained for the anharmonic term have been derived with the theoretical harmonic factors assumed to be correct and a 1% error in the latter would lead to a 15% error in the $(m_e + m_{12})$ term.

Conclusion

The application of the Mössbauer effect in the measurement of elastic Bragg scattering intensities free from inelastic phonon scattering contributions enables the Debye–Waller temperature factor to be found to sufficient accuracy to allow estimates of the amount of anharmonicity present in the atomic vibrations. The variation of the scattered intensities for a number of Bragg peaks was measured from 300 up to 900 K for aluminium and to 1200 K for copper single crystals and estimates of parameters arising from the non-Gaussian distribution of the thermal displacements at the higher temperatures were made and compared with theoretical estimates. The agreement with the general formulae derived by Maradudin & Flinn (1963) was poor, but values derived from the more sophisticated treatment used by Wolfe & Goodman (1969) were much closer.

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Anharmonic Contributions to Bragg Diffraction.
II. Alkali Halides

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Anharmonic contributions to the atomic motion in the alkali halides KCl, NaCl, KBr and LiF have been determined from measurements of the elastic scattering of recoil-less γ-rays in the temperature range 300 to 1300 K. The results are compared with theoretical predictions.

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