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Short Communications

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Anharmonic thermal vibrations in Mg_2Si.

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The recent X-ray diffraction data from Mg_2Si, obtained by Panke & Wölfel (*Z. Kristallogr.* (1969), **129**,9) show systematic differences in the structure factors from those predicted by a model which assumes harmonic thermal vibration of the atoms. These differences indicate an anharmonic component in the thermal vibration of the magnesium atoms, consistent with their tetrahedral site symmetry. An analysis of these data has therefore been carried out in terms of a model which includes anharmonic thermal vibration and a least-squares refinement gave a value of the anharmonicity parameter ($\beta_{Mg} = -2{\cdot}39 \times 10^{-12}$ erg.Å^{-3}) which is similar in magnitude to those found for other systems with the fluorite structure.

The significance of anharmonic thermal vibrations in materials with the fluorite structure has been established by a series of recent accurate neutron diffraction studies on UO_2 (Rouse, Willis & Pryor, 1968), BaF_2 (Cooper, Rouse & Willis, 1968) and CaF_2 and SrF_2 (Cooper & Rouse, 1970). In this structure the anion has a tetrahedral environment which allows an anharmonic contribution to the thermal vibration of the anion, consistent with the introduction of a cubic term βxyz in the potential, where x, y and z are the coordinates defining the instantaneous displacement of the anion (see Dawson, Hurley & Maslen, 1967). The magnitude of the anharmonicity parameter β in these materials is of the order of -3×10^{-12} erg Å^{-3} and the anharmonic component of the thermal vibration results in significant deviations in the Bragg intensities from those predicted by a harmonic model.

For X-ray diffraction the angular dependence of the scattering factors and the predominance of the cation scattering result in the X-ray Bragg intensities for these materials being less dependent on the anharmonic effects, although a detailed analysis of recent accurate X-ray diffraction measurements on CaF_2 (Cooper, 1970*a*) has shown that these also are consistent with an anharmonicity of this magnitude. Panke & Wölfel (1969) have recently carried out a careful X-ray diffraction study of Mg_2Si, which also has the fluorite structure and which has a more favourable scattering factor ratio. It is interesting to note, therefore, that their results show systematic differences from the predictions of a model which assumes harmonic thermal vibration of the atoms, for example the different values obtained for the structure factors of the 933, 771 and 755 reflexions are indicative of anharmonic effects as described above, whereas a harmonic model would require these three reflexions to have equal structure factors. Because of these apparent systematic effects we have therefore reconsidered the experimental data in terms of an anharmonic model.

The X-ray measurements on Mg_2Si were made on both single crystals and powder samples and a comprehensive correction for extinction was carried out. Care was also taken to minimize errors due to multiple diffraction (Panke & Wölfel, 1968). No correction was made for the contribution of thermal diffuse scattering, but it is most probable that such a correction would result only in a change in the derived temperature factors (Cooper & Rouse, 1968; Cooper, 1970*b*). The electron density, which was calculated from the experimental structure factors, indicates spherical magnesium ions but shows that the outer electrons of the silicon ions are distorted towards the nearest magnesium neighbours. The ionic charges were found to be approximately $Mg^{1{\cdot}5+}$ and Si^{1-} and the temperature factors were determined to be $B_{Mg} = 0{\cdot}764$ Å^2 and $B_{Si} = 0{\cdot}548$ Å^2.

The experimental data were reanalysed using a least-squares computer program which can refine parameters associated with both anharmonic thermal vibration and extinction (see Cooper, 1970*a*). The experimental structure factors, as given in the last column of Panke & Wölfel's Table 5 (Panke & Wölfel, 1969), were used, weighted in

accordance with their estimated standard deviations, and theoretical structure factors were calculated using the scattering factors given in *International Tables for X-ray Crystallography* (1962). Initially a harmonic model was assumed and attempts to refine an extinction parameter resulted in a value not significantly different from zero, thus supporting the validity of the extinction correction procedure used. Values obtained for the temperature factors also agreed well with those given by Panke & Wölfel.

Anharmonic thermal vibration will affect primarily the high-angle odd-index reflexions with $h+k+l=4n\pm1$. Refinements using an anharmonic model, with B_{Mg} allowed to vary, resulted in values of β_{Mg} of about $-2{\cdot}5\times10^{-12}$ erg Å^{-3}, irrespective of the number of reflexions included in the analysis in addition to these more sensistive ones, and the other parameters were not changed significantly by the inclusion of the β parameter. It was found, however, that the reliability of the β_{Mg} value was improved by restricting the number of additional reflexions included, particularly since low angle reflexions are more dependent on such factors as the ionic charge and the outer electron distribution. A final analysis was therefore carried out using only the 13 highest-angle odd-index reflexions, *i.e.* from 751 onwards. A harmonic refinement varying only the scale factor, with the temperature factors fixed at the Panke & Wölfel values, gave good agreement with an R index of 0·96%, where

$$R=\Sigma||F_o|-|F_c||/|F_o|.$$

An anharmonic refinement, with only β_{Mg} varied and the scale factor fixed at the value obtained from the harmonic refinement resulted in a final value of $\beta_{Mg}=-2{\cdot}39(\pm0{\cdot}22)\times10^{-12}$ erg Å^{-3} and an R index of 0·79%. The experimental structure factors for these reflexions, together with the final calculated structure factors for the harmonic and anharmonic models are listed in Table 1.

It can be seen that, although the observed differences from the predictions of a harmonic model have little significance individually, they do, in all except two cases, have the sign predicted by the anharmonic model. In addition the agreement between observed and calculated structure factors is improved for all but two of the remaining reflexions. The significance of the overall improvement in the agreement resulting from the introduction of the anharmonicity parameter can be tested using statistical tables, for example those given by Hamilton (1965). The R index ratio in this case is 1·215, so that on the basis of these data the hypothesis that $\beta_{Mg}=0$ can be rejected at the 5% level, but not at the 2½% level.

Table 1. *Observed and calculated structure factors for* Mg_2Si

F_H and F_A are the calculated structure factors for the harmonic and anharmonic models respectively.

h	k	l	F_o	F_H	F_A
7	5	1	14·30	14·23	14·26
5	5	5	14·10	14·23	14·11
9	1	1	13·00	13·04	13·03
7	5	3	13·10	13·04	12·95
9	3	1	12·00	11·98	12·00
9	3	3	10·70	11·04	10·98
7	7	1	10·80	11·04	11·01
7	5	5	11·20	11·04	11·16
9	5	1	10·30	10·20	10·17
7	7	3	10·40	10·20	10·30
9	5	3	9·47	9·45	9·53
11	1	1	8·83	8·78	8·78
7	7	5	8·74	8·78	8·64

It is concluded, therefore, that the experimental data of Panke & Wölfel indicate the existence of an anharmonic contribution to the thermal vibration of the magnesium atoms, consistent with the tetrahedral site symmetry and of similar magnitude to that observed in other systems having the fluorite structure.

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Magnetic symmetry and physical properties.

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The number of independent non-vanishing constants required to describe the six known physical properties, involving a polar vector, has been determined by the character method of Bhagavantam & Suryanarayana for each one of the 58 double-coloured point groups.

Group theory has been successfully applied by Bhagavantam & Suryanarayana (1949), Jahn (1949) and recently by Koptsik (1966) to enumerate the constants needed to describe various physical or magnetic properties in crystals. More recently, a physical significance was given by Krishnamurty & Gopalakrishnamurty (1969*a*) to the number of constants, relating to a magnetic (or physical) property, appearing against the alternating representations of the 32 point groups. Following this, the number of second-, third- and the fourth-order elastic coefficients for each of the 58 double-coloured point groups have been enlisted by Krishnamurty & Gopalakrishnamurty (1969*b*).