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A Neutron Diffraction Study of KCl

By M. J. Cooper and K. D. Rouse

Materials Physics Division, A.E.R.E., Harwell, Berkshire, England

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Accurate integrated intensities for the Bragg reflexion of neutrons by a single crystal of KCl have been measured at room temperature (295 ± 2°K). Measurements were made at a number of wavelengths and corrections were made for extinction and thermal diffuse scattering. The experimental data were analysed in terms of models which include both harmonic and anharmonic components in the thermal vibration of the ions and it is shown that the data indicate a significant anisotropic fourth-order anharmonic component in the thermal vibration of the chlorine ions. The values obtained for the harmonic temperature factors are in excellent agreement with other recent determinations and differences from theoretical values are attributed to isotropic anharmonic contributions. The nuclear scattering amplitude of potassium was refined to $b_K = 0{\cdot}367\ (2) \times 10^{-12}$ cm., assuming a value for the nuclear scattering amplitude of chlorine of $b_{Cl} = 0{\cdot}9580\ (2) \times 10^{-12}$ cm.

Introduction

KCl is commonly used as a standard material in diffraction work and, in particular, has been used in this laboratory for the investigation of certain neutron-diffraction techniques, for example the use of a multi-order white-radiation technique (Wilson & Cooper, 1973). In order to optimize its use in this context the diffraction properties of the material must be characterized with a reasonable accuracy. In addition it is a suitable material for testing certain aspects of theories of diffraction effects, for example those concerned with extinction and anharmonic thermal vibrations, and for the determination of the ratio of the neutron scattering amplitudes for potassium and chlorine. For these reasons we have undertaken an accurate neutron-diffraction study of a single crystal of KCl.

The effects of extinction in both X-ray and neutron diffraction studies have been discussed in detail elsewhere (Cooper & Rouse, 1970). In particular, the dependence of extinction effects on the structure factor, Bragg angle and wavelength are of interest and further accurate diffraction data are of vital importance in testing existing theories of extinction. Since neutron scattering amplitudes are normally independent of the Bragg angle, neutron diffraction measurements are, in general, more powerful than X-ray diffraction measurements in this respect. Such measurements have recently been made on single crystals of CaF_2, SrF_2 (Cooper & Rouse, 1971), ZnS and ZnTe (Cooper, Rouse & Fuess, 1973), but further measurements are clearly desirable.

The analysis of diffraction data in terms of anharmonic thermal vibrations has been discussed in detail in an earlier paper (Cooper, Rouse & Fuess, 1973) in connexion with neutron-diffraction measurements on materials with atoms in tetrahedral sites which have indicated the existence of third-order anharmonic effects. In contrast to these materials, KCl has a structure such that all ions have an octahedral site symmetry. This is centrosymmetric, so that, for a one-particle potential [equation (4)], third-order anharmonic terms are impossible and the lowest-order anharmonic terms are thus fourth-order. Effects of isotropic fourth-order anharmonic thermal vibrations have been observed, for example, by studying the variation of the Debye–Waller factor with temperature. Measurements of this type have been made recently using Mössbauer X-ray diffraction technique on both NaCl (Butt & Solt, 1971) and KCl (Solt, Butt & O'Connor, 1973). Accurate neutron-diffraction measurements of the type described in this paper can be used to investigate the effects of anisotropic components of the thermal vibrations and the present measurements are, we believe, the first observation of significant effects due to anisotropic fourth-order contributions to the thermal vibrations.

Theory

A general structure-factor formalism for interpreting accurate X-ray and neutron-diffraction data has been outlined by Dawson (1967) and has been developed for the special case of neutron-diffraction measurements on materials with the KCl structure by Willis (1969). For a structure with centrosymmetric site symmetry the neutron-diffraction structure factor $F(\mathbf{Q})$ for a particular scattering vector $\mathbf{Q}$, can be written as

$$F(\mathbf{Q}) = \sum_j b_j T_{cj}(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \tag{1}$$

where b_j is the nuclear scattering amplitude of the jth atom at a position $\mathbf{r}_j$ in the unit cell and $T_{cj}(\mathbf{Q})$ is the centrosymmetric thermal-vibration factor.

For the KCl structure the structure factors are finite only if the indices h, k and l are all even or all odd and take one of two forms depending on the indices being even or odd. These are

$$F(\mathbf{Q})=4b_KT_{cK}(\mathbf{Q})+4b_{\mathrm{Cl}}T_{c\mathrm{Cl}}(\mathbf{Q}) \text{ for } h,k,l \text{ even} \tag{2}$$

and

$$F(\mathbf{Q})=4b_KT_{cK}(\mathbf{Q})-4b_{\mathrm{Cl}}T_{c\mathrm{Cl}}(\mathbf{Q}) \text{ for } h,k,l \text{ odd}. \tag{3}$$

Ignoring higher-order terms than fourth-order, the one-particle potential appropriate to an octahedral site symmetry is

$$\begin{aligned} V_j(\mathbf{u}) = {} & V_{oj}+\tfrac{1}{2}\alpha_j(x^2+y^2+z^2)+\gamma_j(x^2+y^2+z^2)^2 \\ & +\delta_j(x^4+y^4+z^4-\tfrac{3}{5}[x^2+y^2+z^2]^2) \end{aligned} \tag{4}$$

where x, y and z are the coordinates defining the instantaneous displacement $\mathbf{u}$ of the jth atom.

The thermal vibration factor $T_{cj}(\mathbf{Q})$ for an atom in a potential field as defined by equation (4) can be derived as

$$\begin{aligned} T_{cj}(\mathbf{Q}) = N_j \exp\left[-\frac{Q^2k_BT}{2\alpha_j}\right] \Bigg\{ & 1-15k_BT\left(\frac{\gamma_j}{\alpha_j^2}\right) \\ & +10(k_BT)^2\left(\frac{2\pi}{a_0}\right)^2\left(\frac{\gamma_j}{\alpha_j^3}\right)(h^2+k^2+l^2) \\ & -(k_BT)^3\left(\frac{2\pi}{a_0}\right)^4\left(\frac{\gamma_j}{\alpha_j^4}\right)(h^2+k^2+l^2)^2 \\ & -\tfrac{4}{5}(k_BT)^3\left(\frac{2\pi}{a_0}\right)^4\left(\frac{\delta_j}{\alpha_j^4}\right) \\ & \times[(h^4+k^4+l^4)-3(h^2k^2+k^2l^2+l^2h^2)]\Bigg\} \end{aligned} \tag{5}$$

where

$$N_j=\left[1-15k_BT\left(\frac{\gamma_j}{\alpha_j^2}\right)\right]^{-1} \tag{6}$$

(see Willis, 1969).

The term in $T_{cj}(\mathbf{Q})$ involving δ_j is the anisotropic component and is best studied by investigating the detailed dependence of the structure factor on the indices h, k and l.

The remaining terms in $T_{cj}(\mathbf{Q})$ constitute the isotropic component and we may note that, of the two terms involving γ_j, that involving γ_j/α_j^3 is normally much larger than that involving γ_j/α_j^4. Thus, if we ignore the latter, and write $e^x=1-x$ for $x\ll 1$, the isotropic component of $T_{cj}(\mathbf{Q})$ is given approximately by

$$T^{i}_{cj}(\mathbf{Q})=\exp\left[-\frac{Q^2k_BT}{2\alpha_j}\left(1-20k_BT\frac{\gamma_j}{\alpha_j^2}\right)\right]. \tag{7}$$

Thus the most significant effect of anharmonic terms in the one particle potential is to give a temperature-squared-dependent contribution to the isotropic thermal-vibration factor. This contribution is equivalent to a contribution to the normal Debye–Waller B factor B_j of

$$(\Delta B_j)_\gamma=-B^{h}_j\,.\,20k_BT\gamma_j/\alpha_j^2\,, \tag{8}$$

where B^{h}_j is the harmonic B factor, given by

$$B^{h}_j=8\pi^2k_BT/\alpha_j\,. \tag{9}$$

The temperature dependence of α_j, γ_j and δ_j is taken into account by the 'quasi-harmonic approximation', which assumes that the change in volume arising from thermal expansion gives rise to a proportional change in the frequencies of the normal modes of vibration. The quasi-harmonic approximation leads to the equations

$$\alpha_j/\alpha_{0j}=\gamma_j/\gamma_{0j}=\delta_j/\delta_{0j}=1-2\gamma_G\chi\Delta T \tag{10}$$

where γ_G is the Grüneisen constant, χ is the volume coefficient of expansion, α_{0j}, γ_{0j}, δ_{0j} are the values of the potential parameters in the absence of expansion and it is assumed that $2\gamma_G\chi\Delta T\ll 1$.

Thus the magnitude of γ_j is best estimated from an experimental determination of B_j as a function of temperature, allowing for the variation due to lattice expansion.

Although equations (7) to (10) have been given to indicate the most significant effects of anharmonic terms in the atomic potential it should be emphasized that the present measurements have been analysed using equation (5) and that no approximations have been made in the form of the thermal-vibration factor.

Experimental measurements

The sample used was a small cube of KCl of edge 1·5 mm, which was cut from a crystal supplied by the Harshaw Chemical Company. Attempts were made to shape a number of similar crystals into spheres but because of the cleavage properties of KCl it proved impossible to obtain spheres of the required size.

A crystallographic $\langle 110\rangle$ axis was aligned vertically and two dimensional *hkk* intensity measurements were made using a Hilger and Watts Mk II automatic neutron diffractometer. Reflexions were scanned in a θ–2θ mode using a rectangular detector aperture which was adjusted to reduce the amount of background scattering detected, without loss of Bragg intensity. A minimum scan range of $\pm 0{\cdot}8°$ was used, but larger scan ranges were used for higher-angle reflexions, as appropriate in order to avoid possible loss of Bragg intensity. No anomalies were observed in the background scattering and background measurements were therefore made using a similar scan with the crystal mis-set by 2°.

Measurements were made at three different wavelengths in order to determine the wavelength-independent parameters more precisely and to check on the consistency of wavelength-dependent effects. The measurements at $\lambda=1{\cdot}142$ Å were preliminary measurements to investigate the suitability of the crystal and these were carried out to a slightly lower precision than the remaining measurements. For the latter, intensities were averaged over a complete two-dimensional set of equivalent reflexions (hkk, $\bar{h}kk$, $h\bar{k}\bar{k}$ and $\bar{h}\bar{k}\bar{k}$). However, because of the excellent agreement observed between equivalent reflexions, it proved possible to include all measurements as part of the accurate study.

Data analysis

(a) *Method of analysis*

The sets of observed data were analysed using the Harwell *TAILS* computer program, as described in an earlier paper (Cooper, Rouse & Fuess, 1973). For spherical or cylindrical crystals effective path lengths through the crystal are calculated from the radius of the crystal. For other shapes of crystal the effective path length for each reflexion must be calculated externally to be read in by the *TAILS* program.

(b) *Results*

Absorption factors and effective path-length values were calculated for all reflexions for the cube-shaped crystal. However, absorption was sufficiently small in this crystal ($\mu R < 0\cdot1$) for A_μ to be effectively the same for all reflexions and for extinction corrections not to vary significantly from those calculated for a spherical crystal of appropriate radius. For the subsequent analysis the absorption factor was therefore considered as part of the scale factor and a spherical approximation was used for the calculation of extinction corrections. Thermal diffuse scattering corrections were calculated using the elastic constant values tabulated by Fedorov (1968).

The parameters which were considered as possible variable quantities were the scale factor, the nuclear scattering amplitude of potassium, the effective domain radius (r^*), the harmonic thermal parameters (α_j) and the anharmonic thermal parameters (γ_j and δ_j). The nuclear scattering amplitude of chlorine was taken to be $b_{\rm Cl} = 0\cdot9580\,(2) \times 10^{-12}$ cm (Koester & Nistler, 1971), but it should be noted that, since the scale factor is refined, only the ratio of the scattering amplitudes of potassium and chlorine can be determined from the analysis.

Of the remaining parameters only the scale factor and the effective domain radius vary with the wavelength. However, the present version of the program does not permit joint refinement of data collected at different wavelengths and initial analysis was carried out treating the data for the various wavelengths separately. Good agreement was obtained for the values of parameters which are independent of wavelength and a weighted mean value was determined in each case. The analysis was then repeated with these parameters fixed at their weighted mean values, in the following order: (i) potassium scattering amplitude, (ii) harmonic thermal parameters, (iii) anharmonic thermal parameters.

The final values of the effective domain radii (r^*) were found to be consistent with the wavelength dependence predicted by the Zachariasen theory [see Cooper & Rouse, 1970, equation (16*d*)]. Final analyses of the data were therefore carried out with domain radius (r) and mosaic spread (g) parameters fixed at values determined from the individual r^* values. The final models are therefore identical for all wavelengths.

In order to consider the significance of effects due to quartic contributions to the thermal vibrations of the atoms three models were considered. Model 1 is a harmonic model with the harmonic thermal parameters refined and the anharmonic thermal parameters zero. Model 2 includes the anisotropic quartic thermal parameters (δ_j) with the harmonic thermal parameters also refined. Model 3 includes both the anisotropic and the isotropic quartic thermal parameters (δ_j and γ_j respectively), but with the harmonic thermal parameters fixed at theoretical values.

Model 2 differs from model 1 only in the inclusion of the anisotropic quartic thermal parameters. Since there is no correlation between the anisotropic parameters and the isotropic parameters there is no difference between the values of the latter for the two models.

Initial analyses for model 2 gave a small value of δ_K which was not significantly different from zero, with no consistency between individual values for the various sets of data. The value of δ_K was therefore subsequently fixed at zero. On the other hand, the individual values obtained for $\delta_{\rm Cl}$ were in excellent agreement, varying only between $0\cdot11$ and $0\cdot15 \times 10^{-12}$ erg Å^{-4}, and were in each case significantly

Table 1. *Neutron diffraction data for* KCl *at* $\lambda = 0\cdot948$ Å

h	k	l	Io	Ic	σ (Io)	y	α
2	0	0	57964	56916	345	0.905	0.004
0	2	2	37288	38027	279	0.936	0.010
2	2	2	29104	28867	175	0.952	0.018
4	0	0	23562	23138	157	0.962	0.028
4	2	2	16065	16086	131	0.974	0.049
0	4	4	11472	11840	114	0.981	0.072
6	0	0	10385	10307	57	0.984	0.084
2	4	4	10152	10288	53	0.984	0.084
6	2	2	7942	7920	68	0.988	0.110
4	4	4	7138	6981	64	0.989	0.123
8	0	0	4412	4417	38	0.994	0.178
6	4	4	3910	3935	36	0.994	0.192
0	6	6	3558	3540	26	0.995	0.206
8	2	2	3537	3554	26	0.995	0.206
2	6	6	3157	3185	33	0.996	0.220
4	6	6	2288	2348	29	0.997	0.262
8	4	4	1918	1941	28	0.997	0.290
10	0	0	1790	1790	19	0.998	0.304
10	2	2	1575	1595	16	0.998	0.330
6	6	6	1588	1570	15	0.999	0.330
10	4	4	969	969	11	0.999	0.400
2	8	8	964	964	11	0.999	0.400
12	0	0	839	839	7	0.999	0.423
4	8	8	814	814	7	0.999	0.423
1	1	1	14427	14400	89	0.976	0.002
3	1	1	6338	6367	62	0.989	0.016
1	3	3	4058	4083	72	0.993	0.035
5	1	1	2877	2897	29	0.995	0.057
3	3	3	2967	2890	28	0.995	0.106
5	3	3	1700	1643	53	0.998	0.133
7	1	1	1259	1290	21	0.998	0.133
1	5	5	1249	1281	22	0.998	0.160
3	5	5	991	1012	47	0.998	0.188
7	3	3	763	814	43	0.999	0.300
9	3	3	309	366	19	1.000	0.300
1	7	7	343	362	19	1.000	0.300
7	5	5	340	360	23	1.000	0.300

larger than their standard deviation. The final value obtained from all sets of data was $\delta_{\mathrm{Cl}}=0{\cdot}13\,(5)\times 10^{-12}$ erg Å^{-4}.

Table 2. *Neutron diffraction data for* KCl *at* $\lambda=1{\cdot}142$ Å

h	k	l	Io	Ic	σ(Io)	y	α
2	0	0	82018	81189	615	0.873	0.004
0	2	2	54217	55135	407	0.913	0.010
2	2	2	42719	42310	320	0.934	0.017
4	0	0	34217	34229	257	0.947	0.026
4	2	2	24435	24188	183	0.963	0.044
0	4	4	17930	18086	136	0.973	0.064
6	0	0	15610	15876	128	0.976	0.075
2	4	4	15823	15845	128	0.976	0.075
6	2	2	12387	12424	114	0.982	0.097
4	4	4	11205	11062	109	0.984	0.108
8	0	0	7292	7362	63	0.990	0.154
6	4	4	6797	6665	61	0.991	0.165
0	6	6	6120	6105	58	0.992	0.176
8	2	2	6202	6129	58	0.992	0.176
2	6	6	5451	5634	39	0.992	0.193
4	6	6	4467	4513	36	0.994	0.226
8	4	4	4279	4097	36	0.995	0.259
10	0	0	4047	4000	36	0.995	0.269
1	1	1	21170	21062	159	0.966	0.002
3	1	1	9360	9459	58	0.985	0.015
1	3	3	6060	6142	58	0.990	0.032
5	1	1	4388	4414	41	0.993	0.052
3	3	3	4365	4405	41	0.993	0.052
5	3	3	2584	2583	28	0.996	0.094
7	1	1	2092	2069	26	0.997	0.117
1	5	5	2070	2056	26	0.997	0.117
3	5	5	1671	1663	21	0.998	0.140
7	3	3	1366	1376	18	0.998	0.162
5	5	5	1152	1145	17	0.998	0.185
9	1	1	1014	1008	8	0.999	0.213
9	3	3	847	808	15	0.999	0.266
1	7	7	789	799	15	0.999	0.266
7	5	5	836	794	15	0.999	0.266

Table 3. *Neutron diffraction data for* KCl *at* $\lambda=1{\cdot}346$ Å

h	k	l	Io	Ic	σ(Io)	y	α
2	0	0	121096	118782	605	0.839	0.004
0	2	2	79680	82185	398	0.888	0.010
2	2	2	65185	63970	326	0.913	0.017
4	0	0	53240	52396	266	0.930	0.025
4	2	2	38245	37911	197	0.950	0.043
0	4	4	28391	29113	142	0.962	0.063
6	0	0	26187	25941	164	0.966	0.073
2	4	4	25935	25892	163	0.966	0.073
6	2	2	21447	21154	108	0.973	0.099
4	4	4	19488	19257	98	0.976	0.110
8	0	0	14683	14671	73	0.982	0.152
8	2	2	13841	14016	69	0.984	0.180
0	6	6	13726	13963	72	0.984	0.180
2	6	6	13983	14218	73	0.983	0.186
1	1	1	32247	31656	182	0.956	0.002
3	1	1	14630	14511	72	0.980	0.015
1	3	3	9417	9604	100	0.987	0.032
5	1	1	7078	7054	24	0.991	0.050
3	3	3	7025	7039	24	0.991	0.050
5	3	3	4438	4404	30	0.994	0.096
7	1	1	3640	3692	28	0.995	0.119
1	5	5	3621	3668	28	0.996	0.119
3	5	5	3145	3158	21	0.997	0.140
7	3	3	2872	2892	22	0.997	0.168
5	5	5	2850	2837	27	0.997	0.185

Table 4. *Neutron structure factors for* KCl

			0·948 Å	1·142 Å	1·346 Å	
h	k	l	F_1	F_2	F_3	F_c
2	0	0	5.092	5.071	5.094	5.045
0	2	2	4.730	4.737	4.703	4.777
2	2	2	4.541	4.544	4.565	4.522
4	0	0	4.321	4.281	4.316	4.282
4	2	2	3.835	3.857	3.854	3.837
0	4	4	3.385	3.424	3.396	3.439
6	0	0	3.271	3.231	3.274	3.259
2	4	4	3.234	3.253	3.258	3.255
6	2	2	2.924	2.915	2.940	2.919
4	4	4	2.792	2.779	2.778	2.761
8	0	0	2.223	2.214	2.226	2.225
6	4	4	2.093	2.120		2.099
0	6	6	1.994	1.991	1.972	1.989
8	2	2	1.988	2.004	1.980	1.992
2	6	6	1.874	1.851	1.866	1.882
4	6	6	1.575	1.587		1.595
8	4	4	1.423	1.463		1.431
10	0	0	1.364	1.372		1.364
10	2	2	1.213			1.221
6	6	6	1.218			1.211
10	4	4	0.876			0.876
2	8	8	0.873			0.873
12	0	0	0.751			0.751
4	8	8	0.739			0.739
1	1	1	2.282	2.286	2.301	2.280
3	1	1	2.040	2.034	2.053	2.044
1	3	3	1.827	1.821	1.815	1.833
5	1	1	1.639	1.640	1.648	1.645
3	3	3	1.665	1.636	1.641	1.643
5	3	3	1.344	1.321	1.326	1.321
7	1	1	1.174	1.195	1.180	1.188
1	5	5	1.169	1.188	1.177	1.184
3	5	5	1.049	1.063	1.059	1.061
7	3	3	0.923	0.949	0.950	0.953
5	5	5		0.854	0.853	0.851
9	1	1		0.774		0.772
9	3	3	0.567	0.633		0.618
1	7	7	0.598	0.611		0.615
7	5	5	0.595	0.628		0.613

Because of severe correlation problems when data have been collected at one temperature only it is not possible to refine the isotropic quartic anharmonic thermal parameters at the same time as the harmonic thermal parameters. It was therefore necessary to fix the latter in the analysis for model 3, the values used being those given by Reid & Smith (1970), which are considered to be the most reliable theoretical values. The values of the isotropic quartic parameters are therefore appropriate only to these values of the harmonic parameters and for this reason we consider that model 2 constitutes the most appropriate model for a detailed discussion of the present measurements.

Discussion

The experimental data are summarized in Tables 1 to 3. These Tables list the observed and calculated background-corrected intensities, the standard deviations of the observed intensities based on counting statistics and the values of the extinction and thermal diffuse scattering factors for each reflexion. The calculated intensities are those given by model 2, which gave the best overall fit to the observed data. The derived values of the structure factors for this model are given in Table 4.

In order to give an indication of the overall agreement, the values of the discrepancy index

$$R_I^w=\sum_i\,(w_i^2|I_{oi}-I_{ci}|)/\sum_i\,(w_i^2 I_{oi}) \qquad (11)$$

where $w_i=1/\sigma(I_{oi})$, are listed for the various sets of data in Table 5. The final values of the fundamental parameters are listed in Table 6 for the three models considered.

Table 5. *Discrepancy index values* (%)

	0·948 Å	1·142 Å	1·346 Å
Model 1	1·30	1·64	0·85
Model 2	0·87	1·34	0·80
Model 3	0·98	1·40	0·72

It can be seen from Table 5 that there is excellent agreement between the observed structure factors derived from the various sets of data. Extinction effects were relatively small with very few reflexions being reduced in intensity by more than 5% because of extinction. The measurements as a whole agree well with the Zachariasen (1967) theory of extinction as extended by the authors (Cooper & Rouse, 1970). The observed values of the effective domain radius r^* are listed in Table 7 and the values of the domain radius r and the mosaic spread parameter g which give r^* values in the best agreement with the individually refined values are given in Table 6. These r^* values are also listed in Table 7 and it can be seen that the agreement is excellent. It is therefore possible to use a single model for the extinction properties to account for the observations at all wavelengths.

The present measurements provide an accurate value of the ratio of the nuclear scattering amplitudes of potassium and chlorine, *i.e.* $b_{\rm K}/b_{\rm Cl}=0{\cdot}383\ (2)$, which is in exact agreement with the value of 0·383 (3) obtained by Bacon & Plant (1968) from neutron diffraction measurements on a powdered sample of KCl. Since the magnitudes of the various corrections involved are different for the single crystal and powder techniques, this agreement supports the validity of the analyses. Recently Koester & Nistler (1971) have determined precise values of a number of nuclear scattering amplitudes using a refractometer technique. These include the value of $b_{\rm Cl}=0{\cdot}9580\ (2)\times10^{-12}$ cm, from which the above ratio gives $b_{\rm K}=0{\cdot}367\ (2)\times10^{-12}$ cm (see Cooper & Rouse, 1972). This is in good agreement with the value of $0{\cdot}371\ (2)\times10^{-12}$ cm determined recently by Koester & Knopf (1972).

Anisotropic anharmonic effects were investigated by extending the harmonic model (model 1) by the inclusion of the anisotropic quartic parameters δ_j (model 2). Since there is no correlation between the anisotropic and isotropic parameters none of the parameters of model 1 changed in value. A significant value was obtained for $\delta_{\rm Cl}$, *viz.* $\delta_{\rm Cl}=0{\cdot}13\ (5)\times10^{-12}$ erg Å^{-4}, which is consistent with the octahedral site symmetry. The value obtained for $\delta_{\rm K}$, although of similar magnitude, was not significantly different from zero.

Table 7. *Effective domain radius values* ($\times10^{-5}$ cm) *for* KCl

	λ (Å)	r^*	$\sigma(r^*)$	$r^*_{\rm calc}$
Models 1 and 2	0·948	0·62	0·10	0·64
	1·142	0·80	0·10	0·73
	1·346	0·81	0·09	0·81
Model 3	0·948	0·73	0·10	0·74
	1·142	0·89	0·10	0·84
	1·346	0·92	0·09	0·92

The values obtained for the conventional harmonic temperature factors B^h_j, given by equation (9), are compared with some previously determined experimental and theoretical values in Table 8. Most of the previous experimental values have been derived from X-ray diffraction measurements, but only the more recent of these have included corrections for the contribution of thermal diffuse scattering (TDS) to the measured intensities. If TDS corrections are ignored the experimental values of the temperature factors will be too small (Cooper & Rouse, 1968). Since the full detector aperture dimensions are not known it is not possible to estimate the error in the temperature factors reliably for the earliest X-ray measurements. However, using the angular dimensions quoted by Nilsson (1957) and assuming a square detector aperture we estimate that, for the James & Brindley (1928) measurements, this error is of the order of $\Delta B_j\simeq -0{\cdot}16$ Å^2. It can be seen from Table 8 that both of the early X-ray determinations, for which no TDS corrections were applied, give B_j values considerably lower than those given by the other determinations. However, no indication is given of the reliability of the early figures and it is probable that this is such that the differences, allowing for the TDS contributions and possible uncertainties in the effects of extinction, are not significant.

Table 6. *Final parameters for* KCl

	Model 1	Model 2	Model 3	
$b_{\rm K}$	0·367 (0·002)	0·367 (0·002)	0·367 (0·002)	$\times10^{-12}$ cm
$\alpha_{\rm K}$	1·468 (0·006)	1·468 (0·006)	1·654	$\times10^{-12}$ erg Å^{-2}
$\alpha_{\rm Cl}$	1·475 (0·005)	1·475 (0·005)	1·605	$\times10^{-12}$ erg Å^{-2}
$\delta_{\rm K}$	0	0	0	$\times10^{-12}$ erg Å^{-4}
$\delta_{\rm Cl}$	0	0·13 (0·05)	0·16 (0·07)	$\times10^{-12}$ erg Å^{-4}
$\gamma_{\rm K}$	0	0	−0·59 (0·02)	$\times10^{-12}$ erg Å^{-4}
$\gamma_{\rm Cl}$	0	0	−0·40 (0·02)	$\times10^{-12}$ erg Å^{-4}
$B_{\rm K}$	2·175 (0·009)	2·175 (0·009)	1·929	Å^2
$B_{\rm Cl}$	2·165 (0·007)	2·165 (0·007)	1·994	Å^2
r	1·31 (0·90)	1·31 (0·90)	1·36 (0·71)	$\times10^{-5}$ cm
g	772 (269)	772 (269)	930 (320)	

The recent X-ray determinations, for which TDS corrections were applied, are in excellent agreement with the present values, as are the values obtained from neutron measurements from a powdered sample. However, the superior reliability of the single-crystal neutron-diffraction values is clearly apparent.

The present B_j values are about 10% larger than the theoretical values. However, Buyers & Smith (1968) point out that the theoretical values contain a part, although not a well defined one, of the anharmonic corrections. Thus it would appear reasonable to suppose that the discrepancy between the recent experimental values and the theoretical values arises from the isotropic anharmonic contributions which are not taken into account in the former. A discrepancy of similar magnitude was observed for a recent experimental determination of the Debye–Waller factor for nickel (Cooper & Taylor, 1969).

Willis (1969) has estimated the magnitude of the isotropic anharmonic effects in KCl from the temperature dependence of the results of James & Brindley (1928), deriving from these a value of $\gamma_0 \simeq -0{\cdot}6 \times 10^{-12}$ erg Å^{-4} (assuming $\gamma_0 = \gamma_K = \gamma_{Cl}$). Since the present measurements were made at one temperature only, it is not possible to determine γ_j values from them in the same way. However, by fixing the harmonic B_j^h values at the theoretical values (model 3) it was possible to estimate the magnitude of the isotropic harmonic parameters which would account for the discrepancy between the experimental and theoretical B_j values. The values obtained, *i.e.* $\gamma_K = -0{\cdot}59\ (2) \times 10^{-12}$ erg Å^{-4} and $\gamma_{Cl} = -0{\cdot}40\ (2) \times 10^{-12}$ erg Å^{-4}, are in excellent agreement with the estimated value of Willis (1969). However, it must be emphasized that the present values have been determined assuming the theoretical harmonic B_j^h values to be correct. Any error in the latter will result in a corresponding error in the γ_j values; for example, a 1% error in the B_j^h values will give a 10% error in the γ_j values.

The relative merits of the three models considered can be evaluated from the ratios of the R values given in Table 5, using the significance tables of Hamilton (1965). The R-value ratio for model 2 and model 1 is 1·49 for the shortest-wavelength data, but decreased systematically for the longer-wavelength data, as would be expected from the reduction in the number of high-index reflexions which can be measured. However, even at the longest wavelength the improvement resulting from the inclusion of the anisotropic anharmonic thermal parameter δ_{Cl} is significant at the 0·10 level; for the shorter wavelengths it is significant at levels less than 0·005. The R-value ratios for model 3 and model 2 indicate that there is no significant difference in the fitting of the experimental data by these two models. This is consistent with the theoretical considerations and emphasizes the fact that the isotropic anharmonic thermal parameters can be estimated from the present data only if the harmonic thermal parameters are fixed at appropriate values.

These significance tests show that the value obtained for the anisotropic anharmonic thermal parameter of chlorine is indeed significant and this would appear to be the first time that significant effects arising from such a component in the thermal motion have been observed. The present measurements also provide very precise values of the harmonic temperature factors (B_j). These are about 10% higher than the theoretical values, but it is reasonable to suppose that these differences are due to isotropic anharmonic effects and estimation of the magnitude of the latter, based on these differences, are consistent with a previous estimate derived from the variation of the mean temperature factor with temperature.

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Table 8. *Harmonic temperature factors* B_j^h *for* KCl

Authors	Method*	T (°K)	TDS	B_K (Å^2)	σ	B_{Cl} (Å^2)	σ
James & Brindley (1928)	SCX	295	No	1·71		1·71	
Wasastjerna (1946)	PX	293	No	1·92		1·78	
Patomaki & Linkoaho (1969)	PX	300	Yes	2·08	0·05	2·06	0·05
Jayalakshmi & Viswamitra (1970)	SCX	298	Yes	2·15		2·15	
Taylor & Willis (1973)	PN	295	Yes	2·00	0·10	2·08	0·04
Present measurements	SCN	295	Yes	2·175	0·009	2·165	0·007
Buyers & Smith (1968)	Th	295	—	1·902		1·956	
Merisalo & Inkinen (1968)	Th	300	—	1·94		1·98	
Reid & Smith (1970)	Th	295	—	1·929		1·994	

* SC Single crystal X X-ray Th Theoretical
P Powder N Neutron

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Electron Diffraction Study of Short-Range-Order Diffuse Scattering from Disordered Cu–Pd and Cu–Pt Alloys

By Kenichi Ohshima and Denjiro Watanabe

Department of Physics, Tohoku University, Sendai, Japan

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The short-range-order diffuse scattering from disordered Cu–Pd and Cu–Pt alloys has been studied by electron diffraction using thin foils prepared from bulk specimens. Twofold and fourfold splittings of diffuse scattering are observed at 100, 110 and equivalent positions in the composition ranges from about 13 to 60 at.% Pd in the Cu–Pd system and up to about 45 at.% Pt in the Cu–Pt system. The separation of the split maxima increases with Pd or Pt content. A close investigation has revealed that the split maxima correspond to the intersections of slightly curved diffuse streaks around the 100 and 110 positions. These results can be interpreted well using the Fermi-surface-imaging theory proposed by Krivoglaz, indicating that the interaction potential in these alloys mainly originates from conduction electrons, and that the diffuse scattering reflects the form of the Fermi surface, *i.e.* the flatness normal to the ⟨110⟩ directions.

1. Introduction

The short-range order in binary alloys can be studied by observing the distribution of diffuse scattering, and the short-range-order parameters representing the pair correlations of atoms are available from the quantitative intensity measurements on single crystals (Cowley, 1950; Clapp & Moss, 1966, 1968; Moss & Clapp, 1968; Wilkins, 1970). However, until recently the electron diffraction method was not considered to be suitable for this purpose, compared with the X-ray and neutron diffraction methods mainly because of the difficulty in quantitative intensity measurement in electron diffraction. Moreover, it was known that the distributions of diffuse scattering observed by electron diffraction for some alloys were different from those observed with X-rays. For example, for disordered Cu_3Au, CuAu and $CuAu_3$ alloys a cross-like distribution consisting of four diffuse spots was observed in electron diffraction (Raether, 1952; Marcinkowski & Zwell, 1963; Sato, Watanabe & Ogawa, 1962; Watanabe & Fisher, 1965), whereas a disk-like or nearly spherical or egg-shaped distribution without fine structure was concluded from X-ray diffractometer observations (Cowley, 1950; Roberts, 1954; Batterman, 1957). For these reasons, little attention had unduly been paid to the results of electron diffraction studies. However, the disagreements were removed recently by Moss (1966). He observed a cross-like distribution from disordered Cu_3Au in X-ray diffraction photographs also, in conformity with the electron diffraction observations.

The importance of the electron diffraction observation has recently increased significantly, since it was pointed out by Krivoglaz (1969) and Moss (1969) that the form of the Fermi surface of a disordered alloy is reflected in the distribution of short-range-order diffuse scattering through anomalies which are similar to those predicted by Kohn for phonon scattering and are due to the pair-interaction potential caused by conduction electrons in the alloy. This correlation between the diffuse-scattering intensity distribution and the Fermi