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## On Anharmonicity in Cadmium

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### Abstract

Recent X-ray diffraction data on cadmium [Rossmanith (1978). *Acta Cryst.* **A34**, 497–500] have been reanalysed using a temperature factor based on an anharmonic one-particle potential to fourth order for the atoms, and values for the anharmonic parameters have been obtained. The fourth-order parameters  $\alpha_{40}$  and  $\beta_{20}$  are found not to be significantly different from zero, while the other fourth-order parameter  $\gamma_{00}$  is found to be strongly correlated to the extinction correction and harmonic parameters. The third-order antisymmetric parameter is found to have a value of  $57 \pm 16 \text{ eV nm}^{-3}$ , which is in reasonable agreement with a recent measurement. The application of the extinction correction is shown to affect substantially the values for the potential parameters.

### Introduction

The determination from X-ray diffraction data of anharmonic parameters in a one-particle-potential model for the atomic vibrations of metals is now well established. It is sometimes possible to evaluate antisymmetric anharmonic components of the potential from measurements of so-called quasi-forbidden reflections: On the other hand, if a complete set of Bragg reflection data at one temperature is available, it is

possible in principle to determine all the anharmonic parameters. This has recently been demonstrated in tetragonal tin, where Merisalo & Jarvinen (1978) determined the parameter for the antisymmetric component in the one-particle potential to be  $\alpha_{32+} = (390 \pm 30) \text{ eV nm}^{-3}$  from a measurement on three quasi-forbidden reflections, whereas Field (1978) obtained a value of  $\alpha_{32+} = (370 \pm 40) \text{ eV nm}^{-3}$  from an analysis of Bragg reflection data.

In the case of cadmium, there has been a recent estimate of the antisymmetric potential parameter from a measurement on a quasi-forbidden reflection by Merisalo, Peljo & Soininen (1978). Also, a single-crystal X-ray investigation of cadmium has been carried out by Rossmanith (1978) and a set of structure factors published (Rossmanith, 1978, Supplementary Publication). The data of Rossmanith have been reanalysed by the present author with a one-particle potential to determine the anharmonic parameters and to compare the parameter for the antisymmetric component with that found by Merisalo, Peljo & Soininen (1978).

### Theory

Cadmium crystallizes in a hexagonal structure, with space group  $P6_3/mmc$ . The lattice constants given by Rossmanith (1978) are  $a = 2.977$  and  $c = 5.612 \text{ \AA}$ ,

giving a  $c/a$  ratio of 1.89. There are two atoms per unit cell with site symmetry  $\bar{6}m2$ .

The theory used in the analysis was that given by Merisalo & Larsen (1977) in their analysis of the hexagonal metal zinc. The one-particle potential appropriate to the site symmetry in  $A3$  structures is

$$V(\mathbf{u}) = V_0 + u^2(\alpha_{20} K_{20} + \beta_{00}) + u^3 \alpha_{33} K_{33} + u^4(\alpha_{40} K_{40} + \beta_{20} K_{20} + \gamma_{00}), \quad (1)$$

where  $\mathbf{u}$  represents the displacement and the  $K$ 's represent symmetry-adapted harmonics. Only two anharmonic parameters were found to be significantly different from zero in the analysis. The temperature factor used in the analysis was, in the notation of Merisalo & Larsen,

$$\begin{aligned} \tau = N^{-1} \exp[-\frac{1}{2}(s_1^2 + s_2^2 + s_3^2)] \\ \times \left\{ 1 + \frac{i\alpha_{33}}{k_B TA^3} (s_1^3 - 3s_1 s_2^2) \right. \\ - \frac{8\gamma_{00}}{k_B TA^4} (s_1^4 + s_2^4 - 8s_1^2 s_2^2 + 2s_1^2 s_2^2 + 8) \\ - \frac{\gamma_{00}}{k_B TB^4} (s_3^4 - 6s_3^2 + 3) \\ \left. + \frac{2\gamma_{00}}{2k_B TA^2 B^2} (1 - s_3^2)(s_1^2 + s_2^2 - 2) \right\}, \end{aligned}$$

where  $N$  is a normalization constant,

$$A^2 = \frac{2\beta_{00} - \alpha_{20}}{k_B T}, \quad B^2 = \frac{2(\beta_{00} + \alpha_{20})}{k_B T} \\ s_1 = \frac{2\pi(2h + k)}{Aa\sqrt{3}}, \quad s_2 = \frac{2\pi k}{Aa}, \quad s_3 = \frac{2\pi l}{Bc}.$$

The mean-square vibration amplitudes in the crystal axis directions may be determined from the harmonic parameters as

$$u_a^2 = \frac{k_B T}{2(\beta_{00} - \frac{1}{2}\alpha_{20})} \quad \text{and} \quad u_c^2 = \frac{k_B T}{2(\beta_{00} + \alpha_{20})}.$$

### Analysis

The data provided by Rossmannith (1978, Supplementary Publication) consist of measurements on 367 reflections with from two to twelve symmetry-related reflections measured for each of the 49 independent reflections. Rossmannith treated her results as a case of high extinction and applied an anisotropic extinction correction before calculating r.m.s. vibration amplitudes.

In the present work, four models were used in the analysis of Rossmannith's data. Firstly, the data as

corrected by Rossmannith for anisotropic extinction were reanalysed with a harmonic model, that is, allowing the scaling factor  $k_s$  and the harmonic potential parameters  $\alpha_{20}$  and  $\beta_{00}$  to vary. This is referred to as model 1.

The anharmonic model (model 2) applied to the extinction corrected data was one in which the five parameters  $k_s$ ,  $\alpha_{20}$ ,  $\beta_{00}$ ,  $\gamma_{00}$  and  $\alpha_{33}$  were allowed to vary simultaneously.

Since Rossmannith had applied an anisotropic extinction correction to her data, it was felt that anharmonic effects may be partially or wholly masked by the extinction correction. Extinction-free data covered 308 measurements on 39 independent reflections in the range  $4.1 < \sin \theta/\lambda < 8.1 \text{ nm}^{-1}$ . This data subset was analysed, after removal of the extinction correction, using a harmonic model (model 3) and an anharmonic model (model 4) in which the four parameters  $k_s$ ,  $\alpha_{20}$ ,  $\beta_{00}$  and  $\alpha_{33}$  were allowed to vary.

In the analyses quoted here, a weighted least-squares fitting procedure was used. The index used to assess the fit of the calculated intensities to the observed data was

$$R = \left[ \frac{\sum_i \frac{1}{\sigma_i^2} (I_{oi} - I_{ci})^2}{\sum_i \frac{1}{\sigma_i^2} I_{oi}^2} \right]^{1/2},$$

where  $I_{oi}$  was the  $i$ th observed intensity, taken as the square of the observed structure factor quoted by Rossmannith,  $I_{ci}$  was the  $i$ th calculated intensity, and  $1/\sigma_i^2$  was the weighting assigned to the  $i$ th intensity.

The value  $\sigma_i$  for each reflection was taken to be the r.m.s. deviation from the mean of the observed intensities for the relevant group of symmetry-related reflections which included that particular reflection.

In finding the values of  $I_{ci}$ , the scattering factor of cadmium was calculated from the nine-parameter-fit tables of Doyle & Turner (1968).

The significance of the improved fit of the anharmonic models 2 and 4 over the respective harmonic models 1 and 3 was assessed with the  $R$ -factor-ratio tables given in *International Tables for X-ray Crystallography* (1974).

### Results

A summary of the results obtained for the four refinements outlined above is given in Table 1. In the table  $u_a$  and  $u_c$  refer to the r.m.s. vibration amplitudes in the crystal axis directions. The entry 'Level at which anharmonic model significant' refers to that level, from the  $R$ -factor-ratio tables in *International Tables for X-ray Crystallography* (1974), at which the decrease in  $R$  factor for each anharmonic model relative to the corresponding harmonic model was significant.

Table 1. *Values of parameters refined for various models*

		Model			
		1 (harmonic)	2 (anharmonic)	2 (harmonic)	4 (anharmonic)
		Extinction correction applied		No extinction correction	
Harmonic parameters	$\alpha_{20}$ (eV nm <sup>-2</sup> )	-40.1 ± 0.1	-41.1 ± 0.1	-43.0 ± 0.1	-43.1 ± 0.1
	$\beta_{00}$ (eV nm <sup>-2</sup> )	73.0 ± 0.1	72.2 ± 0.1	76.4 ± 0.1	76.5 ± 0.1
Anharmonic parameters	$\gamma_{00}$ (eV nm <sup>-4</sup> )	-	930 ± 200	-	-
	$\alpha_{33}$ (eV nm <sup>-3</sup> )	-	26 ± 13	-	57 ± 16
	$u_a$ (pm)	11.60 ± 0.01	11.67 ± 0.01	11.36 ± 0.01	11.35 ± 0.01
	$u_c$ (pm)	19.59 ± 0.06	20.15 ± 0.07	19.44 ± 0.06	19.44 ± 0.06
	$u_c/u_a$	16.89 ± 0.07	17.27 ± 0.07	17.11 ± 0.07	17.13 ± 0.07
	Level at which anharmonic model significant	-	0.005	-	0.005

### Discussion

As can be seen, the anharmonic models 2 and 4 provide a significantly better fit to the data than the corresponding harmonic models 1 and 3.

It might be supposed that an anisotropic extinction correction would have an effect on the antisymmetric anharmonic parameter  $\alpha_{33}$ , and indeed there is some difference between the values refined *via* models 2 and 4. The value of  $\alpha_{33}$  in cadmium has been found by Merisalo, Peljo & Soininen (1978) from an investigation of the 'quasi-forbidden' reflection 303 to be  $81 \pm 12$  eV nm<sup>-3</sup>. The value of  $57 \pm 16$  eV nm<sup>-3</sup> obtained with model 4 in the present analysis confirms from independent data the existence of a small value of  $\alpha_{33}$ .

The antisymmetric term in the potential indicates asymmetry of the vibrations in the basal plane in the structure. In cadmium, the potential is reduced and the amplitude of vibration is correspondingly increased, in the directions in the basal plane towards the sides with rectangular holes between neighbouring atoms. In the opposite directions, that is towards the sides with triangular holes between neighbouring atoms, the potential is increased and the amplitude of vibration decreased. A similar phenomenon has been noted in zinc by Merisalo & Larsen (1979), who obtained a value of  $\alpha_{33} = -1120 \pm 190$  eV nm<sup>-3</sup> for that metal. The negative sign here is not significant in that it is determined by the centre of symmetry taken as origin in the calculations. In the present work, the atoms were described as being at positions  $\pm\frac{1}{6}, \mp\frac{1}{6}, \pm\frac{1}{4}$ , and the value of  $\alpha_{33}$  obtained was positive. If the atoms had been described as being at  $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$  as used by Merisalo & Larsen,  $\alpha_{33}$  would have had the opposite sign.

It is clear from Table 1 that the parameter  $\gamma_{00}$  is strongly influenced by the application of the extinction correction, since a large positive value is refined from the data corrected for extinction (model 2), while  $\gamma_{00}$  is insignificant in the refinement in which the extinction correction was removed (model 4). The parameter  $\gamma_{00}$ , as can be seen from (1), is a straight-forward isotropic anharmonic parameter. It might be expected that this

parameter would have a small negative value, indicating 'softening' of the vibrations from harmonic. A negative fourth-order isotropic anharmonic parameter has been found recently, for example, in the one-particle potential for potassium by Bednarz & Field (1982a) and is suggested at high temperatures in lithium (Bednarz & Field, 1982b). The relatively large positive value for  $\gamma_{00}$  obtained from model 2 in the present analysis suggests that the extinction correction applied by Rossmannith overcorrected the observed data, particularly for the low-angle reflections.

It should be noted that the r.m.s. vibration amplitudes  $u_a$  and  $u_c$  obtained here, with the exception of  $u_c$  for models 1 and 2, are slightly smaller by a percent or two than those quoted by Rossmannith (1978). This is probably a consequence of the weighted fit used in this analysis giving more emphasis to higher-angle reflections, and may provide some further evidence that the extinction correction applied by Rossmannith resulted in an overcorrection of the intensities of the low-angle data. The same reason probably accounts for the ratios of  $u_c$  to  $u_a$  being greater than those calculated by Rossmannith (1978).

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