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Determination of the One-Particle Potential for an Atom with Highly Anharmonic Thermal Motion

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Abstract

Analytical expressions are derived relating the coefficients (α , β , γ , and δ) of the anharmonic one-particle-potential (OPP) model at a cubic site to the parameters of the higher cumulant expansion of the Debye–Waller factor. These expressions are used to derive the shape of the potential for the Al(4) site in the structure of $\text{VAl}_{10.42}$ from refinements of X-ray data measured at 100 K and room temperature, including third and fourth cumulant thermal parameters. Reasonable potentials are obtained at both temperatures. A negative value of β indicates a softening of the potential in the $\langle 111 \rangle$ directions in contradiction to the results of previous pseudopotential calculations. A single set of potential parameters is obtained by least-squares fit to the cumulants at both temperatures. Deviations from the fit indicate a lower temperature dependence for the anharmonic terms than predicted by the OPP model. Corrections for quantum statistical effects are small at both temperatures.

Introduction

Aside from interest in anharmonic motion itself, an accurate description of the thermal motion is required in many applications which utilize precise diffraction data, such as measuring the electron density distri-

bution in crystals. When high-resolution measurements are present in the data set, the neglect of anharmonic motion will introduce additional noise in experimental density maps (see, for example, Stevens, 1979; Stevens, DeLucia & Coppens, 1980). In addition, multipole modeling, which may be used to derive an estimate of the static electron distribution, requires a proper model of thermal smearing to avoid correlations with parameters describing the electron distribution.

Deviations from harmonic thermal motion may be accounted for in the temperature factor in several ways. A general expansion of the temperature factor in terms of higher cumulants has been introduced by Johnson (1969),

$$T(\mathbf{h}) = \exp \left\{ \frac{i^2}{2!} {}^{(2)}\kappa^{ij} h_i h_j + \frac{i^3}{3!} {}^{(3)}\kappa^{ijk} h_i h_j h_k + \frac{i^4}{4!} {}^{(4)}\kappa^{ijkl} h_i h_j h_k h_l + \dots \right\}, \quad (1a)$$

or equivalently,

$$T(\mathbf{h}) = \exp \left\{ -2\pi^2 b^{ij} a_i^* a_j^* h_i h_j - i \frac{4\pi^3}{3} c^{ijk} a_i^* a_j^* a_k^* h_i h_j h_k + \frac{2\pi^4}{3} d^{ijkl} a_i^* a_j^* a_k^* a_l^* h_i h_j h_k h_l + \dots \right\}, \quad (1b)$$

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where summation of repeated indices is implied. Extension of existing least-squares refinement programs to include higher cumulants is easily implemented. On the other hand, the behavior of the cumulants as a function of temperature is not predicted by the model.

An alternative for incorporation of anharmonic effects is based on the one-particle-potential (OPP) model. Each atom is assumed to vibrate independently in the average potential of its neighbors, given by

$$V(\mathbf{u}) = V_0 + \frac{1}{2}\alpha\mathbf{u}^2 + \beta u_1 u_2 u_3 + \gamma \mathbf{u}^4 + \delta(u_1^4 + u_2^4 + u_3^4 - \frac{3}{5}\mathbf{u}^4) \quad (2)$$

for a cubic site (Willis, 1969). In the high-temperature limit ($T > \theta_D$), the probability distribution is given by

$$P(\mathbf{u}) = \exp[-V(\mathbf{u})/k_B T] / \int_{-\infty}^{\infty} \exp[-V(\mathbf{u})/k_B T] d\mathbf{u} \quad (3)$$

and the temperature factor by

$$T(\mathbf{h}) = \int_{-\infty}^{\infty} P(\mathbf{u}) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}) d\mathbf{u}. \quad (4)$$

Assuming small deviations from a harmonic potential, and using $e^x \simeq 1 + x$ when x is small, gives

$$\exp[-V(\mathbf{u})/k_B T] = \exp\left(\frac{-\alpha}{2k_B T} \mathbf{u}^2\right) \left[1 - i \frac{\beta}{k_B T} u_1 u_2 u_3 - \frac{\gamma}{k_B T} \mathbf{u}^4 - \frac{\delta}{k_B T} (u_1^4 + u_2^4 + u_3^4 - \frac{3}{5}\mathbf{u}^4) \right]. \quad (5)$$

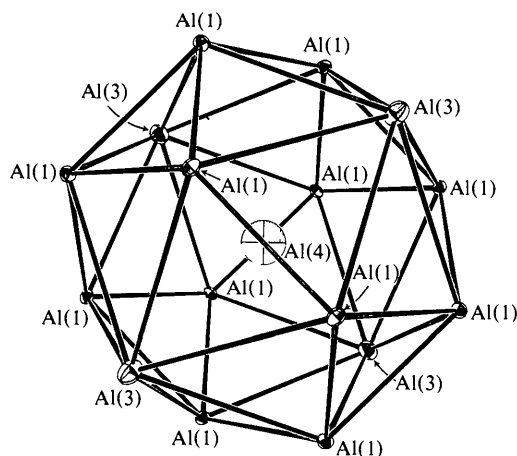


Fig. 1. Plot of the coordination polyhedron surrounding the Al(4) site in VAl_{10} . Thermal ellipsoids are plotted at the 50% probability level (100 K). Four nearest-neighbor Al(3) atoms are located 3.1330(4) Å (100 K) from the center in the $\langle 111 \rangle$ directions. Twelve Al(1) atoms are located only slightly farther [3.1484(5) Å] from the Al(4) site and arranged in groups of three capping each face of the tetrahedron formed by the Al(3) atoms.

In this form, standard integration formulas may be used, yielding

$$T(\mathbf{h}) = N \exp\left[-\frac{k_B T}{\alpha} \frac{(2\pi)^2}{a_0^2} \mathbf{h}^2\right] \times \left\{ 1 - k_B T \left(\frac{15\gamma}{\alpha^2} - \frac{\beta^2}{2\alpha^3} \right) + (k_B T)^2 \left(\frac{10\gamma}{\alpha^3} - \frac{\beta^2}{2\alpha^4} \right) \left(\frac{2\pi}{a_0} \right)^2 \mathbf{h}^2 + i(k_B T)^2 \frac{\beta}{\alpha^3} \left(\frac{2\pi}{a_0} \right)^3 h_1 h_2 h_3 - (k_B T)^3 \left(\frac{2\pi}{a_0} \right)^4 \left(\frac{\gamma}{\alpha^4} \right) \mathbf{h}^4 - \frac{2}{5}(k_B T)^3 \left(\frac{2\pi}{a_0} \right)^4 \left(\frac{\delta}{\alpha^4} \right) [h_1^4 + h_2^4 + h_3^4 - 3(h_1^2 h_2^2 + h_1^2 h_3^2 + h_2^2 h_3^2)] + (k_B T)^3 \left(\frac{2\pi}{a_0} \right)^4 \left(\frac{\beta^2}{2\alpha^5} \right) \times (h_1^2 h_2^2 + h_1^2 h_3^2 + h_2^2 h_3^2) \right\} \quad (6)$$

(Moss, 1979; Mair, 1980). Thus, the OPP model predicts the behavior of each contribution to the anharmonic temperature factor as the temperature changes. Corrections to the OPP model due to the effects of quantum statistical averaging at low temperatures have been derived by Mair & Wilkins (1976) which are valid to about $T > \theta_D/4$.

The validity of the OPP model may be tested by analyzing diffraction data collected at more than one temperature. Several such studies have been reported on simple solids. (See, for example, Moss, McMullan & Koetzle, 1980; McIntyre, Moss & Barnea, 1980; Harada, Suzuki & Hoshino, 1976; Cooper, Rouse & Fues, 1973.) However, only small deviations from the harmonic potential have been observed in these studies, with the fourth-order terms often insignificant or not included. The extent to which the OPP model is valid for highly anharmonic motion has not been tested. Adequate descriptions for highly anharmonic motion will be required for many applications such as the analysis of torsional modes (Coppens, 1980), ionic conductors (Cava, Reiding & Wuensch, 1977), and mode softening in anticipation of phase transitions.

In the course of electron density studies of aluminum alloys containing transition metals (Kontio & Coppens, 1981; Kontio, Stevens, Coppens, Brown, Dwight & Williams, 1980) we have collected high-resolution X-ray intensities from a single crystal of VAl_{10} at 100 K and room temperature. Previous structural studies

(Brown, 1957; Ray & Smith, 1957) have shown that the structure contains a partially occupied aluminum site with $\bar{4}3m$ symmetry (Fig. 1). An anomalous low-temperature heat capacity has been interpreted by Caplin & Nicholson (1978) as arising from well defined local modes associated with a highly anharmonic potential for this site. An analysis of the thermal motion for the aluminum atom at this site is presented here. A detailed description of the electron density distribution will be presented elsewhere (Kontio, Stevens, Boehme & Coppins, 1982).

Theory

For a cubic $\bar{4}3m$ site, the allowed parameters in the cumulant expansion to fourth order are b^{11} , c^{123} , d^{1111} , d^{1122} (*International Tables for X-ray Crystallography*, 1974). These may be related to the parameters of the OPP model using the approximation $1 + x \simeq e^x$ for the OPP temperature factor and equating terms with the same \mathbf{h} dependence. This gives a set of four equations,

$$\begin{aligned} -2\pi^2 {}^{(2)}\kappa^{11} &= \frac{-2\pi^2}{a_0^2} b^{11} \\ &= \frac{-k_B T}{2\alpha} \left(\frac{2\pi}{a_0}\right)^2 + (k_B T)^2 \left(\frac{2\pi}{a_0}\right)^2 \\ &\quad \times \left(\frac{10\gamma}{\alpha^3} - \frac{\beta^2}{2\alpha^4}\right) \end{aligned} \quad (7a)$$

$$\begin{aligned} \frac{-4\pi^3}{3} {}^{(3)}\kappa^{123} \cdot 6i &= \frac{-4\pi^3}{3} 6ic^{123} a_0^{-3} \\ &= i(k_B T)^2 \left(\frac{2\pi}{a_0}\right)^3 \frac{\beta}{\alpha^3} \end{aligned} \quad (7b)$$

$$\begin{aligned} \frac{2\pi^4}{3} {}^{(4)}\kappa^{1111} &= \frac{2\pi^4}{3} d^{1111} a_0^{-4} \\ &= -(k_B T)^3 \left(\frac{2\pi}{a_0}\right)^4 \left(\frac{\gamma}{4} + \frac{2}{5} \frac{\delta}{\alpha^4}\right) \end{aligned} \quad (7c)$$

$$\begin{aligned} \frac{2\pi^4}{3} {}^{(4)}\kappa^{1122} \cdot 6 &= \frac{2\pi^4}{3} 6d^{1122} a_0^{-4} \\ &= (k_B T)^3 \left(\frac{2\pi}{a_0}\right)^4 \left(\frac{2\gamma}{\alpha^4} - \frac{6}{5} \frac{\delta}{\alpha^4} - \frac{\beta^2}{2\alpha^5}\right). \end{aligned} \quad (7d)$$

Solving (7b)–(7d) for β , γ , and δ gives

$$\beta = -\frac{c^{123}}{(k_B T)^2} \alpha^3 \quad (8a)$$

$$\gamma = -\frac{\alpha^4}{(k_B T)^3} \left[\frac{d^{1111} + 2d^{1122}}{40} - \frac{\alpha}{k_B T} \frac{(c^{123})^2}{10} \right] \quad (8b)$$

$$\delta = -\frac{\alpha^4}{(k_B T)^3} \left[\frac{d^{1111} - 3d^{1122}}{24} + \left(\frac{\alpha}{k_B T}\right) \frac{(c^{123})^2}{4} \right] \quad (8c)$$

and substitution into (7a) yields a cubic equation for α ,

$$\begin{aligned} \alpha^3 - \alpha^2 \frac{(d^{1111} + 2d^{1122})}{2(c^{123})^2} (k_B T) + \alpha \frac{b^{11}(k_B T)^2}{(c^{123})^2} \\ - \frac{(k_B T)^2}{(c^{123})^2} = 0, \end{aligned} \quad (8d)$$

which may be solved in the usual manner. Thus, from a higher cumulant refinement, the parameters α , β , γ , and δ of the one-particle potential may be determined.

When $T < \theta_D$, quantum statistical effects must be considered. For the aluminum [Al(4)] at the $\bar{4}3m$ site in VAl_{10} , $b^{11} = 0.042$ (2) \AA^2 at 100 K, so $\theta_M \simeq 110$ K and the high-temperature OPP model is no longer valid. According to Mair & Wilkins (1976), the quantum statistical OPP temperature factor, to fourth order in \mathbf{h} , is given by

$$\begin{aligned} T(\mathbf{h}) = \exp \left[-\left(\frac{2\pi}{a_0}\right) \mathbf{h}^2/4b \right] &\left[1 - \left(\frac{5}{4} \frac{\bar{c}}{b_0^3} + \frac{a^2}{32b_0^4}\right) \right. \\ &\times \left(\frac{2\pi}{a_0}\right)^2 \mathbf{h}^2 - \frac{ia}{8b_0^3} \left(\frac{2\pi}{a_0}\right)^3 h_1 h_2 h_3 \\ &+ \left(\frac{\bar{c}}{16b_0^4} + \frac{a^2}{320b_0^5}\right) \left(\frac{2\pi}{a_0}\right)^4 \mathbf{h}^4 \\ &+ \left(\frac{\bar{d}}{16b_0^4} - \frac{1}{128} \frac{a^2}{b_0^5}\right) \left(\frac{2\pi}{a_0}\right)^4 \\ &\left. \times (h_1^4 + h_2^4 + h_3^4 - \frac{3}{5} \mathbf{h}^4) \right] \end{aligned} \quad (9)$$

where

$$\begin{aligned} \alpha &\equiv m\omega^2, \quad a = -\frac{\beta}{\hbar\omega} a_3^{(1)} \\ b_0 &= \frac{m\omega}{\hbar} \tanh\left(\frac{1}{2} \frac{\hbar\omega}{k_B T}\right) \\ b &= b_0 - a_{22} - \bar{c}_{12}, \quad \bar{c}_{12} = -\frac{5}{3} \frac{\gamma}{\hbar\omega} c_2^{(1)} \\ \bar{c} &= \bar{c}_{14} + \frac{1}{5} a_{24}, \quad \bar{c}_{14} = -\frac{\gamma}{\hbar\omega} c_4^{(1)} \\ \bar{d} &= \bar{d}_{14} - \frac{1}{2} a_{24}, \quad \bar{d}_{14} = -\frac{\delta}{\hbar\omega} d_4^{(1)}, \end{aligned} \quad (10)$$

which converges to (6) as the reduced temperature $\hbar\omega/k_B T$ goes to zero (high-temperature limit). The terms $a_3^{(1)}$, $a_{22}^{(2)}$, $a_{24}^{(2)}$, $c_2^{(1)}$, and $c_4^{(1)} = d_4^{(1)}$ are functions of

the reduced temperature defined by Mair & Wilkins (1976). From the form of this equation, it is obvious that the set of four quantum statistical equations corresponding to (7a)–(7d) can no longer easily be solved in the same manner. In this case, the values of α , β , γ , and δ have been determined by a least-squares refinement using the values of b^{11} , c^{123} , d^{1111} , and d^{1122} as observations.

As formulated, the values describing the potential should be independent of temperature, except for some possible softening due to expansion of the lattice as the temperature is increased (Willis, 1969). It is then straight forward to include cumulants determined at more than one temperature as observations and refine a single set of temperature-independent α , β , γ , and δ

values. By weighting the least-squares fit by $\omega_i = 1/\sigma^2$, the uncertainty in the values of the cumulants is properly accounted for.

Experiment

X-ray intensity measurements were collected with an Enraf–Nonius CAD-4F diffractometer at the State University of New York at Buffalo using a single crystal of VAl_{10} from the same batch as the crystal in the original structure determination (Brown, 1957). Experimental parameters are listed in Table 1. Further details of the experiment will be reported elsewhere (Kontio, Stevens, Boehme & Coppens, 1982).

Previous studies found occupancies of 0.1 (Brown, 1957) and 0.5 (Ray & Smith, 1957) for the aluminum atom at the Al(4) site. Therefore, in this study the occupancy of the site was varied along with positional and anisotropic thermal parameters of all atoms (as allowed by symmetry), yielding an occupancy of 0.84 (1) at 100 K, which corresponds to a stoichiometry of $\text{VAl}_{10.420(5)}$. This is in good agreement with a composition of $\text{VAl}_{10.41}$ calculated from the analysis (15.3% V, 84.6% Al) reported by Brown (1957). To avoid bias from the valence electron distribution the thermal parameters have been determined in refinements in which only high-order data ($\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$) have been included. Results of the various refinements are summarized in Table 2. A plot of the

Table 1. Summary of experimental parameters

Space group	<i>Fd3m</i>	
Z	16	
$\lambda(\text{MoK}\alpha_1)$	0.70930	
Crystal shape	Regular octahedron	
	0.40 mm (maximum dimension)	
Data set	I	II
Temperature	293 (1) K	100 (5) K
Cell constant, a_0	14.502 (5) Å	14.471 (2) Å
N_{obs} (total)	5768	6406
N_{obs} (unique)	1249	1509
$(\sin \theta/\lambda)_{\text{max}}$	1.22 Å ⁻¹	1.36 Å ⁻¹
R_I^*	2.05%	2.22%

$$* R_I = \sum (\langle I \rangle - I_i) / \sum I_i$$

Table 2. Least-squares refinement results

<i>T</i> = 100 K				
Sin θ/λ range (Å ⁻¹)	0.0–1.36	0.65–1.36	0.65–1.36	0.65–1.36
Al(4)	at <i>x</i> = 0.375			
Occupancy	0.84 (1)	0.84	0.84	0.84
b^{11} (Å ²)	0.0481 (9)	0.0495 (12)	0.0464 (10)	0.0417 (20)
c^{123} (Å ³)			0.0049 (5)	0.0045 (2)
d^{1111} (Å ⁴)				–0.0036 (6)
d^{1122} (Å ⁴)				0.0011 (1)
N_{obs}	1509	1314	1314	1314
N_v	17	16	17	19
<i>R</i> (%)	3.00	3.02	2.89	2.78
R_w (%)	4.15	3.76	3.57	3.42
GOF	1.86	1.61	1.53	1.47
<i>T</i> = 293 K				
Sin θ/λ range (Å ⁻¹)	0.0–1.22	0.65–1.22	0.65–1.22	0.65–1.22
Al(4)	at <i>x</i> = 0.375			
Occupancy	0.85 (1)	0.85	0.85	0.85
b^{11} (Å ²)	0.0738 (12)	0.0929 (26)	0.0707 (15)	0.0547 (94)
c^{123} (Å ³)			0.0104 (18)	0.0097 (7)
d^{1111} (Å ⁴)				–0.0118 (3)
d^{1122} (Å ⁴)				0.0024 (5)
N_{obs}	1059	859	859	859
N_v	17	16	17	19
<i>R</i> (%)	3.85	4.76	4.68	4.64
R_w (%)	4.04	3.86	3.67	3.58
GOF	1.74	1.48	1.41	1.37

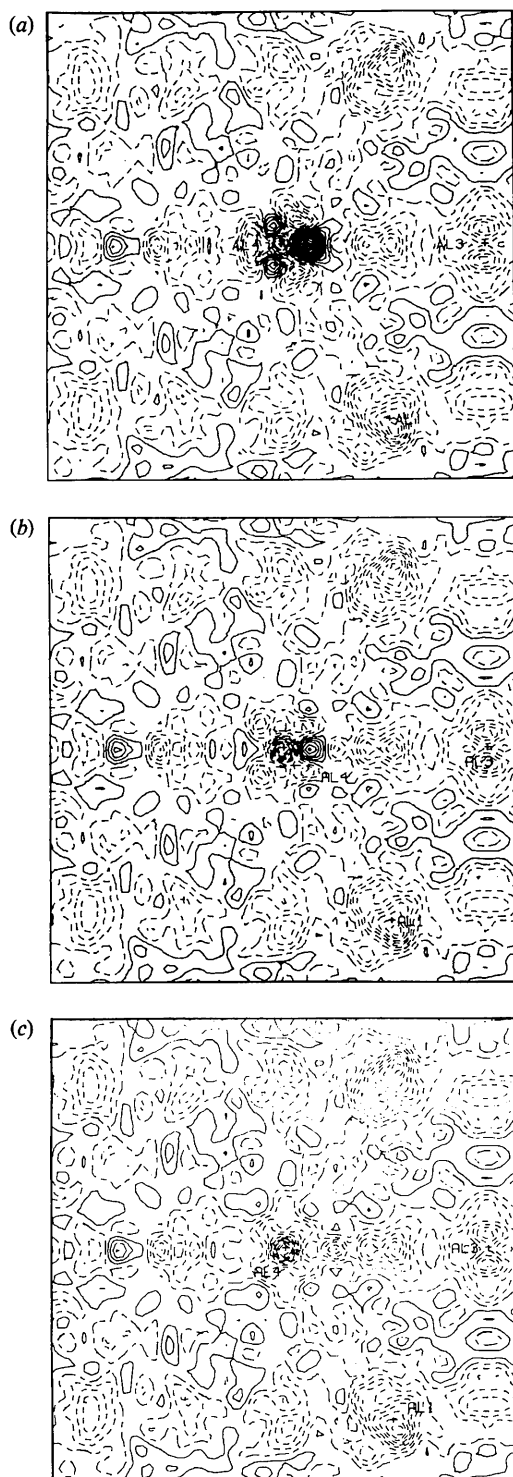


Fig. 2. Plot of the difference electron density distribution at 100 K in a plane defined by the Al(4), Al(3) and Al(1) positions and centered at the Al(4) site. Contours are plotted at $0.20 e \text{ \AA}^{-3}$ intervals, with zero and negative contours broken. (a) After refinement including second cumulant thermal parameters only. (b) After refinement including second and third cumulants. (c) After refinement including second, third, and fourth cumulants.

difference electron density at the Al(4) site following this refinement is shown in Fig. 2(a). Large peaks are located near the Al(4) site in the $\langle 111 \rangle$ directions indicating a large component of the probability distribution arising from a third-order term in the temperature factor.

Fig. 2(b) shows the difference density after refinement including the c^{123} parameter. Although most of the residual density has been accommodated there still remains a sharp feature near the Al(4) site. Inclusion of the fourth-order terms d^{1111} and d^{1122} removes this feature, leaving only a slight negative region centered on the Al(4) site (Fig. 2c). Very similar maps are obtained using the room-temperature data.

Results

Solving the high-temperature equations (8a)–(8d) using the values of b^{11} , c^{123} , d^{1111} , and d^{1122} given in Table 2 yields the values of α , β , γ , and δ listed in Table 3. Also listed in Table 3 are the corresponding values obtained by solving the quantum statistical equations (9), (10) by least-squares refinement. Although the potential parameters derived at the two temperatures are somewhat different, they are physically reasonable. The signs are consistent, and the potentials remain positive as $|\mathbf{u}| \rightarrow \infty$.

The negative sign of β corresponds to a softening of the potential in the $\langle 111 \rangle$ direction, towards the nearest-neighbor Al(3) atoms and away from three Al(1) atoms arranged about the $\langle \bar{1}\bar{1}\bar{1} \rangle$ direction. This is consistent with peaks in the difference density map, Fig. 2(a), and opposite to the result of the calculation reported by Caplin & Nicholson (1978) which predicts a minimum of the potential in the $\langle \bar{1}\bar{1}\bar{1} \rangle$ direction.

In Figs. 3(a) and (b) the resulting potentials at both temperatures are compared with the corresponding harmonic potentials. In Fig. 3(c) the potential at 100 K as obtained with the quantum statistical equation is

Table 3. *OPP parameters obtained from the high-temperature (HT) and quantum statistical (QS) equations*

α , β , γ , and δ are given in units of J \AA^{-2} , J \AA^{-3} , J \AA^{-4} , and J \AA^{-4} respectively, all $\times 10^{20}$.

	HT	QS
$T = 100 \text{ K}$		
α	2.33 (16)	2.36 (16)
β	-2.98 (59)	-3.09 (60)
γ	0.77 (9)	0.80 (9)
δ	2.26 (52)	2.38 (53)
$T = 293 \text{ K}$		
α	4.05 (29)	4.05 (29)
β	-3.96 (84)	-3.97 (84)
γ	1.11 (33)	1.12 (33)
δ	2.26 (78)	2.27 (78)

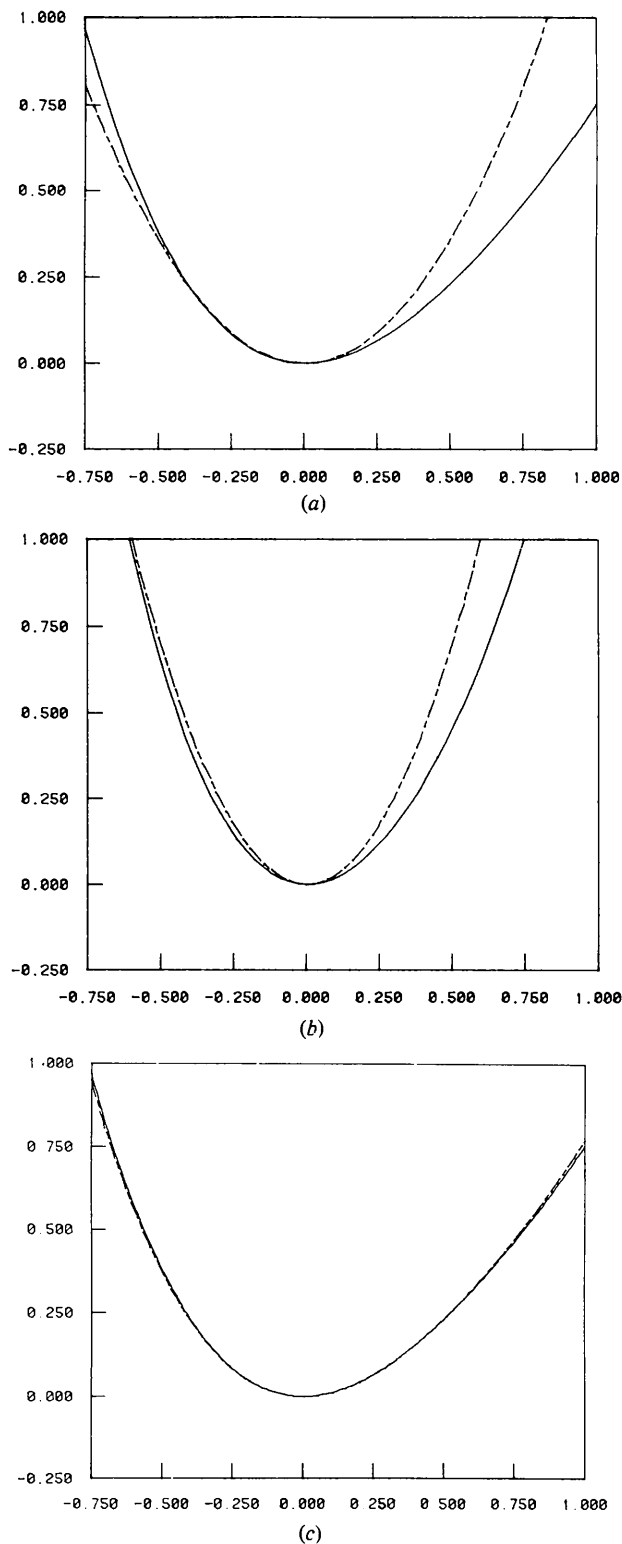


Fig. 3. Plot of the one-particle potential along the $\langle 111 \rangle$ direction as obtained from the quantum statistical equation. The corresponding harmonic potential is given as a broken line. (a) 100 K. (b) Room temperature. (c) Comparison of QS and HT (broken line) results at 100 K.

compared with the result in the high-temperature limit. The difference in the potential is found to be slight for $\theta_M/T \approx 0.9$ at 100 K.

The results of a refinement in which the cumulant temperature factors at both temperatures are fit with a single set of OPP parameters are given in Table 4 along with the observed and calculated values of the cumulants. The fit is reasonably good with a r.m.s. σ/Δ value of ~ 5 . However, a systematic trend is observed, with the magnitude of the observed values always being less than the calculated values at room temperature and greater at 100 K. The high-order terms in the temperature factor thus show a lower dependence on temperature than predicted by the OPP model.

The Al-Al distances in the cage change relatively little going from 100 to 293 K. It therefore seems unreasonable to attribute the observed behavior of the temperature factors to a significant change in the potential. The deviation from the usual expression for the OPP temperature factor observed here is more likely to be due to the unusually large cubic and quartic terms. In this case, the expansion of (4) about the second-order term is no longer valid (see Coppens, 1980, for another example). In fact, to produce a double-well potential similar to the one reported by Caplin & Nicholson (1978) a negative value of α' is required. Unfortunately, the required integrals for the calculation of (3) and (4), for large β , γ , or δ are not easily evaluated. An analysis using numerical integration, however, is possible (Stevens & Kontio, 1982). Alternative forms of the potential which are not expansions about the harmonic case (Mair, 1982) may also be more successful for highly anharmonic systems.

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Table 4. OPP parameters from joint refinement on cumulants at both temperatures using QS equation

b^{11} , c^{123} , d^{1111} , and d^{1122} are given in units of \AA^2 , \AA^3 , \AA^4 , and \AA^4 , respectively.

α , β , γ , and δ are given in units of J \AA^{-2} , J \AA^{-3} , J \AA^{-4} , and J \AA^{-4} respectively, all $\times 10^{20}$.

	Observed	Calculated	σ
b_{293}^{11}	0.0547	0.0573	0.0094
c_{293}^{123}	0.0097	0.0101	0.0007
d_{293}^{1111}	-0.0118	-0.0122	0.0003
d_{293}^{1122}	0.0024	0.0142	0.0005
b_{100}^{11}	0.0417	0.0317	0.0020
c_{100}^{123}	0.0045	0.0011	0.0002
d_{100}^{1111}	-0.0036	-0.0005	0.0006
d_{100}^{1122}	0.0011	0.0001	0.0001
α	3.80 (11)		
β	-3.25 (30)		
γ	0.97 (6)		
δ	1.33 (30)		

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Intensity Formula for Single Bragg Reflection, Including Corrections for the Effects of Extinction and Thermal Diffuse Scattering

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Abstract

Two existing intensity formulae of a single Bragg reflection which include corrections for the effects of extinction and thermal diffuse scattering are discussed on the basis of energy-transfer equations for secondary extinction. It is shown that one of them, which has been recommended by Cooper & Rouse [In *Thermal Neutron Diffraction* (1970), edited by B. T. M. Willis, Oxford Univ. Press], is not valid.

1. Introduction

In the accurate analysis of density distribution by means of X-ray and neutron diffraction from single crystals, the most remarkable progress made in the last decade comes from the fact that the observed inte-

grated intensities can now be corrected for extinction and thermal diffuse scattering. In the actual analysis, at present, the integrated Bragg intensity is represented by two slightly different formulae in which corrections for the effects of absorption, polarization, extinction and thermal diffuse scattering are included. However, there has been no discussion about the difference between these two formulae, except for a comment given by Cooper & Rouse (1970). Consequently the choice seems to have depended upon the convenience to the analyst. The purpose of this paper is to reconsider what sort of scattering process is really represented by each formula and to recommend that one of them be used for the refinement as representing more plausibly the scattering process.

2. Expressions for the integrated Bragg intensity

In corrections for the effect of extinction as well as thermal diffuse scattering to the observed integrated

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