

the fact that the end-group packing energy is less than in a normal crystal or in polytypes. In our opinion, this may be due to the presence, on the (001) faces of these crystals, of growth spirals repeating periodically the stacking sequence which depends on the content of the exposed ledge. In this way, near the anomalous interfaces, stability is mainly provided by the side-packing energy which remains unaltered. Furthermore, the highly repulsive forces at the interface may be cancelled if the interlayer spacings are increased by a few tenths of an Å or by the rearrangement of relaxed end-groups which was not taken into account in our model.

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Temperature Effects on the X-ray Scattering Factors of Crystals in the LCAO Approximation

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Abstract

A new convolution method is presented for a rigorous LCAO calculation of the lattice-vibration effects on the X-ray scattering factors of crystals. The theory is applied to a lithium hydride crystal and a good agreement with experiment is obtained.

Introduction

Previous calculations of the X-ray scattering factors of crystals within the LCAO approximation have included

the lattice vibrations in a similar way to the free ion (or free atom) picture (Aikala & Mansikka, 1970, 1971, 1972; Grosso & Parravicini, 1978). These calculations have involved the conception of crystal ions (or atoms). This inconsistency is avoided in the present work where the lattice vibrations are treated rigorously in the LCAO approximation with a convolution method.

The most suitable crystal for an experimental check of this method is lithium hydride because it is the simplest ionic crystal with only four electrons per ion pair. Recently, several theoretical investigations have been published on this crystal. These include studies on directional and isotropic Compton profiles (Aikala,

1976; Paakkari, Halonen & Aikala, 1976; Grosso, Parravicini & Rosta, 1976) and magnetic susceptibility (Grosso & Parravicini, 1978). All these investigations utilize an ionic picture of the LiH crystal and employ the LCAO (Linear Combination of Atomic Orbitals) approximation, and the non-orthogonal ionic wave functions are orthogonalized symmetrically to each other.

The scattering factors of LiH have been calculated by Waller & Lundqvist (1953), Westin, Waller & Lundqvist (1962), Hurst (1959), Kahane, Felsteiner & Opher (1973) and Grosso & Parravicini (1978). The first three calculations were only qualitative and in the fourth the comparison with the experimental data of Calder, Cochran, Griffiths & Lowde (1962) was performed in a simple way and considerable deviations occurred for some reflexions. The last one, however, shows good agreement with experiment.

The authors have earlier calculated the scattering factors for several ionic crystals within the LCAO approximation (Aikala & Mansikka, 1970, 1971, 1972; Mansikka & Aikala, 1973).

The numerical results in Table 1 have been published earlier as a preliminary report (Mikkola, Mansikka & Aikala, 1976).

Theoretical

We start our theoretical consideration from the well-known expression of the coherent X-ray scattering factor of a crystal

$$F(\mathbf{K}) = \int_{V_0} \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3 \mathbf{r} \quad (1)$$

for the reflexion \mathbf{K} . Here, $\rho(\mathbf{r})$ denotes the crystalline charge density, and V_0 is the volume of the unit cell. The density $\rho(\mathbf{r})$ can be written as a superposition

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \rho_1(\mathbf{r} - \mathbf{R}), \quad (2)$$

where $\rho_1(\mathbf{r} - \mathbf{R})$ is the contribution of the unit cell characterized by the lattice vector \mathbf{R} . Substituting (2) into (1) and changing the order of summation and integration yield

$$F(\mathbf{K}) = \sum_{\mathbf{R}} \int_{V_0} \rho_1(\mathbf{r} - \mathbf{R}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3 \mathbf{r}. \quad (3)$$

Replacing $\mathbf{r} - \mathbf{R}$ by \mathbf{r} in each of the integrals, one obtains the integral representation

$$F(\mathbf{K}) = \int_{V_c} \rho_1(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3 \mathbf{r}, \quad (4)$$

where V_c represents the volume of a crystal.

By choosing one of the ions in the unit cell as the origin of \mathbf{r} , one can write

$$\rho_1(\mathbf{r}) = \rho_a(\mathbf{r}) + \rho_b(\mathbf{r} - \mathbf{R}_1) \quad (5)$$

for non-primitive crystals having a two-atom basis. Here, \mathbf{R}_1 stands for the position vector of the nearest neighbour to the central crystal ion a . Equations (4) and (5) now give

$$F(\mathbf{K}) = \int_{V_c} \rho_a(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3 \mathbf{r} + e^{i\mathbf{K}\cdot\mathbf{R}_1} \int_{V_c} \rho_b(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3 \mathbf{r}. \quad (6)$$

For example, we can immediately find that the phase factor $e^{i\mathbf{K}\cdot\mathbf{R}_1}$ takes the values $+1$ or -1 for the NaCl structure depending on the parity of the reciprocal-lattice point \mathbf{K} .

The basic problem is how to find reasonable expressions for the overlapping localized densities ρ_a and ρ_b . One possible choice is based on the LCAO method by defining the concept of a crystal ion. By employing Löwdin's orthogonalization technique, one can write the localized crystal-ion densities to represent ρ_a and ρ_b as follows (Aikala & Mansikka, 1970):

$$\rho_i(\mathbf{r}) = 2\varphi_0^*(\mathbf{r}) \sum_g (\Delta^{-1})_{0,g} \varphi_g(\mathbf{r} - \mathbf{R}_g) \quad (i = a, b) \quad (7)$$

for a LiH crystal. Here, $(\Delta^{-1})_{0,g}$ denote the elements of the inverse of the overlap matrix, φ_g is the one-electron wave function of the ion at \mathbf{R}_g , while the factor two comes from the summation over the two spin states. The generalization of (7) into other crystals is straightforward.

We consider next the effect of the lattice vibrations on the above quantities by introducing the displacements $\boldsymbol{\mu}_g$ of the ions from their equilibrium positions. Thus one can write

$$\rho_i(\mathbf{r}, \boldsymbol{\mu}) = \varphi_0^*(\mathbf{r} - \boldsymbol{\mu}_0) \sum_g (\Delta^{-1})_{0,g} (\boldsymbol{\mu}_0, \boldsymbol{\mu}_1, \dots) \times \varphi_g(\mathbf{r} - \mathbf{R}_g - \boldsymbol{\mu}_g). \quad (8)$$

Let $G(\boldsymbol{\mu}) = G(\boldsymbol{\mu}_0, \boldsymbol{\mu}_1, \dots)$ be the displacement density. Hence, the average charge density is

$$\bar{\rho}_i(\mathbf{r}) = \int \varphi_0^*(\mathbf{r} - \boldsymbol{\mu}_0) \sum_g (\Delta^{-1})_{0,g} (\boldsymbol{\mu}) \times \varphi_g(\mathbf{r} - \mathbf{R}_g - \boldsymbol{\mu}_g) G(\boldsymbol{\mu}) \prod_{g'} d^3 \boldsymbol{\mu}_{g'}. \quad (9)$$

In (9) there are an enormous number of displacement variables in each $(\Delta^{-1})_{0,g}$. Owing to the inversion symmetry of the system, various terms of the sum can, however, be integrated over $\boldsymbol{\mu}_{g'}$ for $g' \neq 0, g$ by neglecting $\boldsymbol{\mu}$ in the argument of $(\Delta^{-1})_{0,g}$ without making an error larger than $O(\boldsymbol{\mu}^2)$. Thus there are only two displacement arguments per term which may be important. However, one has in (9) a convolution, which, as a smoothing operation, is not sensitive to the details of the functions to be convoluted. Therefore a satisfactory approximation will be obtained if $(\Delta^{-1})_{0,g}$

(μ) in (9) is replaced by the static-lattice value $(\Delta^{-1})_{0,g}$. Within this approximation one gets

$$\bar{\rho}_i(\mathbf{r}) = \sum_g (\Delta^{-1})_{0,g} \int \varphi_0^*(\mathbf{r} - \mu_0) \times \varphi_g(\mathbf{r} - \mathbf{R}_g - \mu_g) \prod_{g'} G_{g'}(\mu_{g'}) d^3 \mu_{g'}, \quad (10)$$

where the ions are taken to be independent oscillators. Hence, the displacement density can be written in the product form, and the integration of (10) term by term gives

$$\begin{aligned} \bar{\rho}_i(\mathbf{r}) &= (\Delta^{-1})_{0,0} \int |\varphi_0(\mathbf{r} - \mu_0)|^2 G_0(\mu_0) d^3 \mu_0 \\ &+ \sum_{g \neq 0} (\Delta^{-1})_{0,g} \int \varphi_0^*(\mathbf{r} - \mu_0) \varphi_g(\mathbf{r} - \mathbf{R}_g - \mu_g) \\ &\times G_0(\mu_0) G_g(\mu_g) d^3 \mu_0 d^3 \mu_g. \end{aligned} \quad (11)$$

The first term in (11) is a one-centre contribution and it contains the temperature damping factor in the form of the Fourier transform

$$\int G_0(\mu_0) e^{i\mathbf{K} \cdot \mu_0} d^3 \mu_0, \quad (12)$$

which, in the harmonic approximation, gives the conventional Debye-Waller factor of Gaussian type e^{-BK^2} . The inverse transform of this gives the displacement density, which is Gaussian, too.

In the case of the two-centre term in (11), it is not possible to get a simple temperature damping factor, but convolution operations must be carried out explicitly before making the Fourier transform. Thus we get the expression

$$\begin{aligned} F_i(\mathbf{K}) &= \int \rho_i(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d^3 \mathbf{r} \\ &= (\Delta)_{0,0}^{-1} e^{-BK^2} f_i(\mathbf{K}) \\ &+ \int e^{-i\mathbf{K} \cdot \mathbf{r}} \sum_{g \neq 0} (\Delta^{-1})_{0,g} \tilde{\varphi}_0^*(\mathbf{r}) \tilde{\varphi}_g(\mathbf{r} - \mathbf{R}_g) d^3 \mathbf{r}, \end{aligned} \quad (13)$$

where $\tilde{\varphi}_g$ denotes the convolution of φ_g and G_g and $f_i(\mathbf{K})$ is the Fourier transform of $|\varphi_0|^2$.

Practical procedures

In the present case the wave functions of the ions are of the s type. Hence the convolution $\tilde{\varphi}$ of φ and G can be written

$$\tilde{\varphi}(r) = (\zeta/\pi)^{3/2} \int \exp[-\zeta(r-r')^2] \varphi(r') d^3 r', \quad (14)$$

where $\zeta = 1/4B$ (B = the Debye-Waller exponent). By evaluating the integral (14) in the spherical polar coordinates with the z' axis parallel to \mathbf{r} , we easily obtain

$$\begin{aligned} \tilde{\varphi}(r) &= (\zeta/\pi)^{1/2} (1/r) \int_0^\infty \{ \exp[-\zeta(r-r')^2] \\ &- \exp[-\zeta(r+r')^2] \} r' \varphi(r') dr'. \end{aligned} \quad (15)$$

Integral (15) may conveniently be evaluated by means of numerical integration.

A practical method for the computation of the two-centre contributions to the scattering factors is to expand the corresponding charge density in terms of the invariant cubic harmonics (Altmann & Cracknell, 1965), and by fitting the radial parts on the Slater-type basis functions. The Fourier transform can now be obtained using known analytical formulae (the cubic harmonics behave like the spherical ones). In order to determine the above expansion one has to calculate the radial parts $\rho_{l,m}(r)$ of the expansion. By means of the normalized invariant cubic harmonics $C_l^m(\hat{\mathbf{r}})$ we can write

$$\rho_{l,m}(r) = \tilde{\varphi}_0(r) \sum_{g \neq 0} (\Delta^{-1})_{0,g} \int C_l^{m*}(\hat{\mathbf{r}}) \tilde{\varphi}_g(\mathbf{r} - \mathbf{R}_g) d^2 \hat{\mathbf{r}}. \quad (16)$$

For the calculation of the integral

$$\int C_l^{m*}(\hat{\mathbf{r}}) \tilde{\varphi}_g(\mathbf{r} - \mathbf{R}_g) d^2 \hat{\mathbf{r}},$$

we first expand the function

$$\tilde{\varphi}_g(|\mathbf{r} - \mathbf{R}_g|) = \tilde{\varphi}_g[(r^2 - 2rR_g \hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g + R_g^2)^{1/2}]$$

in terms of the Legendre polynomials

$$\varphi_g[|(r^2 - 2rR_g \hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g)^{1/2}] = \sum_{l=0}^{\infty} u_l(R_g, r) P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g), \quad (17)$$

where (by denoting $\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g = \cos \theta$)

$$\begin{aligned} u_l(R_g, r) &= \frac{2l+1}{2} \int_0^\pi \tilde{\varphi}_g[(r^2 - 2rR_g \cos \theta + R_g^2)^{1/2}] \\ &\times P_l(\cos \theta) \sin \theta d\theta. \end{aligned} \quad (18)$$

Thus the integrals to be evaluated are of the type

$$\int C_l^{m*}(\hat{\mathbf{r}}) P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g) d^2 \hat{\mathbf{r}}.$$

By using the formula

$$P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g) = \frac{4\pi}{2l+1} \sum_{m'=-l}^l Y_l^{m'*}(\hat{\mathbf{R}}_g) Y_l^{m'}(\hat{\mathbf{r}}),$$

we obtain

$$\begin{aligned} &\int C_l^{m*}(\hat{\mathbf{r}}) P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}_g) d^2 \hat{\mathbf{r}} \\ &= [4\pi/(2l+1)] \sum_{m'} Y_l^{m'*}(\hat{\mathbf{R}}_g) \int C_l^{m*}(\hat{\mathbf{r}}) Y_l^{m'}(\hat{\mathbf{r}}) d^2 \hat{\mathbf{r}} \\ &= [4\pi/(2l+1)] C_l^{m*}(\hat{\mathbf{R}}_g). \end{aligned} \quad (19)$$

In the last step we have utilized the fact that C_l^m is a linear combination of the Y_l^m 's over m .

Because of the invariance of the C_l^m 's in the operations of the cubic point group, each equivalent

neighbour gives an equal contribution to the sum. Thus the total expansion can be written

$$\tilde{\psi}_0 \sum_{g \neq 0} (\Delta^{-1})_{0,g} \tilde{\psi}_g = \sum_{l,m} \rho_{l,m}(r) C_l^m(\hat{\mathbf{r}}), \quad (20)$$

where

$$\begin{aligned} \rho_{l,m}(r) &= 2\pi \tilde{\psi}_0(r) \sum_{g'} (\Delta^{-1})_{0,g'} N_{R_{g'}} C_l^{m*}(\hat{\mathbf{R}}_{g'}) \\ &\quad \times \int_0^\pi \tilde{\psi}_g [(r^2 - 2rR_{g'} \cos \theta + R_{g'}^2)^{1/2}] \\ &\quad \times P_l(\cos \theta) \sin \theta d\theta. \end{aligned} \quad (21)$$

Here the summation index g' labels the different groups of equivalent lattice points, while the coefficient $N_{R_{g'}}$ represents the number of equivalent points. The θ integration is conveniently carried out by numerical methods.

Having computed the radial parts, the Fourier transforms can be performed by

$$\begin{aligned} &\int e^{-i\mathbf{K}\cdot\mathbf{r}} \rho_{l,m}(r) C_l^m(\hat{\mathbf{r}}) d^3 \mathbf{r} \\ &= 4\pi (-i)^l C_l^m(\hat{\mathbf{K}}) \int_0^\infty r^2 j_l(Kr) \rho_{l,m}(r) dr, \end{aligned} \quad (22)$$

which is easily obtained by using the expansion of the plane wave $e^{i\mathbf{K}\cdot\mathbf{r}}$ into spherical harmonics. In (22), the j_l 's denote the spherical Bessel functions. Finally, when the $\rho_{l,m}$'s are expressed by Slater-type functions (STO's), the integration can be carried out using known analytical formulae, and in consequence some laborious numerical integrations are avoided (Flannery & Levy, 1969).

The fitting of theoretical values to experimental data

According to the above treatment the structure factor can be written as follows:

$$\begin{aligned} F(\mathbf{K}) &= \exp(-B_a K^2) F_a(\mathbf{K}) \\ &\quad + \exp(-B_b K^2) F_b(\mathbf{K}) + F_2(B_a, B_b, \mathbf{K}), \end{aligned} \quad (23)$$

where $F_a(\mathbf{K})$ and $F_b(\mathbf{K})$ represent the one-centre contributions of the ions a and b , respectively, while F_2 is the sum of the two-centre contributions. The phase factor $e^{-i\mathbf{K}\cdot\mathbf{R}_1}$ appearing in (6) is here included in the quantities F_a , F_b and F_2 . To fit the theoretical values of $F(\mathbf{K})$ to the experimental values corresponding to temperature T , an additional fitting parameter, namely a scale coefficient, is introduced to account for the possible scale error of experimental data. Thus, one has to solve by the method of least squares the Debye-

Waller factors B_a and B_b and the scale-error parameter ε so as to give optimal approximate equality:

$$\begin{aligned} &[\exp(-B_a K^2) F_a(\mathbf{K}) + \exp(-B_b K^2) F_b(\mathbf{K}) \\ &\quad + F_2(B_a, B_b, \mathbf{K})](1 + \varepsilon) = F_{\text{exp}}(\mathbf{K}). \end{aligned} \quad (24)$$

Because the one-centre terms are dominant, the solution can be carried out iteratively: first approximations of the above parameters can be obtained using the conventional method by determining the DW factors and ε for the total static structure factor, then the convolutions are evaluated and new estimates are obtained keeping the F_2 term as a constant. The operation is then repeated until convergence to the desired accuracy is obtained.

Results and discussion

The numerical results of the application of the above theory and computational procedures to the LiH crystal ($\text{Li}^+ : 1s^2$, $\text{H}^- : 1s^2$) are presented in Table 1. The calculations were carried out by employing Clementi's free ion HF wave function for Li^+ and the simple free-ion variational function for H^- . The ionic wave functions were orthogonalized to each other taking into account 42 different orders of neighbours, and the resulting inverse overlap matrix Δ^{-1} of the above cluster of ions was solved exactly. The cubic harmonic expansion was evaluated including the first five non-zero terms, *i.e.* up to the order $l = 10$.

Table 1. *One-centre (F_1) and unconvoluted two-centre (F_2) contributions to the static scattering factors of LiH due to the positive (F^+) and negative (F^-) ions, the temperature-corrected scattering factors of LiH calculated with the present convolution method, and the experimental data measured by Calder *et al.* (1962)*

hkl	F_1^-	F_2^-	F_1^+	F_2^+	F_{conv}	F_{obs}
1 1 1	0.681	-0.027	1.780	-0.029	1.068	1.086
2 0 0	0.497	-0.056	1.702	-0.025	2.040	2.032
2 2 0	0.198	-0.022	1.439	-0.015	1.441	1.454
3 1 1	0.122	0.006	1.282	-0.011	0.973	0.960
2 2 2	0.106	-0.010	1.235	-0.010	1.112	1.096
4 0 0	0.066	-0.004	1.074	-0.007	0.887	0.888
3 3 1	0.049	-0.001	0.973	-0.006	0.684	0.671
4 2 0	0.045	0.000	0.943	-0.006	0.722	0.738
4 2 2	0.032	0.000	0.836	-0.004	0.593	0.600
3 3 3	0.026	-0.001	0.767	-0.003	0.480	0.474
5 1 1	0.026	-0.002	0.767	-0.004	0.480	0.472
4 4 0	0.019	0.000	0.671	-0.003	0.412	0.414
5 3 1	0.016	0.000	0.612	-0.003	0.343	0.354
4 4 2	0.016	0.000	0.607	-0.002	0.348	0.359
6 0 0	0.016	-0.002	0.607	-0.002	0.346	0.349
6 2 0	0.013	-0.001	0.552	-0.002	0.294	0.299
5 3 3	0.011	0.000	0.516	-0.002	0.250	0.248
6 2 2	0.011	-0.001	0.504	-0.002	0.251	0.250
4 4 4	0.009	0.000	0.463	-0.002	0.215	0.209
5 5 1	0.008	0.000	0.435	-0.002	0.184	0.182
7 1 1	0.008	-0.001	0.435	-0.001	0.185	0.179

Table 2. *The Debye–Waller exponents and the normalization factors for a LiH crystal obtained by fitting the theoretical scattering factors to the experimental data of Calder et al. (1962) in various approximations*

A means the present convolution treatment, in *B* the two-centre terms are included in the various one-centre terms, and in *C* no temperature damping at all is applied to the two-centre terms.

	$B_{\text{H}^-} (\text{\AA}^2)$	$B_{\text{Li}^+} (\text{\AA}^2)$	ϵ (%)
<i>A</i>	0.9525 ± 0.1946	1.1270 ± 0.0203	2.81 ± 0.47
<i>B</i>	0.9421 ± 0.1990	1.1268 ± 0.0203	2.80 ± 0.46
<i>C</i>	0.9138 ± 0.1901	1.1240 ± 0.0199	2.99 ± 0.46

We may now see from the data of Table 1 that the agreement between theory and experiment (Calder, Cochran, Griffiths & Lowde, 1962) is good for all reflexions. We also find that the present theoretical scattering factors show a slight dependence on crystallographic directions, an effect which is also predicted by the experimental data.

In order to see whether it is essential or not to treat the two-centre terms by the present convolution method (*A*), the temperature corrections of these contributions were also determined with two other methods. In one of these methods (*B*), the two-centre terms were included in the crystal-ion contributions as in the work of Aikala & Mansikka (1970, 1971, 1972) and in the other (*C*) no temperature correction at all was applied to the small two-centre contributions. The corresponding Debye–Waller and scale factors are given in Table 2. The results for the scattering and Debye–Waller factors show no essential differences between various approximations. The main reason for this result is of course that the two-centre terms give only a slight contribution to the total scattering factor. This may also partly arise from the smoothing effects due to the employed expansion in cubic harmonics and the fitting of the radial density terms to the STO functions. Although the relative influence of the convolution treatment in the two-centre terms is very large,

the effect on the total scattering factors is unimportant because of the small relative magnitude of the two-centre contributions. The changes in the two-centre terms in different approximations are compensated by small variations in the fitting parameters B_{H^-} , B_{Li^+} and ϵ . This is the reason why the results of Grosso & Parravicini (1978) are in good agreement with experiment. Thus, when comparing the present theoretical data with experimental data, it is sufficient to use the static scattering factors of the crystal ions (including two-centre contributions) given in Table 1 and the parameters B_{H^-} , B_{Li^+} and ϵ in the fitting procedure.

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