

Anharmonic Non-Gaussian Contribution to the Debye–Waller Factor. II. KCl

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(Received 2 October 1972; accepted 23 October 1972)

Mössbauer γ -ray diffraction data obtained by the technique of O'Connor & Butt [*Phys. Lett.* (1963), 7, 233–235] are analysed to deduce the anharmonic fourth-order term in the Debye–Waller factor for KCl and to estimate the third-order anharmonic coupling constant in this way. The theoretical treatment assumes that the displacement correlation function can be approximated by its large-distance asymptotic value. For the anharmonic coupling parameter ϕ^{111} an estimate of -6.2×10^{13} erg cm $^{-3}$ is found, which differs by a factor of about 6 from that given previously by Leibfried & Ludwig.

Introduction

Departure from the Gaussian shape of the Debye–Waller factor as a function of $\sin \theta/\lambda$ is one of the most prominent effects of lattice anharmonicity since it shows the limits of even the best quasi-harmonic approximation. Such deviation from the Gaussian appears, for cubic crystals, through the fourth (and higher) powers of $\sin \theta/\lambda$ in the exponent of the Debye–Waller factor. In a previous paper (Butt & Solt, 1971) a simple theoretical treatment was presented for calculating the quartic non-Gaussian term, and it was applied to experimental results on NaCl. It was shown that by using accurate *elastic* diffraction intensity data for different scattering angles within a wide temperature range, direct information on the anharmonic coupling constants can be obtained. Since a somewhat detailed discussion can be found in the above reference, here only some essential points of the theoretical model will be mentioned. The γ -ray diffraction peak intensity at momentum transfer \mathbf{k} ($|\mathbf{k}| = 4\pi \cdot \sin \theta/\lambda$) is given by‡

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

where the Debye–Waller factor $f(\mathbf{k}, T)$ defined through the ionic displacement vector \mathbf{u} can be expressed as

$$f(\mathbf{k}, T) = \langle \exp \{i\mathbf{k} \cdot \mathbf{u}\} \rangle_T = \exp \left\{ -\frac{1}{2} \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle_T + \frac{1}{24} [\langle (\mathbf{k} \cdot \mathbf{u})^4 \rangle_T - 3 \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle_T^2] + O(k^6) \right\}. \quad (1)$$

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‡ The difference between the Debye–Waller factors of the different kinds of ions is, for the present purpose, assumed to be negligible. This was seen to be irrelevant even for NaCl; thus for KCl the difference for form factors can safely be ignored. The notation $\langle \rangle_T$ means thermal average at temperature T .

To evaluate the quartic term the following two assumptions have been used:

- (i) In the *harmonic* lattice, the displacement correlation function for two ions at different sites is entirely determined by the acoustical sound waves;
- (ii) Anharmonic forces can be represented by nearest-neighbour central interactions.

This treatment is, in fact, a simplified version of that given by Wolfe & Goodman (1969) though with the advantage that some of the relevant physical parameters enter here in a more explicit way. The experiments were performed by the Mössbauer γ -ray diffraction technique (O'Connor & Butt, 1963) which allows measurement of the strictly elastic component of the diffraction intensity.

The main result of this work is that the experimentally observed quartic term for KCl shows, in fact, the expected behaviour as a function of temperature between 293 and 523°K, though with a much higher amplitude than could be expected on the basis of previous estimates for the anharmonic coupling constants. This result is thus completely analogous to that obtained in the foregoing work for NaCl.

Results

The present analysis has been focused on the $|\mathbf{k}|^4$ term in the exponent of $f(\mathbf{k}, T)$, which is completely absent when a harmonic or quasi-harmonic description for the lattice vibrations applies. In the present case, with \mathbf{k} pointing in the [100] direction, the quantity of interest is therefore

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

For this, one has the approximation expression (Butt & Solt, 1971)

$$D(T) = \frac{(k_B T)^3}{8(4\pi C_{44} d)^4} \left[\frac{\phi^{1V}}{3} A_{xx}(b) - \frac{(\phi^{111})^2}{4\pi C_{44} d} B_{xx}(b) \right] \quad (3)$$

where T is the absolute temperature, u_x is the ionic displacement in the [100] direction, d is the nearest-neighbour distance at $T=0$, C_{44} is the conventional notation for the shear modulus, φ^{III} and φ^{IV} are the third and fourth derivatives of the repulsive interaction potential and $A_{xx}(b)$ and $B_{xx}(b)$ are simple lattice sums (Butt & Solt, 1971) determined by the structure and depending only on the quantity

$$b = \frac{\langle u_x^2 \rangle_T}{\langle u_x^{(nn)} u_x \rangle_T}$$

where in the denominator one has the displacement correlation function for nearest-neighbour ions. Using the value of Buyers & Smith (1968) for $\langle u_x^2 \rangle_T$ one gets $b = 1.36 \pm 0.02$, and this gives for the lattice sums A_{xx} and B_{xx} the values 0.37 and 0.40 respectively. Using

then the data $C_{44} = 0.63 \times 10^{11}$ erg. cm $^{-3}$ (Leibfried, 1955) and $d = 3.11$ Å (Leibfried & Ludwig, 1961) one comes up with the expression

$$D(T) = \left\{ \frac{\varphi^{\text{IV}}}{\tilde{\varphi}^{\text{IV}}} 0.12 - \left(\frac{\varphi^{\text{III}}}{\tilde{\varphi}^{\text{III}}} \right)^2 1.33 \right\} 1.78 \times 10^{-8} \left(\frac{T}{\Theta_0} \right)^3$$

where the quantities $\tilde{\varphi}^{\text{III}} = -0.95 \times 10^{13}$ erg cm $^{-3}$, $\tilde{\varphi}^{\text{IV}} = 0.11 \times 10^{22}$ erg cm $^{-4}$ and $\Theta_0 = 257^\circ\text{K}$ have been introduced as appropriate scaling units, being actually the calculated values of Leibfried & Ludwig (1961) for Debye temperature and anharmonic coupling parameters.

On the other hand, the quantity to be measured is the strictly elastic part of the diffraction peak intensity $I(\mathbf{k}, T)$ at different temperatures T and different reflexions klm . If one has, e.g., data for the $k_1 = 200$ and $k_2 = 400$ reflexions at room temperature T_0 and at other points T , by simple algebra one gets for the anharmonic part

$$\begin{aligned} [D(T) - D(T_0)] &= \frac{1}{2} \left\{ \frac{1}{(k_1 d)^2 - (k_2 d)^2} \right. \\ &\times \left[\frac{1}{(k_1 d)^2} \log \frac{I(k_1, T)}{I(k_1, T_0)} - \frac{1}{(k_2 d)^2} \log \frac{I(k_2, T)}{I(k_2, T_0)} \right] \left. \right\} \\ &= \frac{1}{32\pi^4} \frac{1}{3} \left[\frac{1}{4} \log \frac{I[(400), T]}{I[(400), T_0]} - \log \frac{I[(200), T]}{I[(200), T_0]} \right]. \quad (4) \end{aligned}$$

To determine the strictly elastic part of the peak intensity, the Mössbauer γ -ray diffraction technique (O'Connor & Butt, 1963; Butt & O'Connor, 1967) seems to be extremely well adapted, since inelastic contributions are not present even in the rough data. Some details of the Mössbauer diffraction set-up used for obtaining the present data were given in the previous paper (Butt & Solt, 1971) and here only the results for KCl are discussed. In Fig. 1(a) and (b) the intensity $I(\mathbf{k}, T)$ is plotted at two reflexions *versus* temperature, while Fig. 2 shows the exponent of the Debye-Waller factor divided by $(k/4\pi)^2 = (\sin \theta/\lambda)^2$. In harmonic or quasi-harmonic approximation the two curves should coincide, both giving $16\pi^2 \{ \langle u_x^2 \rangle_{T_0} - \langle u_x^2 \rangle_T \}$ and the difference represents precisely the non-Gaussian behaviour of the Debye-Waller factor. (One notices that, at these temperatures, the deviation of the curves from the straight line itself is an effect of anharmonicity, but this can be described at least partly within the frame of a quasiharmonic theory.) Finally, Fig. 3 shows $[D(T) - D(T_0)]$, as processed from the data according to (4), *versus* $(T/\Theta_0)^3$. It is difficult to check accurately the predicted linearity since the statistical uncertainties (of about 1–2%) are, especially for the 200 reflexion, considerably blown up by the small value of $(\sin \theta/\lambda)^2$ in the final result. (The same can also be seen in Fig. 2.) Comparison with the theory can be made by determining the slope of the line in Fig. 3, which for the above reasons is obviously difficult, and the approxi-

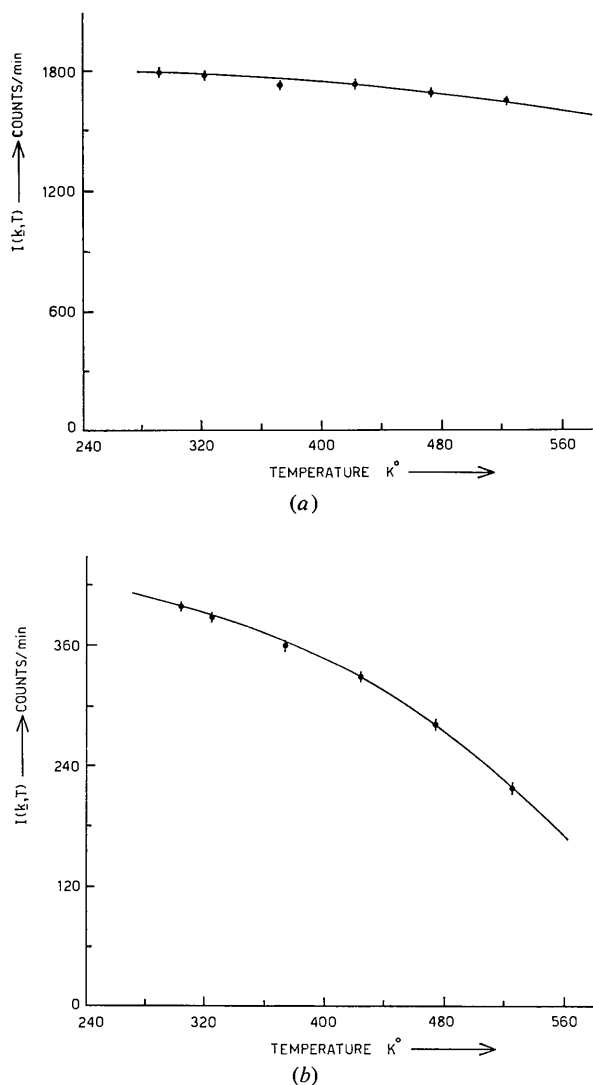


Fig. 1. Elastic (zero-phonon) scattered intensity $I(\mathbf{k}, T)$ from KCl at different scattering angles *versus* temperature: (a) for the 200 reflexion; (b) for the 400 reflexion.

mate value of $-1.0 \pm 0.4 \times 10^{-6}$ is rather uncertain. One can go still further and estimate the anharmonic force constant φ^{III} by assuming that $\varphi^{III}/\bar{\varphi}^{III}$ and $\varphi^{IV}/\bar{\varphi}^{IV}$ are of the same order of magnitude and therefore

$$D(T) \simeq - \left(\frac{\varphi^{III}}{\bar{\varphi}^{III}} \right)^2 2.374 \times 10^{-8} \left(\frac{T}{\theta_0} \right)^3$$

which leads to

$$\varphi^{III} \simeq (6.5 \pm 1.5) \bar{\varphi}^{III} = -(6.2 \pm 1.4) \times 10^{13} \text{ erg cm}^{-3}.$$

Owing to the small numerical coefficient before $\varphi^{IV}/\bar{\varphi}^{IV}$, that ratio is almost completely uncertain and, in turn, it plays a much less important role in this anharmonic term. The final result is very similar to that obtained for NaCl, where the estimate of φ^{III} has given 4.2 times the value found by Leibfried & Ludwig (1961).

As to the accuracy of the above values, one should mention that, in addition to the statistical errors already discussed, no extinction effects were accounted for in the data processing. This was already noted in connexion with the results for NaCl (Butt & Solt, 1971) and the corresponding error should obviously be greater here where no data for the 600 reflexion were available and we had to use those for the 200 reflexion. Therefore, to check the above values, experiments at higher-order reflexions are required, the need for these being indicated already by the 200 data for NaCl which seemed not to be accurate enough for a similar discussion.

Conclusion

The temperature dependence of the fourth-order anharmonic term $D(T)$ in the Debye-Waller factor for KCl was theoretically estimated and was measured within the range 293–523 °K. The experimental data seem to show the predicted trend, though the amplitude of the variation with temperature is much larger than expected. As a consequence, the third-order anharmonic coupling constant obtainable from the present data turns out – within a statistical accuracy of approximately 25% – to be about six times as large as that predicted by Leibfried & Ludwig. The disagreement, or at least part of it, may be connected with experimental uncertainties like statistical errors and neglect of extinction effects.

Still, the very fact that, just as for NaCl, though by using different reflexions, the ratio $\varphi^{III}/\bar{\varphi}^{III}$ for KCl was also found to be much larger than unity, indicates that the departure from the results of Leibfried & Ludwig (1961) may be a real one. If this is the case, one has, of course, to choose between the two sets of values for φ^{III} and also explain why they differ from each other so greatly. In this connexion, besides emphasizing again the need for further experimental work to test accurately the values given above, we may mention that the present method, principally, seems to be one of the simplest and most direct ways of determining the anharmonic coupling coefficients.

Two of the authors (NMB and GS) are indebted to Professor Abdus Salam, Professor P. Budini, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics and to the Swedish International Development Authority for financial support. They are grateful to Professors I. Waller and S. Lundqvist for valuable discussions. NMB takes pleasure in acknowledging the hospitality and kindness of Professor P. B. Moon during the experimental part of this work at Birmingham University. GS is grateful to the Central Research Institute for Physics of the Hungarian Academy of Sciences and NMB to the Pakistan Atomic Energy Commission for leave of absence.

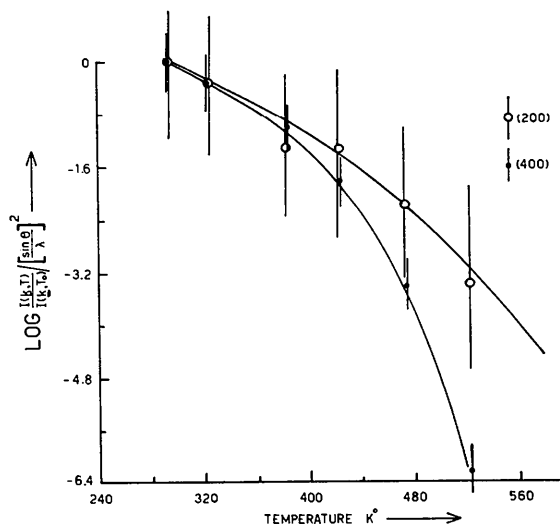


Fig. 2. The quantity $\log [I(\mathbf{k}, T)/I(\mathbf{k}, T_0)]/(\sin \theta/\lambda)^2$ versus temperature for the 400 and 200 reflexions. For harmonic or quasiharmonic lattice vibrations both curves give $16\pi^2 \{ \langle u_x^2 \rangle_{T_0} - \langle u_x^2 \rangle_T \}$ and should therefore coincide.

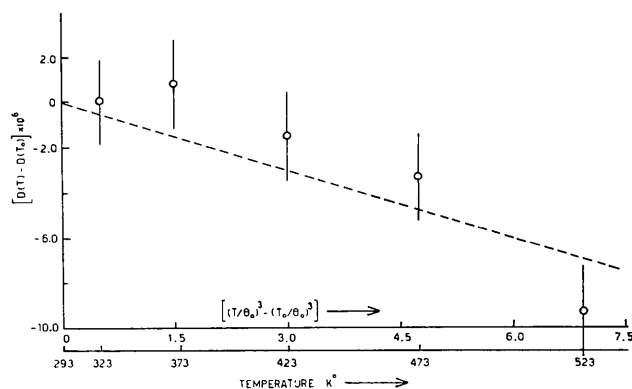


Fig. 3. Deviation from the Gaussian form of the Debye-Waller factor versus temperature as deduced from the experiments. $T_0 = 293$ °K. Zero slope would correspond to Gaussian behaviour.

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On the Application of Phase Relationships to Complex Structures. V. Finding the Solution

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(Received 23 August 1972; accepted 27 September 1972)

Multiresolution direct methods for solving crystal structures lead to many plausible sets of phases and some means of determining the correct set is necessary. For centrosymmetric structures, figures of merit are usually quite discriminating and the examination of only one or two E maps is necessary. For non-centrosymmetric structures, figures of merit are unreliable and the necessity of examining a large number of E maps can sometime prove to be an almost insuperable obstacle to finding the correct structure. A procedure is described for overcoming this difficulty. The Cooley–Tukey fast-Fourier-transform technique is used to compute E maps and all peaks greater than a certain height are located. A selection of the highest of these peaks, whose number is chosen by the program user, is then analysed with respect to bond lengths and angles. Favourable projections of coherent groups of peaks are output on the line printer in the form of integers representing the ranking order of the peaks and in positions which represent an undistorted projection of the group. Computing time is of the order of one minute per set of phases and the examination of a set of 32 maps and finding the correct solution takes about 30 minutes.

Figures of merit

Some direct methods of solving crystal structures systematically produce a large number of plausible sets of phases (*e.g.* Germain & Woolfson, 1968) but even when a unique solution is sought ambiguities in phase determination are encountered which lead eventually to a multiresolution situation. In such cases it is the normal practice to use various figures of merit to rank the solutions in order of plausibility and then to examine the E maps in ranking order until the correct solution is found.

The correctness, or otherwise, of an E map would be judged by the presence of reasonably related groups of peaks which could be interpreted in terms of the expected chemistry of the material. To examine the three-dimensional E map the usual procedure is to draw contours of sections on sheets of glass or transparent plastic material and to view a stack of the sheets. Even then the interpretation of the map is complicated by the fact that a single molecule or other coherent

structural unit may appear in fragments in various parts of the contoured region.

It is a matter of experience that figures of merit are quite good for indicating the correct set of signs for centrosymmetric structures – normally one need examine no more than two or three maps – but the situation is very much worse with non-centrosymmetric structures. Various figures of merit have been used, for example the ‘absolute figure of merit’ (Germain, Main & Woolfson, 1971), R_{Karle} (Karle & Karle, 1966) and the zero check (Cochran & Douglas, 1957). For particular structures one or other of these may turn out to be more discriminating than the other two but often none of them is reliable and the correct set of phases may be well down in the ranking order.

The automatic interpretation of E maps

With the availability of the Cooley–Tukey fast Fourier transform algorithm it is feasible to compute a large number of E maps – for an average structure and with