

Single Crystal Structure Study of α -Ag₂HgI₄: Evidence for Anharmonic Vibration*

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X-ray diffraction intensities have been measured for two single crystals of α -Ag₂HgI₄ at 66°C using MoK α radiation monochromated by reflection from a 002 graphite face. It is found that improvement on the simple zincblende description could be made either by considering all ions to be displaced by about 0.25 Å along tetrahedral directions or by applying existing anharmonic theory for thermal motions. Although all ions are on appropriate sites to contribute to anharmonic effects, only a single anharmonic parameter, representing a weighted difference of two individual parameters, could be evaluated. The anharmonic treatment gives substantially better agreement for critical reflections of the class $h + k + l = 4n \pm 1$.

Introduction

There exists a well-recognized need for single crystal structural data for cation-disordered structures with simple anion arrangements (face-centered or body-centered cubic). Many of these compounds are solid electrolytes comprising some of the oldest and best ionic conductors known, e.g., AgI and Ag₂HgI₄. A detailed knowledge of their structures would be highly desirable for understanding their unusual properties, particularly their conductivity behavior; yet in practically all cases the structural characterization has been for polycrystalline material only. Generally, there is considerable difficulty in obtaining single crystals of the high temperature conducting form. In the case of Ag₂HgI₄, however, a single crystal of the conducting cubic α -phase results from heating a single crystal of the tetragonal β (room temperature) phase through the transition temperature at 50°C (1, 2). Accordingly, we have undertaken a single crystal X-ray diffraction investigation of α -Ag₂HgI₄ after the successful growth of crystals of β -Ag₂HgI₄ and a study of its struc-

ture and transformation behavior (2).

There is general acceptance of the original Ketelaar (3) description of α -Ag₂HgI₄ as a zincblende-type structure with random distribution of the three cations in the four tetrahedral sites of that structure. A modification of that description was suggested by Hoshino (4) from a quantitative X-ray intensity study of polycrystalline specimens. Hoshino pointed out that abnormally high temperature factors are called for with the zincblende model and that a better accounting of the "anomalous intensity" behavior would be given by a model that allowed the cations to be displaced along tetrahedral directions from the ideal positions of the zincblende structure. More significantly, Hoshino remarked that the meaning of such a model could be the possibility of anharmonic vibrations associated with the cations.

The availability of single crystals has allowed us to make a more quantitative and definitive assessment of the following features of the α -Ag₂HgI₄ structure: (1) the adequacy of the simple Ketelaar model; (2) the possible occupancy by cations of sites other than the tetrahedral ones; and (3) the nature of the thermal motion, particularly the possibility of anharmonic motion.

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Experimental

The preparation of crystals has been described in our previous publication on β - Ag_2HgI_4 (2). The tendency of crystals to deteriorate, especially when heated in air, made for considerable difficulty in obtaining accurate intensity data for the α -phase. It was found necessary to enclose crystals in thin-walled capillaries, thereby increasing the background sufficiently to prohibit any serious study of diffuse scattering. A greater annoyance was the necessity to examine many crystals since many of them would show changes in intensity and in physical appearance before completion of the data collection at temperatures above 50°C. Two crystals proved satisfactory with respect to stability and provision of a complete set of intensity data. Both crystals were needlelike with [110] as the needle axis and {111} and {100} as principal faces (in terms of the cubic cell of the α -phase). One crystal (No. 1) was 0.0835 cm long with a mean diameter of 0.008 cm; the dimensions of the other crystal (No. 2) were 0.038 cm for length and 0.004 cm for mean diameter. Temperatures above 50°C were attained by blowing a heated stream of air over the specimen.

X-ray intensity measurements were made at 63–69°C for all reflections within one half of the sphere of reflection of radius of $\sin \theta/\lambda = 0.77$ with a GE 490 automated diffractometer and $\text{MoK}\alpha$ radiation (0.7107 Å) monochromatized by reflection from the (002) face of a graphite crystal. The θ – 2θ scan mode was used with steps of $0.05^\circ 2\theta$ over a scan range of 3° plus the α_1 – α_2 dispersion. Twenty-eight independent reflections were examined. Absorption corrections were applied with the program HORSE (5) using $\mu = 310.5 \text{ cm}^{-1}$ and equivalent reflections were averaged to give the final data set. A disagreement index (6),

$$R_F = \sum_n \sum_i |F_n - F_{i,n}| / \sum_{n,i} F_n$$

was 0.053 for Crystal 1 and 0.045 for Crystal 2;

$$F_n = \sum w_i F_i / \sum W_i$$

and the summation is over each of the i measurements of the unique reflection F_n . If the following criterion was met, F_i was

accepted as observed: $(I-B) > 2\sigma(I) = 2[1 + B + (0.02I)^2]$, where I and B are net and background counts, respectively. All 28 independent reflections were observed for Crystal 2, but only 25 of these were considered as observed for Crystal 1. The lattice parameter for $66 \pm 3^\circ\text{C}$ was $a = 6.35(1) \text{ \AA}$ for both crystals.

Analysis of data—Harmonic Approximation

After application of Lorentz-polarization corrections the resultant F^2 or F values were used in least-squares analyses, complemented by Fourier and difference Fourier syntheses. The weights were derived from $\sigma(I)$ which was determined by the deviations from the mean value for equivalent reflections as well as by the counting statistics.

The scattering factors were those of Cromer and Waber (7) for Ag^+ , Hg^{2+} and I^- , corrected for anomalous dispersion according to Cromer (8). Scattering factors for neutral atoms were also tried, but they gave no significant difference in the structural parameters. Generally, an average scattering factor for the cation (f_M) was used, i.e.,

$$f_M = \frac{2f_{\text{Ag}^+} + f_{\text{Hg}^{2+}}}{4},$$

as well as an averaged dispersion correction. In some least-square calculations the two cations were treated separately and only the parameters of Ag^+ were varied while the Hg^{2+} parameters retained the values found for Ag^+ in the previous cycle and the process continued until convergence. The two procedures gave essentially identical results.

The Ketalaar Model

The adequacy of the simple zincblende structure type description (i.e., with I^- at (000) + F.C., three cations at (1/4, 1/4, 1/4) + F.C.; and isotropic thermal parameters) was tested first. Apparent refinement was attained but with large thermal parameters and with R values that were not excessively large, but larger than expected from the quality of the data. The results for the two crystals were:

	$B_I(\text{\AA}^3)$	$B_M(\text{\AA}^3)$	R	R_w
Crystal 1	5.1	7.9	0.055	0.079
Crystal 2	4.8	7.6	0.052	0.076

B_M is the thermal parameter for the averaged cation;

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \frac{\{\sum W(|F_o| - |F_c|)^2\}^{1/2}}{(\sum W|F_o|^2)^{1/2}}$$

No improvement by way of reduction of the discrepancy indices could be made by various modifications of the simple zincblende model. These included deviations from stoichiometry either in variations of the Ag⁺/Hg²⁺ ratio or the ratio of cations to iodide ions; use of neutral scattering factors; and inclusion of octahedral or the interstitial tetrahedral sites for occupancy by cations.

Nonetheless, a better model seemed to be called for upon detailed examination of the calculated structure factors. Most notable was a systematic discrepancy with observed $|F|$ for reflections with h, k, l odd. In all cases, the observed $|F|$ was too small for $h + k + l = 4n + 1$ and too large for $h + k + l = 4n - 1$. Attempted refinement with h, k, l odd reflections alone did not reduce R below 0.050 in contrast to the situation for the reflections with h, k, l even. In particular, for hko data alone, the R values for crystals 1 and 2, respectively, were 0.029 and 0.036, but the parameters from that refinement then yielded R values of 0.071 and 0.072 for hkl odd data.

The Displacement Model

A more satisfactory model suggested by Hoshino (4), allows the ions to be displaced along tetrahedral directions away from the

special positions of (000) and (1/4, 1/4, 1/4).

The fourfold positions 4(a) and 4(c) of space group $F\bar{4}3m$ are thereby replaced by the 16-fold positions 16(e), $xxx, x\bar{x}\bar{x}, \bar{x}x\bar{x}, \bar{x}\bar{x}x$. Presumably, then, there is a statistical distribution of the ions among these sites.

For our single crystal data, substantially better agreement between observed and calculated structure factors was attained when both metal and iodide ions were considered to be in the 16-fold positions. Hoshino for his powder data had considered displacement of the cations only and arrived at a value of 0.45 Å for the magnitude of the displacement. We find displacements of about half that magnitude (0.22–0.27 Å) for the iodide ion as well as the cations. As expected, the thermal parameters are smaller when the ions are displaced from the ideal positions. The isotropic B values range from 2.5 to 3.0 Å³ for I⁻ and 6.0–6.6 Å³ for the cations. The best intensity agreement is attained, however, when anisotropic thermal parameters are used. The results of anisotropic least squares refinements are given in Table I and the structure factors in Table II.

The displacement model, then, is quite satisfactory in accounting for the X-ray intensities of α -Ag₂HgI₄, much more so than the ideal zincblende type structure. It represents a physical description that is not impossible and one that has been suggested for the high-temperature structures of CuI (9) and CuBr (10). Nonetheless, a literal acceptance

TABLE I

COORDINATE AND THERMAL PARAMETERS—DISPLACEMENT MODEL OF α -Ag₂HgI₄

Space group $F\bar{4}3m - T_d^2$
 $4I^-$ and $4M$ in $16e - xxx, x\bar{x}\bar{x}, \bar{x}x\bar{x}, \bar{x}\bar{x}x$
 $M = (2Ag^+ + Hg^{2+})/4$

	x	$\beta_{11} = \beta_{22} = \beta_{33}$	$\beta_{12} = \beta_{13} = \beta_{23}$
Crystal 1	I ⁻ -0.025 (1)	0.0150 (10)	-0.0019 (10)
	M 0.275 (1)	0.0373 (40)	0.0076 (58)
Crystal 2	I ⁻ -0.0207 (5)	0.0198 (4)	0.0033 (10)
	M 0.275 (2)	0.0412 (31)	0.0132 (48)

Anisotropic temperature factors are expressed as:

$$\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$$

TABLE II
STRUCTURE FACTORS ($\times 10$)— α -Ag₂HgI₄—DISPLACEMENT MODEL ($F_{000} \times 10 = 3870$)

<i>h k l</i>	Crystal 1		Crystal 2	
	$ F_o $	$ F_c $	$ F_o $	$ F_c $
1 1 1	2293	2195	2042	2185
2 0 0	407	378	422	383
2 2 0	2227	2248	2167	2231
3 1 1	1428	1363	1405	1352
2 2 2	410	353	380	346
4 0 0	1431	1469	1479	1446
3 3 1	937	920	879	909
4 2 0	317	326	319	323
4 2 2	1023	1006	997	1001
3 3 3	722	705	704	699
5 1 1	609	646	633	641
4 4 0	734	698	710	703
5 3 1	470	474	471	471
4 4 2	209	231	218	204
6 0 0	208	231	218	248
6 2 0	468	473	497	477
5 3 3	300	282	295	289
6 2 2	155	179	164	175
4 4 4	372	347	350	355
5 5 1	228	214	225	224
7 1 1	231	222	240	233
6 4 0	117	131	124	123
6 4 2	258	236	258	249
5 5 3	196	214	191	198
7 3 1	155	146	160	162
8 0 0			178	162
7 3 3			141	135
8 2 0			83	89
	$R = 0.041$		$R = 0.035$	
	$R_w = 0.054$		$R_w = 0.044$	

of this description is not demanded. A valid interpretation is that the specific location of four atom centers tetrahedrally about an ideal position is merely an approximate way of describing a more general concentration of electron density along the tetrahedral directions. In particular, the possibility of anharmonic motion comes to mind. Anharmonic vibrations have been found recently (11, 12) to be present in several crystals, especially for ions situated on sites of $\bar{4}3m$ symmetry, as is the case for α -Ag₂HgI₄. As a matter of fact, the first purported evidence for anharmonic motion in CaF₂ (13) was based mainly on the

fact that a tetrahedral displacement effect of the fluorides in sites of $\bar{4}3m$ symmetry was indicated. Also, Hoshino (4) made the specific suggestion that for α -Ag₂HgI₄, the displacement effects might be attributable to anharmonicity although no quantitative treatment of anharmonic effects was then available. Since then, there has been evolved a theoretical treatment of anharmonic motion by Willis and co-workers (11) and by Dawson (12) which has been applied most extensively to fluorite structures. We have employed the same treatment in considering anharmonic motion in α -Ag₂HgI₄.

Anharmonic Analysis

A detailed exposition of the theory of anharmonic effects and the application to zincblende structures has been given by Cooper, Rouse, and Fuess (14). We have followed this treatment with the necessary modifications arising from our use of complex X-ray scattering factors rather than real nuclear scattering amplitudes. The explicit structure factor expressions and the definitions of terms are given in the appendix. The main feature of the anharmonic analysis is that significant contributions to X-ray intensities from anharmonicity are to be expected only for reflections with hkl all odd for which the anharmonic contribution involves the parameter $\beta' = \beta_I - \beta_M(\alpha_I/\alpha_M)^3$ and the index product hkl . Furthermore, the sign of the contribution to the intensity is dependent on whether $h + k + l = 4n + 1$ or $4n - 1$. The X-ray intensity data for α -Ag₂HgI₄ comply with these conditions: (1) the intensities of reflections with one index zero (and hence, $hkl = 0$) are accounted for satisfactorily by the usual harmonic analysis; (2) the largest discrepancies between calculated and observed intensities on the harmonic basis occur for the odd index reflections; (3) in each case, on the harmonic basis, the calculated intensity is too small when $h + k + l = 4n + 1$ and too large when $h + k + l = 4n - 1$. The intensity discrepancies for h, k, l odd were minimized by introducing β' as indicated by Eq. 17 in the Appendix. A value of $\beta' = 2.6 \times 10^{-12}$ erg/Å³ for Crystal 1 and $\beta' = 2.4 \times 10^{-12}$ erg/Å³ for

Crystal 2 reduced the respective R values from 0.072 to 0.032 and from 0.071 to 0.032, i.e., to R values comparable to those for hko reflections (0.029 and 0.036). The β' values were determined not from a least square analysis but on the basis of the smallest resulting R for different values of β' , varied in increments of 0.2×10^{-12} erg/Å³. The list of the final $|F|$ values for the anharmonic treatment for both crystals is given in Table III and the values of the pertinent parameters in Table IV.

A critical test of anharmonic effects concerns the relative F values of pairs of reflections

TABLE III

STRUCTURE FACTORS ($\times 10$) FOR ANHARMONIC MODEL
($F_{000} \times 10 = 3870$)

hkl	Crystal 1		Crystal 2	
	$ F_o $	$ F_c $	$ F_o $	$ F_c $
2 0 0	407	369	422	367
2 2 0	2227	2229	2167	2245
4 0 0	1431	1452	1479	1478
4 2 0	317	311	319	314
4 4 0	734	685	710	712
6 0 0	208	223	218	228
6 2 0	468	481	497	506
6 4 0	117	146	124	154
8 0 0	—	—	178	196
8 2 0	—	—	83	99
2 2 2	410	340	380	341
4 2 2	1023	989	997	1012
4 4 2	209	231	218	230
6 2 2	155	186	164	190
4 4 4	372	358	350	366
6 4 2	258	255	258	266
1 1 1	2293	2255	2042	2092
3 1 1	1428	1396	1405	1326
3 3 1	937	900	879	880
3 3 3	722	725	704	694
5 1 1	690	646	633	634
5 3 1	470	487	471	474
5 3 3	300	285	295	291
5 5 1	228	229	225	230
7 1 1	231	248	240	258
5 5 3	196	224	191	218
7 3 1	155	175	160	172
7 3 3	—	—	141	157
	$R = 0.037$		$R = 0.037$	
	$R_w = 0.033$		$R_w = 0.038$	

TABLE IV

PARAMETER VALUES FOR ANHARMONIC MODEL

	Crystal 1	Crystal 2	
B_I	4.8 (0.2)	4.6 (0.2)	Å ³
B_M	7.6 (0.7)	7.4 (0.6)	Å ³
α_I	0.77 (0.16)	0.80 (0.16)	$\times 10^{-12}$ erg Å ⁻²
α_M	0.49 (0.06)	0.50 (0.16)	$\times 10^{-12}$ erg Å ⁻²
β'	2.6 (0.2)	2.4 (0.2)	$\times 10^{-12}$ erg Å ⁻³

occurring at the same $\sin\theta/\lambda$. These are, of course, equivalent in the harmonic case in the absence of any anomalous dispersion effects, but can be quite different according to anharmonic theory. There are three such pairs in the α -Ag₂HgI₄ data. Their $|F|$ values are given in Table V where it is evident that the observed differences are real and correspond to those given by the anharmonic treatment, although the pair (551), (711) is borderline. On the other hand, the small differences in the harmonic treatment, due to dispersion corrections, are in the wrong direction.

Discussion

Both the static displacive model and the anharmonic treatment account for the observed structure factors more satisfactorily than the strict zincblende model with harmonic motions. Although the R values are quite close to one another for the two cases, the anharmonic treatment is preferable on physical grounds. A definitive choice could be made on the basis of intensity behavior with temperature, but we found it impractical to make such studies for α -Ag₂HgI₄ because of the increasing tendency of crystals to deteriorate with increase of temperature. There is little doubt, however, that the anharmonic model is a satisfactory one for α -Ag₂HgI₄.

The critical β' parameter appears reasonable as to magnitude and sign. There is no independent basis for deciding on its absolute magnitude, but the value for α -Ag₂HgI₄ is of the same order as that for ZnS and ZnTe (14) for which β' is 4×10^{-12} erg Å⁻³. Although the individual β' s could not be evaluated, the site symmetry indicates β_I is positive and

TABLE V
 F_{hkl} ($\times 10$) FOR PAIRS OF REFLECTIONS WITH EQUAL $h^2 + k^2 + l^2$

hkl	Crystal 1			Crystal 2		
	$ F_o $	$ F_c _A^a$	$ F_c _H^b$	$ F_o $	$ F_c _A^a$	$ F_c _H^b$
{ 3 3 3	722 (9)	725	590	704 (13)	694	623
{ 5 1 1	609 (18)	646	613	633 (13)	634	647
{ 7 1 1	231 (8)	248	212	240 (5)	253	235
{ 5 5 1	228 (4)	229	220	225(7)	233	243
{ 5 5 3	196 (4)	224	154	191 (9)	213	174
{ 7 3 1	155 (5)	175	159	160 (7)	172	179

^a $|F_c|_A$ —calculated structure factor—anharmonic

^b $|F_c|_H$ —calculated structure factor—harmonic

β_M is negative and that $\beta' = \beta_I - \beta_M(\alpha_I/\alpha_M)^3$ is positive as found. It would seem that the individual β 's could be obtained if rather accurate intensities for reflections with $h + k + l = 4n + 2$ were available. An attempt to utilize our data for $h + k + l = 4n + 2$ reflections was not successful due to the smallness of the intensity values and their greater inaccuracy.

The α values are quite low, or conversely the B values are quite high. The significance of such high values of B as are found for $\alpha\text{-Ag}_2\text{HgI}_4$ may be somewhat questionable in terms of simple Debye-Waller theory. Perhaps it is more meaningful to focus on the low value of α as indicating a large mean-square displacement of the atoms and to regard the relation $B_j = (8\pi^2 k_B T / \alpha_j)$ as merely a formal way of relating to the usual harmonic treatment. It is, of course, inherent in the anharmonic treatment, in contrast to the static displacive mode, that the relatively large B values of the harmonic treatment are retained (12).

At any rate, it is interesting that the anharmonic treatment can be successfully applied to a case where the B 's and the atomic displacements are so large. Heretofore, the demonstration of anharmonic effects has been for situations where the atomic displacements have been much less than considered here and where the isotropic B values have been about 1 \AA^2 or less. By the same token, it has been necessary to obtain intensities of

utmost accuracy to discern effects of anharmonicity. The considerably larger effects for $\alpha\text{-Ag}_2\text{HgI}_4$ have allowed the evaluation of anharmonic parameters with intensities that are not quite of the accuracy demanded in previous investigations.

With regard to the high mobility of silver ions in $\alpha\text{-Ag}_2\text{HgI}_4$ it is expected that the motions of the ions would be along the tetrahedral directions toward the empty octahedral sites since the migration of silver ions must proceed alternately through tetrahedral and octahedral sites (15). The passage of ions through centers of triangular faces would not require any close approach of Ag^+ to I^- . The minimum distance would be 0.942 of the normal Ag-I separation on the basis of the geometry of fixed positions. The approach distance could be even larger if cooperative motions of the iodide ions are taken into account.

It would be interesting to examine other simple structures that are good ionic conductors (e.g., AgI) for the existence of anharmonicity. It would seem reasonable that large anharmonic motions would be characteristic of these types of ionic conductors.

Appendix—Anharmonic Theory

Following the development of Cooper, Rouse, and Fuess (14) which uses the structure factor formalism of Dawson (12), the structure factor for a scattering vector $Q = 2\pi S$ is expressed in terms of the scattering factors

$f_j(Q)$ and the thermal vibration factors $T_j(Q)$ of the atom positions r_j in the unit cell as follows:

$$F(Q) = \sum_j f_j(Q) T_j(Q) \exp(iQ \cdot r_j). \quad (1)$$

In the general case both $f_j(Q)$ and $T_j(Q)$ may be complex and may be expressed as:

$$f_j(Q) = f_{cj}(Q) + if_{aj}(Q) \quad (2)$$

$$T_j(Q) = T_{cj}(Q) + iT_{aj}(Q), \quad (3)$$

where c and a identify centrosymmetric and anticosymmetric components, respectively.

Equation (1) then becomes

$$\begin{aligned} F(Q) &= \sum_j (f_{cj} + if_{aj})(T_{cj} + iT_{aj}) \exp(iQ \cdot r_j) \\ &= \sum_j [(f_{cj}T_{cj} - f_{aj}T_{aj})(\cos Q \cdot r_j + i \sin Q \cdot r_j) \\ &\quad - (f_{aj}T_{cj} + f_{cj}T_{aj})(\sin Q \cdot r_j - i \cos Q \cdot r_j)]. \end{aligned} \quad (4)$$

For the zinblende type structure, the structure factors take one of three forms, depending on the index sum $h + k + l$ being equal to $4n$, $4n + 2$, or $4n \pm 1$.

With the iodide ions at 000 and the cations, designated by M , at $1/4, 1/4, 1/4$, the following relationships apply to the three groups of reflections

(a) $h + k + l = 4n$

$\cos Q \cdot r_j = 1; \sin Q \cdot r_j = 0$ for all atoms

$$\begin{aligned} F(Q) &= 4[(f_{cI}T_{cI} - f_{aI}T_{aI}) \\ &\quad + (f_{cM}T_{cM} - f_{aM}T_{aM})] \\ &\quad + 4i[(f_{aI}T_{cI} + f_{cI}T_{aI}) \\ &\quad + (f_{aM}T_{cM} + f_{cM}T_{aM})]. \end{aligned} \quad (6)$$

(b) $h + k + l = 4n + 2$

$\cos Q \cdot r_I = 1, \sin Q \cdot r_I = 0$

$\cos Q \cdot r_M = -1, \sin Q \cdot r_M = 0$

$$\begin{aligned} F(Q) &= 4[(f_{cI}T_{cI} - f_{cM}T_{cM}) \\ &\quad - (f_{aI}T_{aI} - f_{aM}T_{aM})] \\ &\quad + 4i[(f_{aI}T_{cI} - f_{aM}T_{cM}) \\ &\quad + (f_{cI}T_{aI} - f_{cM}T_{aM})]. \end{aligned} \quad (7)$$

(c) $h + k + l = 4n \pm 1$

$\cos Q \cdot r_I = 1, \sin Q \cdot r_I = 0$

$\cos Q \cdot r_M = 0, \sin Q \cdot r_M = \pm 1$

$$\begin{aligned} F(Q) &= 4[(f_{cI}T_{cI} - f_{aI}T_{aI}) \\ &\quad \mp (f_{aM}T_{cM} + f_{cM}T_{aM})] \\ &\quad + 4i[(f_{aI}T_{cI} + f_{cI}T_{aI}) \\ &\quad \pm (f_{cM}T_{cM} - f_{aM}T_{aM})]. \end{aligned} \quad (8)$$

The contribution to the Bragg intensity by anharmonic thermal vibrations is then given as follows

$$\begin{aligned} h + k + l &= 4n \\ \Delta(F^*(Q)F(Q)/16) &= T_{aI}^2(f_{cI}^2 + f_{aI}^2) \\ &\quad + T_{aM}^2(f_{cM}^2 + f_{aM}^2) + 2T_{aI}T_{aM}(f_{aI}f_{aM} + \\ &\quad + f_{cI}f_{cM}) - 2(f_{aI}f_{cM} - f_{aM}f_{cI}) \\ &\quad \times (T_{aI}T_{cM} - T_{aM}T_{cI}). \end{aligned} \quad (9)$$

$$\begin{aligned} h + k + l &= 4n + 2 \\ \Delta(F^*(Q)F(Q)/16) &= T_{aI}^2(f_{cI}^2 + f_{aI}^2) \\ &\quad + T_{aM}^2(f_{cM}^2 + f_{aM}^2) - 2T_{aI}T_{aM}(f_{aI}f_{aM} + \\ &\quad + f_{cI}f_{cM}) + 2(f_{aI}f_{cM} - f_{aM}f_{cI}) \\ &\quad \times (T_{aI}T_{cM} - T_{aM}T_{cI}). \end{aligned} \quad (10)$$

$$\begin{aligned} h + k + l &= 4n \pm 1 \\ \Delta(F^*(Q)F(Q)/16) &= T_{aI}^2(f_{cI}^2 + f_{aI}^2) \\ &\quad + T_{aM}^2(f_{cM}^2 + f_{aM}^2) \pm 2T_{aI}T_{aM}(f_{aI}f_{cM} - \\ &\quad - f_{aM}f_{cI}) \pm 2(f_{aI}f_{aM} + f_{cM}f_{cI}) \\ &\quad \times (T_{aI}T_{cM} - T_{aM}T_{cI}). \end{aligned} \quad (11)$$

The only significant contribution by anharmonic terms occurs for the case $h + k + l = 4n \pm 1$ and is given almost completely by

$$\begin{aligned} \Delta(F^*(Q)F(Q)/32) &= \pm (f_{aI}f_{aM} + f_{cM}f_{cI}) \\ &\quad \times (T_{aI}T_{cM} - T_{aM}T_{cI}). \end{aligned} \quad (12)$$

This expression can then be rewritten in terms of the parameters α and β occurring in the one particle potential appropriate to tetrahedral site symmetry, which is

$$V_j(u) = V_{oj} + 1/2 \alpha_j(x^2 + y^2 + z^2) + \beta(xyz) \quad (13)$$

where x, y, z are the coordinates defining the instantaneous displacement u of the j th atom and x_j is related to the mean-square displacement of the atom in this potential. α_j is related to the conventional harmonic factor B_j as follows

$$B_j = 8\pi^2 k_B T / \alpha_j \quad (14)$$

The thermal factors T_{c_j} and T_{a_j} are:

$$T_{c_j}(q) = \exp(-Q^2 k_B T / 2\alpha_j) \quad (15)$$

$$T_{a_j}(Q) = (\beta_j (k_B T)^2 / \alpha_j^3) \left(\frac{2\pi}{a}\right)^3 T_{c_j}(Q) hkl \quad (16)$$

where a is the unit cell parameter.

Substitution of Eqs. (15) and (16) in (12) gives

$$\begin{aligned} \Delta \left(\frac{F^*(Q)F(Q)}{32} \right) &= \pm (f_{aI}f_{aM} + f_{cI}f_{cM}) \\ &\times \exp\left(\frac{Q^2 k_B T}{2\alpha_M}\right) \times \exp\left(\frac{-Q^2 k_B T}{2\alpha_I}\right) k_B^2 T^2 \\ &\times \left(\frac{2\pi}{a}\right)^3 hkl \left[\beta_M - \beta_I \left(\frac{\alpha_M}{\alpha_I}\right)^3 \right] \frac{1}{\alpha_M^3}. \quad (17) \end{aligned}$$

The effective anharmonic thermal parameter that is determinable is $\beta' = \beta_M - \beta_I \left(\frac{\alpha_M}{\alpha_I}\right)^3$, a weighted difference of the two individual β parameters.

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