it leaves the sphere of reflexion. Fig. 5 shows the geometry; the arc AA' is the track of a reciprocal-lattice point rotated about R, and $RA=r$, and $RR=RM=MA$, the radius of the circle which the spehre of reflexion cuts in the n-layer net. Then

$$\cos\eta=[r^2/\{2\times(RR)^2\}]-1\;.$$

Thus, a reflexion generated at A will appear in the top half of the record with z-coordinate$=z_t$, corresponding to φ; and, after the crystal has been rotated by $2\times\eta$, the reflexion at A' will appear on the lower half of the film with z coordinate$=z_1$, corresponding to $(\varphi+2\times\eta)$; or, $z_1=z_t+\eta$.

A program written in FORTRAN IV for an ICL 1905 computer to perform the operations analysed above is available from the author.

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Anharmonic Non-Gaussian Contribution to the Debye–Waller Factor for NaCl

By N. M. Butt

Pakistan Institute of Nuclear Science and Technology, Rawalpindi, Pakistan

and G. Solt

Central Research Institute for Physics, Budapest 114, *P.O. Box* 49, *Hungary*

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Measurement and theoretical estimate of the anharmonic non-quadratic contribution to the Debye–Waller factor for NaCl are reported. For the experiment the Mössbauer γ-ray diffraction technique was used to find the elastic diffracted intensity separated from the thermal diffuse scattering. The theoretical treatment makes use of the asymptotic form of the displacement correlation functions to give simple explicit expressions for the non-quadratic term. The role of the relevant lattice dynamical parameters is discussed. The deviation from the Gaussian form of the Debye–Waller factor is shown to be large enough to be observed, and the possibility of estimating the third-order anharmonic coupling constant from such a measurement is indicated.

Introduction

As is well known, the Debye–Waller factor governing the intensity of elastic scattering processes in a crystal defined as

$$f(\mathbf{k},T)=\langle e^{i\mathbf{ku}}\rangle_T$$

can generally be written in the cumulant expansion form

$$f(\mathbf{k}T)=\exp\{-\tfrac{1}{2}\langle(\mathbf{ku})^2\rangle_T+\tfrac{1}{24}[\langle(\mathbf{ku})^4\rangle_T \\ -3\langle(\mathbf{ku})^2\rangle_T^2]+O(\mathbf{k}^6)\} \quad (1)$$

where $\mathbf{k}$ is the change in the wave-vector of the scattered quantum, $\mathbf{u}$ is the displacement of the scattering atom from the lattice equilibrium position and the bracket means thermal averaging over the dynamical states of the crystal. If the lattice sites have inversion symmetry, the odd powers in (1) are absent. Higher than fourth-order terms will be neglected here.

The physical information contained in the Debye–Waller factor is particularly clear if the dynamics of the lattice can be described entirely by using the harmonic approximation, when only the quadratic term appears in the exponent and one has a Gaussian distribution in $\mathbf{k}$ with a width determined by the mean-square displacement of the atoms. It was suggested a long time ago that careful investigation of the Debye–Waller factor can be a very useful tool to study anharmonic properties of crystals. The anharmonic coupling leads to a change in the mean-square displacement as compared with the harmonic value, and also gives rise to the quartic (and higher-order) terms in (1). The presence of the quartic term representing the deviation from the Gaussian behaviour is an inherent effect of lattice anharmonicity, in the sense that it cannot be removed by a simple renormalization in the frame of a harmonic theory. Though earlier work (Maradudin & Flinn, 1963) suggested that only the change in the value of the quadratic term can be large enough to be observed and the quartic term is very small, the approximation giving that result turned out (Wolfe & Goodman, 1969) to underestimate the quartic term. In fact, the calculations of the latter authors for copper show that the anisotropy of the Debye–Waller factor caused by the quartic term is large enough to be observable at the present experimental accuracy. At the same time, the numerical value of the change in the quadratic term, as calculated for KBr (Cowley & Cowley, 1966) as well as for copper, turned out to be much smaller than expected from an *a principio* estimate as a consequence of a cancellation between different contributions; therefore, the clear-cut separation of harmonic and anharmonic quadratic terms becomes extremely difficult.

In spite of its smallness, therefore, the quartic term in (1) is of particular interest, since it can be expected to give direct information on the deviation from quasi-harmonic lattice dynamics, and the different dependence on scattering angle allows it to be separated from the harmonic part of the Debye–Waller factor. Exact theoretical expressions for the non-Gaussian contribution have been given in the early work of Maradudin & Flinn, but accurate calculations could be performed only recently by Wolfe & Goodman using the method of displacement correlation functions in real space. A very simple approximate version of this method, showing, however, explicitly the role of the different physical parameters involved, was used here to calculate the quartic term for NaCl, with the result that it is rather large to be observed, and a reasonable choice of the anharmonic coupling parameters makes the theory fit the experimental results reported here. Since, for determining non-quadratic terms, the elastically scattered X-ray intensity must be measured with high accuracy, to eliminate the thermal diffuse scattering (O'Connor & Butt, 1963) the diffraction technique using Mössbauer radiation has been used. In the following, a short description of the experimental procedure is given and then the results for NaCl are discussed in the frame of a simple theoretical treatment.

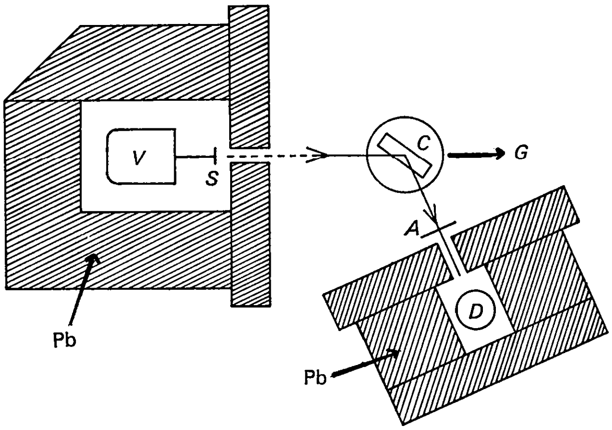


Fig. 1. Mössbauer γ-ray diffractometer set-up. V=electromagnetic vibrator, $S={}^{57}$Co source, C=single crystal, G=goniometer table, A=resonant absorber ^{57}Fe, $D=\gamma$-ray proportional counter, Pb=lead shielding.

Experimental method

The essential apparatus is a Mössbauer γ-ray diffractometer, which is, in fact, an X-ray counter diffractometer where the X-ray source is replaced by a Mössbauer γ-ray source of ^{57}Co. The schematic representation of this apparatus is given in Fig. 1. The single crystal of NaCl ($1\times2\times0{\cdot}2$ cm) with (200) planes parallel to the face was mounted on the goniometer. The crystal could be heated uniformly in a specially designed furnace. The pure elastic part (zero-phonon line) of the diffracted intensity was determined by the technique developed earlier (O'Connor & Butt, 1963).

A 50 millicurie ^{57}Co source diffused in palladium was used and 14·4 keV ($\lambda=0{\cdot}86$ Å) γ-rays of ^{57}Fe formed by the decay of ^{57}Co were used as Mössbauer resonant γ-rays. A 'black absorber' (90% enriched ^{57}Fe isotope diffused in ammonium–lithium fluoroferrate) with absorber line width about 15 times larger than the natural line width of the 14·4 keV radiation, was used as the resonant energy analyser in the diffracted beam. This absorber was placed in front of the slit of the γ-ray detector D which is a gas-proportional counter filled with xenon at one atmosphere pressure.

Since the diffracted elastic intensity is counted for many hours (so that a statistical accuracy of about 2% could be obtained), a very good thermal insulation is required between the crystal and the metallic goniometer. This was achieved by using a piece of porcelain 1·5 cm long with a low coefficient of thermal conductivity.

The crystal was clamped to a 3 mm thick silver plate which was heated by electric heaters. The silver plate was useful in reducing the temperature gradient across the crystal. The front face of the crystal was subjected to radiation heating by an electric heater placed in front of the crystal such that the incident and diffracted γ-rays are not obstructed. To avoid air currents the crystal was enclosed by a cylindrical shield having two slits (covered with a very thin mica sheet) for the incident and the diffracted beams. This heating system for the crystal was quite satisfactory over the range of temperature up to about 700°K. The temperature was measured by two thermocouples fixed at the two ends of the crystal and the measurements showed a temperature gradient of not more than 2 to 3% even at the highest temperature measured. The temperature of the crystal could be kept at a constant value (within about 1% variation) for many hours by using a temperature-controller.

The measurements of elastic intensity were made for the two orders of reflexion 400 and 600 corresponding to Bragg angles of 17°49′ and 27°19′, respectively. For these high angle data extinction effects were assumed to be negligibly small. The NaCl crystal was first set for the reflexion 400 at the Bragg angle $\Theta=17°49'$ and the detector set at the corresponding scattering angle 2θ to receive the diffracted γ-rays. The resonant black-absorber was, of course, placed at the window of the detector. The intensity was then measured at different temperatures over the whole temperature range mentioned above. The variation of elastic intensity thus measured as a function of temperature of the crystal for the 400 and 600 Bragg reflexions is given in Fig. 2(*a*) and (*b*) on a logarithmic scale, where a strong non-linearity at high temperatures can be noticed. This markedly non-linear behaviour was also observed earlier in the case of KCl and Al single crystals (Butt & O'Connor, 1967), and it means a strong indication of large anharmonicity of the lattice dynamics. Our main aim here was to determine the non-quadratic terms in the Debye–Waller factor, which, to our knowledge, have not yet been observed for the NaCl structure. [Cubic terms arising in the case of fluorite structure observed recently are discussed in detail by Willis (1969).] Therefore, the data were processed so as to give the non-Gaussian contribution directly to the Debye–Waller factor.

Results and discussion

Neglecting the difference between the Debye–Waller factors of the alkali and halide ions, an approximation which for NaCl and KCl can be shown to lead to negligible error in this case, one has from the expression for the intensity

$$I(\mathbf{k}T)\sim|f(\mathbf{k}T)|^2\,,$$

after some algebra, the relation

$$\frac{1}{(k_1d)^2-(k_2d)^2}\times\left\{\frac{1}{(k_1d)^2}\log\frac{I(k_1T)}{I(k_1T_0)}-\frac{1}{(k_2d)^2}\log\frac{I(k_2T)}{I(k_2T_0)}\right\}=2(D(T)-D(T_0)) \tag{2}$$

where

$$D(T)=\tfrac{1}{24}\,\frac{\langle u_x^4\rangle_T-3\langle u_x^2\rangle_T^2}{d^4} \tag{3}$$

and $\mathbf{k}_1$ and $\mathbf{k}_2$ are two different angular positions, T and T_0, two different temperatures for the sample, x denotes the component along the parallel vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ pointing in our case into the [100] crystallographic direction, and d is the nearest neighbour distance in the lattice. In the following T_0 stands for room temperature. The simplest theoretical model still possessing the essential features of the situation envisaged here may be the following:

(i) the displacement correlation functions for the *harmonic* lattice

$$C^l_{xx'}(T)=\langle u^l_x u^0_{x'}\rangle_T \tag{4}$$

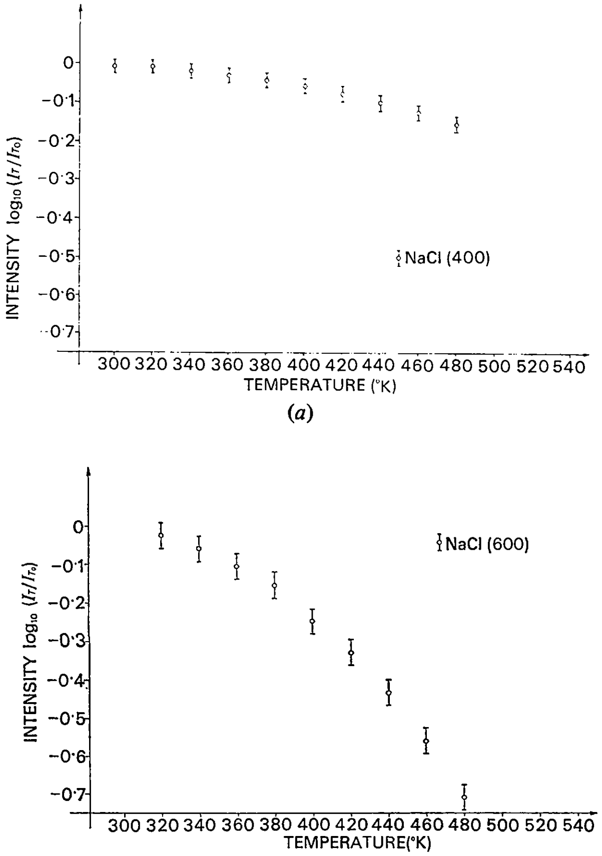
for two ions at different lattice sites $\mathbf{l}\neq0$ are determined entirely by the acoustic normal modes of the crystal;

(ii) in the *anharmonic* part of the Hamiltonian

$$H_A=\frac{1}{3!}\sum_{\substack{lmn\\\alpha\beta\gamma}}V^{\alpha\beta\gamma}_{lmn}u^l_\alpha u^m_\beta u^n_\gamma+\frac{1}{4!}\sum_{\substack{lmnp\\\alpha\beta\gamma\delta}}V^{\alpha\beta\gamma\delta}_{lmnp}u^l_\alpha u^m_\beta u^n_\gamma u^p_\delta \tag{5}$$

the coupling constants $V^{\alpha\beta\gamma}_{lmn}$, $V^{\alpha\beta\gamma\delta}_{lmnp}$ are derived from a pairwise nearest-neighbour interaction when they reduce to the form given by Leibfried & Ludwig (1961) in their Tables II-IV.

Assumption (i) would, of course, follow also from a lattice dynamical model where the difference between alkali and halide ions was completely ignored. However, it should be pointed out that while such a



(*a*)

(*b*)

Fig. 2. Purely elastic (zero-phonon) scattered intensity from NaCl at different scattering angles vs temperature (*a*) for the (400) and (*b*) for the (600) Bragg reflexions.

model would be an oversimplification of the actual physical situation, the assumption as stated above is still reasonable for the following reasons. Most generally, it is obvious from the explicit normal coordinate representation of the correlation function (*e.g.* Maradudin & Flinn, 1963) that the latter is, in fact, strongly biased by the small-frequency lattice modes, and the high-frequency (optical) range of the phonon spectrum is of small importance in determining this particular quantity. Moreover, the larger the distance $|\mathbf{l}|$ between the ions concerned, the better the expression for the asymptotics of $C^{l}_{xx'}$ (Flinn & Maradudin, 1962) works, which implies only frequencies near $q=0$ vanishing at the origin; thus, the large $|\mathbf{l}|$ behaviour of $C^{l}_{xx'}$ is entirely determined by the sound region. To complete the argument, one notices that, as discussed below, the asymptotics turns out to work quite well for any non-zero $\mathbf{l}$; therefore, with the use of an accurate value for $C^{0}_{xx'}$, the assumption (i) seems to be reasonably adequate. Assumptions (i) and (ii), together with the use of the asymptotic form for the displacement correlation function, not only provide a fairly simple way of calculating the quartic contribution to the Debye–Waller factor, but the relevance of the different physical parameters of the crystal becomes apparent in the final result. Though the asymptotic expansion of $C^{l}_{xx'}$ was studied in detail by Flinn & Maradudin (1962), the actual usefulness of such expressions in calculating anharmonic properties was emphasized only recently by Wolfe & Goodman (1969) in finding that the asymptotic formula 'works surprisingly well even for small $|\mathbf{l}|$', namely, for nearest-neighbour distance within 6% of accuracy.

Bearing this in mind, one starts from the general expression,

$$\left.\begin{aligned}
&D(T)=D_1(T)+D_2(T)\,,\\
&D_1(T)=\frac{1}{24d^4(k_BT)}\sum_{\substack{lmnp\\ \alpha\beta\gamma\delta}} V^{\alpha\beta\gamma\delta}_{lmnp}C^{l}_{\alpha x}C^{m}_{\beta x}C^{n}_{\gamma x}C^{p}_{\delta x}\\
&D_2(T)=-\frac{1}{8d^4(k_BT)^2}\sum_{\substack{lmn\alpha\beta\gamma\\ pqr\delta\mu\nu}}\\
&\qquad\times V^{\alpha\beta\gamma}_{lmn}V^{\delta\mu\nu}_{pqr}C^{l}_{\alpha x}C^{m}_{\beta x}C^{p}_{\delta x}C^{q}_{\mu\nu}C^{n-p}_{\gamma\nu}
\end{aligned}\right\}\qquad(6)$$

where the two terms represent the contributions from the fourth- and third-order anharmonic coupling, respectively. According to the discussion given above, one can use with reasonable accuracy the asymptotics of $C^{l}_{xx'}$ for any non-zero $\mathbf{l}$, which, neglecting the anisotropy of the (cubic) lattice, goes over into the isotropic continuum limit.

$$C^{l}_{xx'}(T)=\frac{k_BT}{4\pi C_{44}|\mathbf{l}|}\times\left\{\delta_{xx'}\left[1-\lambda\left(1-\frac{l_x^2}{|\mathbf{l}|^2}\right)\right]+(1-\delta_{xx'})\lambda\frac{l_xl_{x'}}{|\mathbf{l}|^2}\right\}\qquad(7a)$$

while for $\mathbf{l}=0$ one has

$$C^{0}_{xx'}(T)=2B(T)\delta_{xx'}\qquad(7b)$$

with $\lambda=(C_{12}+C_{44})/2C_{11}$, as expressed in terms of the elastic constants, and $B(T)$ is to be taken from an accurate model calculation as given by Buyers & Smith (1968). The error introduced by using this analytic form instead of the actual asymptotics turns out to be irrelevant in the light of the discussion given in the Appendix of the paper by Flinn & Maradudin, where it is shown, for example, that for $\mathbf{l}$ in the (100) direction, the exact and the continuum limit (7*a*) coincide exactly, while the anisotropy for other directions of $\mathbf{l}$ introduces a factor very close to unity. Though the calculation with the use of (7*a*) and (7*b*) is already straightforward, some other approximations of minor importance should be mentioned. Since for NaCl $\lambda=0\cdot255$, in the diagonal terms the term with λ was neglected. The commonly used approximation (*e.g.* Maradudin & Flinn, 1963) of keeping only the leading derivatives in calculating the third- and fourth-order coupling constants has also been made, in view of the short exponential decay of the anharmonic coupling.

Now using equations (6) and (7) and assumption (ii), one has for $D_1(T)$ and $D_2(T)$ the expressions

$$\begin{aligned}
D_1(T)&=\frac{\varphi^{\mathrm{IV}}\,.\,(k_BT)^3}{24(4\pi C_{44}d)^4d^4}\,[A_{xx}(b)+2\lambda^4A_{xy}]\\
D_2(T)&=-\frac{(\varphi^{\mathrm{III}})^2(k_BT)^3}{8(4\pi C_{44}d)^5d^4}\,[B_{xx}(b)+\lambda^3B_{xy}+\lambda^4E_{xy}]
\end{aligned}\qquad(8)$$

where φ^{III} and φ^{IV} are the third- and fourth-order derivatives of the anharmonic repulsive potential taken at the nearest-neighbour distance or, slightly more generally, the constants α_1' and α_1'' of Leibfreid & Ludwig (1962). The dimensionless numbers, A_{xy}, B_{xy} and E_{xy}, are simple lattice sums as defined in the Appendix; the similar quantities $A_{xx}(b)$, $B_{xx}(b)$ depend also on the value

Table 1. *Lattice dynamical data for* NaCl

C_{11} (erg.cm^{-3})	C_{12} (erg.cm^{-3})	C_{44} (erg.cm^{-3})	$\tilde{\varphi}^{\mathrm{III}}$ (erg.cm^{-3})	$\tilde{\varphi}^{\mathrm{IV}}$ (erg.cm^{-4})	d (cm)	Θ_0 (°K)	b
$4\cdot91\times10^{11}$*	$1\cdot22\times10^{11}$*	$1\cdot28\times10^{11}$*	$-1\cdot41\times10^{13}$†	$0\cdot44\times10^{22}$†	$2\cdot78\times10^{-8}$†	325†	$2\cdot21\pm0\cdot03$‡

* Leibfried (1955)
† Leibfried & Ludwig (1961)
‡ Buyers & Smith (1968)

$$b=\frac{C^0_{xx}(T)}{C^{n-n}_{xx}(T)}$$

where $n-n$ means nearest-neighbour distance; the numerator is the calculated value given by Buyers & Smith (1968). It is now easy to understand why the effect can be expected to be quite significant in the case of most alkali halides, in particular, for NaCl. Besides the structure-dependent lattice sums and the essentially atomic characteristics $V^{\alpha\beta\gamma}_{lmn}$, $V^{\alpha\beta\gamma\delta}_{lmnp}$ the quantity $D(T)$ also contains as a factor a high power of the inverse shear modulus C_{44}, which is very small for this case. The reason why precisely the shearing motion of the lattice is essential to build up correlation between ionic displacements is simple. Taking any general direction of **l**, one sees that only those waves with wave-vector orthogonal to this direction contribute to the correlation function; the shifts caused by waves going parallel to **l** sum up to zero.

The lattice dynamical parameters needed in the present calculations are tabulated in Table 1. Using the data of Table 1, it is easy to reduce the expression (8) to the form

$$D_1(T)=\frac{\varphi^{\rm IV}}{\tilde\varphi^{\rm IV}}\left(\frac{T}{\Theta_0}\right)^3 0{\cdot}673\times10^{-8}(A_{xx}(b)+0{\cdot}008A_{xy})$$

$$D_2(T)=-\left(\frac{\varphi^{\rm III}}{\tilde\varphi^{\rm III}}\right)^2\left(\frac{T}{\Theta_0}\right)^3 \times 2{\cdot}08\times10^{-8}(B_{xx}(b)+0{\cdot}01B_{xy}+0{\cdot}004E_{xy}) \qquad (9)$$

where Θ_0 is the Debye temperature from elastic data used merely as a temperature unit and $\tilde\varphi^{\rm III}$ and $\tilde\varphi^{\rm IV}$ are the anharmonic coupling constants of Leibfried & Ludwig (1961) inferred from a phenomenological fitting procedure. Keeping only the leading terms connected with A_{xx} and B_{xx} and using the values 4·54 and 7·09, respectively, for these constants, as computed directly, one has from (3) and (9) for

$\mathbf{k}_1=\frac{2\pi}{d}(300)$ and $\mathbf{k}_2=\frac{2\pi}{d}(200)$ the result as

$$D(T)-D(T_0)=\frac{1}{32\pi^4}\cdot\frac{1}{s}\times\left\{\frac{1}{9}\log\frac{I(300,T)}{I(300,T_0)}-\frac{1}{4}\log\frac{I(200,T)}{I(200,T_0)}\right\}=\alpha\left(\frac{T}{\Theta_0}\right)^3-\left(\frac{T_0}{\Theta_0}\right)^3 \qquad (10a)$$

with

$$\alpha=\left[3{\cdot}06\frac{\varphi^{\rm IV}}{\tilde\varphi^{\rm IV}}-14{\cdot}72\left(\frac{\varphi^{\rm III}}{\tilde\varphi^{\rm III}}\right)^2\right]\times10^{-8}. \qquad (10b)$$

The experimental results are plotted in Fig. 3. As it is seen, the functional dependence of $D(T)-D(T_0)$ *vs.* $(T/\Theta_0)^3-(T_0/\Theta_0)^3$ is reasonably linear. Deviation from linearity is seen at the smaller temperature region where, of course, the linearity of C^l_{xx} in T becomes less and less valid. For the case of $\varphi^{\rm III}=\tilde\varphi^{\rm III}$, $\varphi^{\rm IV}=\tilde\varphi^{\rm IV}$ one has $\alpha=\alpha_{LL}=-1{\cdot}17\times10^{-7}$ where the subscript refers to Leibfried & Ludwig's estimate. The value deduced from the present data is also negative but much higher, $\alpha_{\rm ex}=-2{\cdot}4\times10^{-6}$, suggesting an anharmonic coupling constant $\varphi^{\rm III}$ much larger than estimated earlier. As to $\varphi^{\rm IV}$, one sees from (10*b*) that it plays a less important role in determining α, due to its small numerical coefficient. (The corresponding effect can also be seen in Wolfe & Goodman's Table VIII.) For an estimate, therefore, one can assume $\varphi^{\rm IV}/\tilde\varphi^{\rm IV}=\varphi^{\rm III}/\tilde\varphi^{\rm III}$ which, by use of (10*b*) gives the experimental value for $\varphi^{\rm III}$ as

$$\varphi^{\rm III}_{\rm ex}=4{\cdot}2\tilde\varphi^{\rm III}=-5{\cdot}92\times10^{13}\ {\rm erg.cm^{-3}}. \qquad (11)$$

The ratio $\varphi^{\rm IV}/\tilde\varphi^{\rm IV}$ remains uncertain for the numerical reasons mentioned above; it does not, however, influence appreciably the estimate for $\varphi^{\rm III}$. Bearing in mind the rather indirect way by which the values $\tilde\varphi^{\rm III}$, $\tilde\varphi^{\rm IV}$ were determined, the above result seems not unreasonable. As to the accuracy of this result, one has to note that the simplifications in the theoretical treatment are expected to lead to an error probably not higher than that due to the uncertainty of about 10% in the experimental value of the slope. Since, however, the quartic term itself is relatively small, it is not impossible that extinction effects normally negligible at these scattering angles are responsible, at least by part, for the observed disagreement in $\varphi^{\rm III}$ expressed by (11).

Though refining the calculations does not represent any essential difficulty, at the present stage when one has essentially one parameter measured, the simple treatment given above seemed to us to be appropriate.

Conclusions

The method of Mössbauer diffractometer technique which enables the separation of the inelastic contributions from the elastic (zero-phonon) diffracted intensity was used to investigate anharmonic

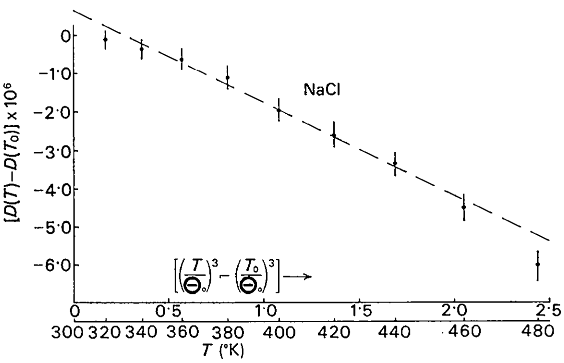


Fig. 3. Deviation from the Gaussian form of the Debye–Waller factor *vs.* temperature as deduced from the experiments. $T_0=300\,°K$. Zero slope would correspond to Gaussian behaviour.

properties of NaCl. The deviation from the Gaussian of the Debye–Waller factor between 300–500 °K was measured by using data for the two reflections (400) and (600). In the frame of a simple theoretical treatment based on the asymptotic form of the harmonic displacement correlation functions, explicit expressions for the quartic term $D(T)$ are given by equations (8) to (10) showing its dependence on the lattice dynamical parameters, in particular on the shear modulus C_{44} and the third and fourth order anharmonic coupling constants. Incidentally, it turns out that in determining $D(T)$, the constant $\varphi^{\rm III}$ plays a decisive role while the dependence on $\varphi^{\rm IV}$ is less important. It is shown that by using *only relative intensity data* for different reflexions and temperatures, the quartic term can be determined from the measurements. The theoretical estimate based on Leibfried and Ludwig's coupling constants leads to $\alpha = -1{\cdot}17 \times 10^{-7}$ which in itself is, in fact, large enough to be observed by using higher-order reflexions and a wide range of temperatures. On the other hand, the present experiments gave a much larger value $\alpha_{\rm ex} = -2{\cdot}4 \times 10^{-6}$, and to explain it one is led to assume $\varphi^{\rm III}$ to be about four times are large as Liebfried & Ludwig's result. Though such value seems to be very high, one should note the somewhat different approximations used in the two cases and also the rather direct way in which $\varphi^{\rm III}$ can be reduced from the observed value of $D(T)$. On the other hand, considering the serious difficulties envisaged in measuring such a delicate effect, repeated measurements at three or more higher-order reflexions would be desirable, since from that set of data one would be able to check the consistency of the results by choosing different pairs of reflexions to obtain $D(T)$.

The theoretical treatment can be generalized by including short-range interactions beyond nearest neighbours and also using the still asymptotic but more accurate, though more implicit, expressions (Flinn & Maradudin, 1962) for the displacement correlation function, accounting for the proper anisotropy of the lattice. In a more refined treatment one should also take into account the difference between the temperature factors for the two kinds of ions. As is shown easily, ignoring that difference leads to a spurious quartic term proportional to the square of the difference between the *quadratic* parts of the individual Debye–Waller factors. The magnitude of this term, however, is much smaller than the actual quartic term due to anharmonicity. This is so for the temperature factors given by Buyers & Smith (1968) or those by Gottlicher (1968). Yet, the large scatter between these two sets of data indicates a basic uncertainty of available data as far as this difference is concerned, and if it is actually larger than found by Gottlicher, the spurious quartic term may be quite large.

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APPENDIX

The lattice sums $A_{\alpha\beta}$ and $B_{\alpha\beta}$, are given as

$$A_{\alpha\beta} = 2\sum_{l}\{(c^{l}_{\alpha\beta})^3 - 3(c^{l}_{\alpha\beta})^2 c^{l+a}_{\alpha\beta} + 3(c^{l}_{\alpha\beta})^2(c^{l+a}_{\alpha\beta})^2 - (c^{l+a}_{\alpha\beta})^3\}c^{l}_{\alpha\beta}$$

$$B_{\alpha\alpha} = 2\sum_{ll'}(c^{l+a}_{\alpha\alpha} - c^{l}_{\alpha\alpha})^2(c^{l'+a}_{\alpha\alpha} - c^{l'}_{\alpha\alpha})^2(c^{l-l'}_{\alpha\alpha} - c^{l-l'}_{\alpha\alpha})$$

where the dimensionless quantities c^l are defined by

$$C^{l}_{xx'}(T) = \frac{k_B T}{4\pi C_{44} d}\, c^{l}_{xx'}$$

and **a** means the vector (100).

Similar expressions define $B_{\alpha\beta}$ and $E_{\alpha\beta}$, $\alpha \neq \beta$. One notices that the expressions are equivalent to those given by Wolfe & Goodman (1969) except for the explicit form of C^{l}_{xy} given by (7).

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