

Debye–Waller Factors of KBr at 4.2 and 295 K

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The Debye–Waller factors of KBr have been determined both by X-ray and by neutron diffraction methods. Previous experiments have been carried out at or above room temperature. No such measurements have been reported at 4.2 K. Neutron diffraction experiments on a KBr powder at 295 and 4.2 K are reported here. The experimental results obtained were $B_K = 2.55 \pm 0.07$, $B_{Br} = 2.20 \pm 0.04 \text{ \AA}^2$ at $T = 295 \text{ K}$, and $B_K = 0.43 \pm 0.05$, $B_{Br} = 0.35 \pm 0.02 \text{ \AA}^2$ at 4.2 K. These values differ from the theoretical estimates of Reid & Smith [*J. Phys. Chem. Solids* (1970), **31**, 2689–2697], based on a quasiharmonic approximation using the shell model. The discrepancy may be attributed to the partial neglect of anharmonicity in the theoretical estimates.

Introduction

The thermal parameters of KBr have been studied by several workers using X-ray diffraction (Meisalo & Inkinen, 1967) and neutron diffraction (Pryor, 1966; Atoji, 1972; Bacon, Titterton & Walker, 1973). Measurements using powder as well as single crystals have been made. Powder neutron diffraction experiments have been done only at room temperature (Pryor, 1966; Atoji, 1972) while no experiments have been reported at 4.2 K. Also, there is considerable disagreement between different experimentalists on the values of the thermal parameters even at room temperature; moreover, some of the measurements are not particularly accurate.

Several uncertainties and possible approximations are involved in room-temperature experimental studies. Two important ones are due to thermal diffuse scattering (TDS) and anharmonic contributions to the Debye–Waller factors. The agreement between the theoretical estimates (Reid & Smith, 1970) and the experimental values (Pryor, 1966; Atoji, 1972) is therefore not completely satisfactory (Table 1).

At low temperature both TDS and anharmonic effects are less important, and therefore it may be more appropriate to make a comparison between experimental determinations and the theoretical estimates at such temperatures.

In the present work the Debye–Waller factors of KBr have been determined at 4.2 K by powder neutron diffraction on a high-resolution two-axis neutron diffractometer. We have also made room-temperature powder measurements using this instrument and report

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Table 1. *The room-temperature B values for KBr*

$B_K (\text{\AA}^2)$	$B_{Br} (\text{\AA}^2)$	Method†	Reference
2.55 ± 0.07	2.20 ± 0.04	Neutron P	Present work (1975)*
2.45 ± 1.5	2.23 ± 1.5	X-ray P	Meisalo & Inkinen (1967)*
2.39 ± 0.05	2.36 ± 0.05	Neutron SC	Bacon, Titterton & Walker (1973)
2.20 ± 0.10	2.28 ± 0.10	Neutron SC	Pryor (1966)*
2.17 ± 0.30	2.67 ± 0.30	Neutron P	Pryor (1966)*
2.60 ± 0.20	2.50 ± 0.20	Neutron P	Atoji (1972)
2.26	2.55	Calculated from 300 K data of physical constants	Pryor (1966)
2.17	2.20	Theory	Buyers & Smith (1968)
2.26	2.46	Theory	Reid & Smith (1970)

* TDS corrected.

† P powder sample, SC single-crystal sample.

results of better accuracy than those reported earlier (Pryor, 1966; Atoji, 1972). Similar experiments for NaCl at room temperature and at 4.2 K have already been published (Butt, Cheetham & Willis, 1973).

Experiment

The diffraction patterns at both temperatures were obtained on the high-resolution two-axis diffractometer PANDA installed at the Harwell PLUTO reactor. The measurements at 4.2 K were made at a neutron wavelength of 1.28 Å using a Ge(511) monochromator at a take-off angle of 70°. The room-temperature measurements were made at a neutron wavelength of 0.954 Å using a Cu(311) monochromator at a take-off angle of 55°.

The data were collected using a bank of three BF₃ detectors. The integrated intensities for most of the reflections had a statistical accuracy of better than 1%. The neutron scattering lengths for K and Br used for calculating the intensities of reflections were those compiled by the Neutron Diffraction Commission of the International Union of Crystallography (Bacon, 1972).

Data analysis and results

For the room-temperature experiment the observed intensities were corrected for TDS by the method of Chipman & Paskin (1959) developed for X-rays. This method could be used because the neutron wavelength used in the experiment was such that the neutron velocity in KBr was larger than the elastic-wave velocity in this material (Willis, 1970).

In the case of a cubic powder the correction due to TDS is given by (Chipman & Paskin, 1959)

$$\sigma = \left(\frac{\pi}{3}\right)^{1/3} aB \left(\frac{\sin \theta}{\lambda}\right)^2 (\cos \theta) \frac{A}{\lambda},$$

where a = lattice parameter, B = Debye-Waller parameter, λ = neutron wavelength, θ = Bragg angle, $A(2\theta)$ = base width (rad) of a Bragg peak. If I_o is the observed integrated intensity (corrected for background), the TDS-corrected intensity is given by

$$(I_o/1 + \sigma).$$

For estimating σ for many reflections we used $\frac{2}{3}$ of the value of B as discussed by Suortti (1967). The data were analysed using the Harwell TAILS computer program (Rouse, 1977) for refining a scale factor and two isotropic harmonic temperature factors. The observed (I_o) and calculated (I_c) intensities in these experiments along with the factor $R = \sum(I_o - I_c)/\sum I_o$ are given in Tables 2 and 3.

Table 2. *The observed and calculated intensities at room temperature*

$$\lambda = 0.954 \text{ \AA}, a = 6.578 \text{ \AA}.$$

hkl	I_o	I_{cal}	σ
1 1 1	9020	8712	0.006
2 2 0	49123	49134	0.021
4 0 0	10313	10135	0.036
3 3 1	3251	3093	0.026
4 2 0	29143	29475	0.047
4 4 0	7153	6926	0.053
5 3 1	2397	2516	0.036
6 0 0/4 4 2	14019	14005	0.037
6 2 2	7566	7599	0.061
4 4 4	2391	2115	0.056
6 4 0	5397	5339	0.070
6 4 2	8887	9040	0.074

$$R = 0.012$$

Table 3. *The observed and calculated intensities at 4.2 K*

$$\lambda = 1.28 \text{ \AA}, a_0 = 6.526 \text{ \AA}.$$

hkl	I_o	I_c
2 0 0	29279	29507
2 2 0	29381	29589
3 1 1	4141	3807
2 2 2	13287	13198
4 0 0	7741	7458
4 2 0	24093	24000
4 4 0	9975	7683
5 3 1	2821	2591
6 0 0/4 4 2	16991	17260
6 2 0	12895	12586
6 2 2	11900	11610
5 5 1	1688	1936
6 4 0	9943	10187
6 4 2	19271	19348
7 3 1/5 5 3	2613	2660

$$R = \sum(I_o - I_c)/\sum I_o = 0.017$$

Discussion

The results obtained at 4.2 K agree with those calculated by Reid & Smith (1970) in that the bromide anion has a smaller mean-square amplitude of vibration, $\langle U_{Br}^2 \rangle$, than that of the lighter potassium cation $\langle U_K^2 \rangle$. The calculated ratio $\langle U_{Br}^2 \rangle / \langle U_K^2 \rangle$ at 5 K is 0.78, and is found experimentally to be 0.80. In absolute terms our values are close to those calculated by Reid & Smith at 35 K. This small difference may reflect the fact that the calculation is based on an extrapolation or possibly that an anharmonic potential is necessary even at this low temperature (Barron, 1965). At temperatures near or above the Debye temperature (high-temperature limit) the B value should become independent of the mass (Jex, Müllner & Dyck, 1974) and depend only on the power of the potential. In the case of a nearest-neighbour potential the B values should be

Table 4. Comparison of experimental B values of KBr at 4.2 and 295 K with the theoretical values of Reid & Smith (1970)

Temperature	Present experiments				Theory (Reid & Smith 1970)	
	Uncorrected B_K (\AA^2)	TDS corrected B_K (\AA^2)	Uncorrected B_{Br} (\AA^2)	TDS corrected B_{Br} (\AA^2)	B_K (\AA^2)	B_{Br} (\AA^2)
295 K	2.45 ± 0.07	2.55 ± 0.07	2.12 ± 0.04	2.20 ± 0.04	2.26	2.46
4.2 K	0.431 ± 0.05		0.35 ± 0.02		0.350	0.272

the same for the NaCl structure (Groenewegen & Huiszoon, 1972; Huiszoon & Groenewegen, 1972). It is interesting to note that the calculated values of Reid & Smith, using the shell model in the quasiharmonic approximation near 125 K, also show this behaviour. Above this temperature the calculations suggest that the lighter ion has the smaller thermal motion. However, the measured values at 295 K (Table 4) disagree slightly in that the bromide anion has a somewhat smaller B value than the cation. This has also been reported by other authors (see Table 1). The explanation could be that additional anharmonic effects, perhaps including a Q^4 term in the analysis, should be incorporated in the calculation.

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Intermolecular Interactions in Crystals of Carboxylic Acids. IV. Empirical Interatomic Potential Functions

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An intermolecular force field for carboxylic acids has been derived by a least-squares fit of the parameters of non-bonded atom–atom potentials and a hydrogen-bond potential to experimental data. The latter include heats of dimerization and dimer structures of formic, acetic and propionic acid, and heats of sublimation and crystal structures of acetic, α and β -oxalic, α and β -fumaric and isophthalic acid. It was found that (exp – 6 – 1) atom–atom potentials and the Lippincott–Schroeder potential for the hydrogen bonds reproduce fairly well the experimental energies as well as the structures. The transferability of the potentials was studied with respect to the crystal structure of allene dicarboxylic acid and to the crystal structure and the lattice energy of formic acid, and was found to be good. A comparison is made with the results of other authors.