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X-ray absorption fine structure study on the anharmonic effective pair potential in ZnO and Zn_{0.1}Mg_{0.9}O

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Abstract. X-ray-absorption fine structure (XAFS) measurements and analysis are presented for ZnO and Zn_{0.1}Mg_{0.9}O at different temperatures from 296 K to 760 K and from 373 K to 771 K, respectively. The anharmonic effective pair potentials of the Zn–O bond in these compounds are found from the analysis of the temperature-dependent XAFS data (Stern E A *et al* 1991 *Phys. Rev. B* **43** 8850). The influence of the local structure parameters on the anharmonic effective pair potential is studied.

1. Introduction

X-ray-absorption fine structure (XAFS) [2, 3] provides a unique and accurate technique for detailed measurements of the local environment around an atom species. Though it is typically used to measure the physical arrangement of nearby atoms in a disordered system, XAFS can also be applied to make accurate measurements of near-neighbour force constants. A simple model, presented in [4] for the near-neighbour pair distribution function, is based on the effective one-dimensional anharmonic potential $U(x) = ax^2/2 + bx^3 + cx^4$ (a , b , c are force constants, x is the deviation of the bond length from the location R_0 of the potential minimum). The effective one-dimensional anharmonic potential $U(x)$ is the ‘potential of mean force’ giving the interaction of two atoms embedded in the environment of the solid. The influence of all other atoms is implicit in $U(x)$ [4].

The effect on XAFS of such a potential was treated through the cumulant expansion [5]. The method of determination of the anharmonic potential between near neighbours with the help of XAFS was suggested by Stern, Livinš and Zhang [1].

In this paper we present the experimental XAFS measurements on ZnO and Zn_{0.1}Mg_{0.9}O at temperatures from 296 K to 760 K and from 373 K to 771 K, respectively. The XAFS measurements at these temperatures are used to characterize the anharmonic potentials for the Zn–O bond in the compounds ZnO and Zn_{0.1}Mg_{0.9}O. The potentials are found from the analysis of the temperature-dependent XAFS data. The influence of local structure parameters, such as bond length and coordination number, on the effective pair potential of the Zn–O bond is investigated. For this purpose, two compounds were chosen with different Zn–O bond lengths: (i) ZnO of the zincite-type structure, in which Zn atom is tetrahedrally coordinated by the oxygen atoms with bond lengths about 1.98 Å; (ii) the solid solution Zn_{0.1}Mg_{0.9}O of the NaCl-type structure, in which the Zn atom is octahedrally coordinated by oxygen atoms with bond lengths about 2.08 Å. In addition, the potential found from the EXAFS analysis for ZnO is used to determine local

thermodynamic properties of the interatomic bond (Zn–O), including the linear coefficient of a thermal expansion, the Debye and Einstein temperatures and the specific heat temperature dependence.

2. Experiment and analysis

We synthesized the compound $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$, in which 10 mol% of chemically pure ZnO and 90 mol% of chemically pure MgO were used as components. It has been shown [6–8] that to form the compound $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$, a temperature of synthesis about 1400 K is necessary. The $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ sample was specified by x-ray diffraction. Both $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ and chemically pure ZnO powdered and mixed with ultra-dispersion graphite. The samples were positioned in a special high temperature cell, which made it possible to measure the spectra at temperatures up to 900 K. The high temperature cell construction ensured a relatively small (1–2 K) temperature gradient in the vicinity of the sample. The temperature was measured with a thermocouple and was controlled automatically. The stability of the temperature was about 2 K.

The Zn K-edge XAFS was measured in transmission on an XAFS spectrometer at the Siberian center of Synchrotron Radiation with the storage ring operating at 2 GeV and 60–90 mA. An Si(111) double-crystal monochromator determined x-ray energy. The intensities of both the incident and transmitted x-ray beams were measured with ionization chambers filled with Ar gas. The XAFS spectra were obtained at the following temperatures: 373, 471, 576, 671, 777 K for ZnO and 373, 465, 570, 762 K for $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$. We limited the temperature ranges for ZnO and $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ $T > T_{room}$ because second-order corrections to the cumulants are important at high temperatures.

The analysis of the XAFS data has been performed following the routine procedure: E_0 was set at the maximum of the first derivative for each scan; the data were normalized to the edge step; and then the XAFS oscillating function, $\chi(k)$, was obtained from the measured spectra by subtracting the background absorption, which was determined by fitting the data above the edge with five cubic splines. The Zn K-edge EXAFS spectra of ZnO and $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ measured at different temperatures are shown in figure 1.

Fourier transforms of $k^2\chi(k)$ are shown in figure 2, evaluated over the range of wave vectors 2.6–11.13 \AA^{-1} for ZnO and 2.4–11.75 \AA^{-1} for $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$. The first shell r -space peak between 0.96 and 2.09 \AA for ZnO and 0.94 and 2.07 \AA for $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ was then transformed back to k -space using a square window. Fitting $\chi(k)$ was carried out in k -space to determine parameters of the first coordination shell: the difference between theoretical and experimental threshold energies (ΔE_0); interatomic distance (R); second, third and fourth cumulants ($\sigma^{(2)}$, $\sigma^{(3)}$, $\sigma^{(4)}$). The back-scattering amplitude and the total phase shift were calculated using FEFF7 software [9]. The quantities ΔE_0 and S_0^2 (S_0^2 is the square of the overlap between the initial (N -electron) and final ($N - 1$ -electron) atomic states) were varied for the scan carried out at the lowest temperature and the obtained values used at higher temperatures. These values ΔE_0 and S_0^2 , respectively, are 4 eV and 0.85 for ZnO and 0.35 eV and 0.85 for $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$. The numbers of neighbouring atoms were set as their crystallographic values: four for ZnO [10] and six for $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ (such as for MgO). The first cumulants were determined as $\sigma^{(1)} = R - R_0$. $R_0 = 1.9754 \text{\AA}$ (average of two near distances $R_0^{(1)} = 1.9695 \text{\AA}$ and $R_0^{(2)} = 1.9813 \text{\AA}$ at $T = 20 \text{ K}$) for ZnO was taken from crystallographic data [10]. The value $R_0 = 2.0786$ for $\text{Zn}_{0.1}\text{Mg}_{0.9}\text{O}$ was determined by an extrapolation of the interatomic distances, derived from EXAFS at all temperatures, to 0 K. The best-fit values of the quantities at all temperatures for both compounds are presented in tables 1 and 2.

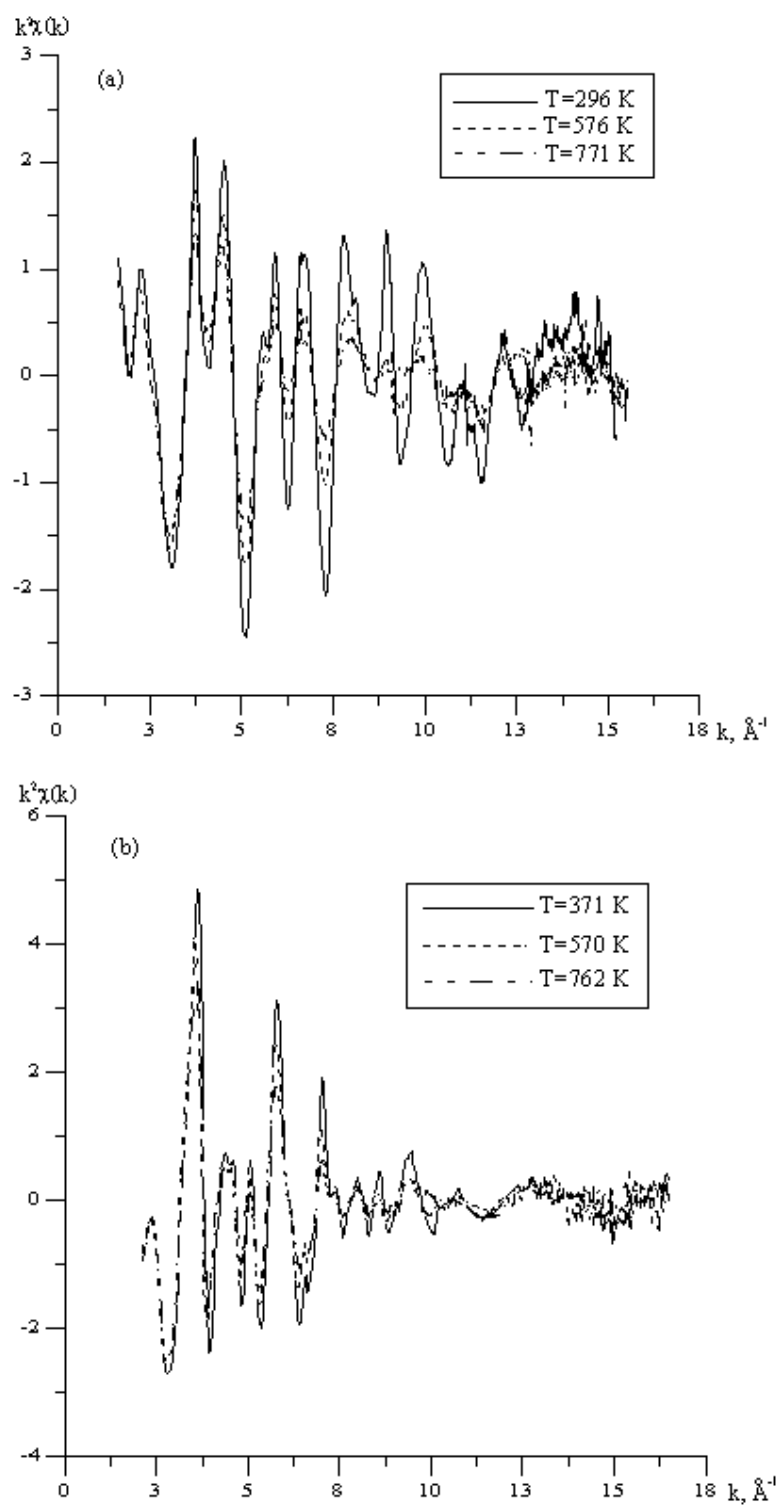


Figure 1. Zn K-edge $k^2\chi(k)$ of ZnO (a) and Zn_{0.1}Mg_{0.9}O (b) at different temperatures.

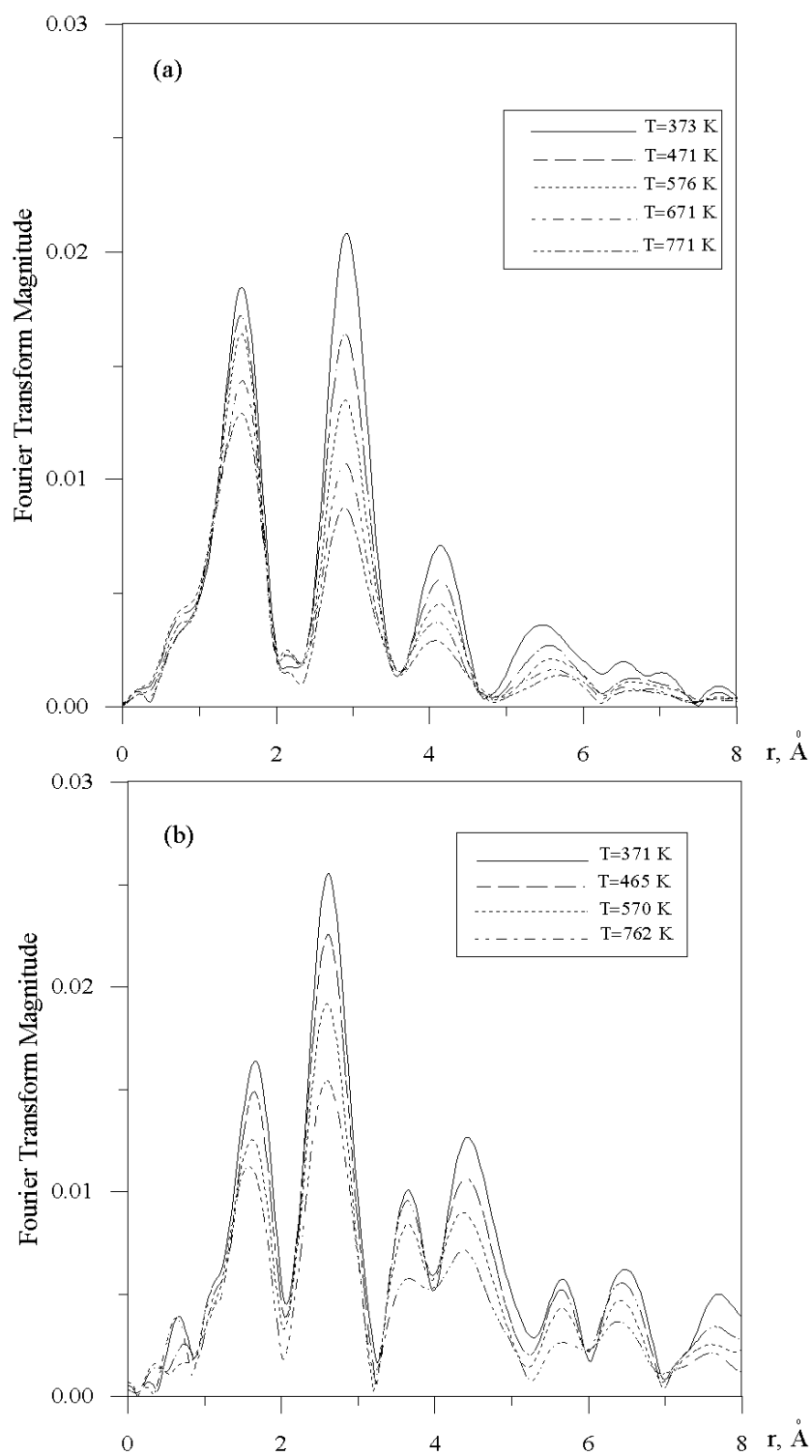


Figure 2. Fourier transforms of Zn K-edge $k^2\chi(k)$ of ZnO (a) and Zn_{0.1}Mg_{0.9}O (b) at different temperatures.

Table 1. Cumulants $\sigma^{(n)}$ for the Zn–O bond in ZnO from XAFS experiment^{a,b}.

| <i>T</i> (K) | $\sigma^{(1)}$ (Å) | $\sigma^{(2)}$ (Å ²) | $\sigma^{(3)}$ (Å ³) | $\sigma^{(4)}$ (Å ⁴) |
|-----------------|--------------------|----------------------------------|----------------------------------|----------------------------------|
| 293 | 0.0034 | 0.00246 | 0.000018 | 0.0000009 |
| 373 | 0.0044 | 0.00341 | 0.000030 | 0.0000010 |
| 471 | 0.0057 | 0.00398 | 0.000051 | 0.0000024 |
| 576 | 0.0071 | 0.00492 | 0.000080 | 0.0000042 |
| 671 | 0.0085 | 0.00580 | 0.000114 | 0.0000060 |
| 771 | 0.0099 | 0.00672 | 0.000157 | 0.0000090 |

^a The first coordination sphere (oxygen) is $N = 4$. The distances R and mean-square displacements σ^2 were determined by fit and their values can be found from experiment 1 as $R = R_0 + \sigma^{(1)}$ ($R_0 = 1.9754 \text{ \AA}[10]$) and $\sigma^2 = \sigma^{(2)}$ for all temperatures.

^b Estimated uncertainty: ± 4 –6%.

Table 2. Cumulants $\sigma^{(n)}$ for the Zn–O bond in Zn_{0.1}Mg_{0.9}O from XAFS experiment^{a,b}.

| <i>T</i> (K) | $\sigma^{(1)}$ (Å) | $\sigma^{(2)}$ (Å ²) | $\sigma^{(3)}$ (Å ³) | $\sigma^{(4)}$ (Å ⁴) |
|-----------------|--------------------|----------------------------------|----------------------------------|----------------------------------|
| 373 | 0.01129 | 0.00763 | 0.000212 | 0.000018 |
| 465 | 0.01538 | 0.01099 | 0.000380 | 0.000033 |
| 570 | 0.02049 | 0.01390 | 0.000650 | 0.000061 |
| 762 | 0.03030 | 0.01813 | 0.001399 | 0.000189 |

^a The first coordination sphere (oxygen) is $N = 6$. The distances R and mean-square displacements σ^2 were determined by fit and their values can be found from experiment 1 as $R = R_0 + \sigma^{(1)} + \Delta R_{off}$ ($R_0 = 2.0786 \text{ \AA}$, $\Delta R_{off} = -0.003 \text{ \AA}$) and $\sigma^2 = \sigma^{(2)}$ for all temperatures.

^b Estimated uncertainty: ± 6 –8%.

It has been shown [1, 4] that the four cumulants can be written in terms of the three lowest order force constants (a , b , c) and the absolute temperature (T):

$$\begin{aligned}
 \sigma^{(1)} &= \Delta R = -\frac{3bk_B T}{a^2} \left[1 + \frac{k_B T}{a^2} \left(45 \frac{b^2}{a} - 32c \right) \right] \\
 \sigma^{(2)} &= \sigma^2 = \frac{k_B T}{a} \left[1 + \frac{k_B T}{a^2} \left(36 \frac{b^2}{a} - 12c \right) \right] \\
 \sigma^{(3)} &\approx \frac{-6b(k_B T)^2}{a^3} \left[1 + \frac{k_B T}{a^2} \left(\frac{144b^2}{a} - 84c \right) \right] \\
 \sigma^{(4)} &\approx \frac{(k_B T)^3}{a^4} \left(108 \frac{b^2}{a} - 24c \right)
 \end{aligned} \tag{1}$$

where k_B is the Boltzmann constant. We applied the Monte Carlo procedure to determine the force constants using the $\sigma^{(1)}$, σ^2 , $\sigma^{(3)}$, $\sigma^{(4)}$ measured at different temperatures. Since an arbitrary near-neighbour distance was used to generate the theoretical XAFS, a constant offset to the near-neighbour distance (ΔR_{off}) [4] was allowed to be varied and added to ΔR . A value of ΔR_{off} was zero for ZnO and -0.003 \AA for Zn_{0.1}Mg_{0.9}O. In order to estimate the accuracy of the procedure we calculated sigma values through the obtained force constants using the formulas (1) and then compared these values with the initial values of the cumulants. Both sets of the cumulants are presented in figure 3 for ZnO for Zn_{0.1}Mg_{0.9}O.

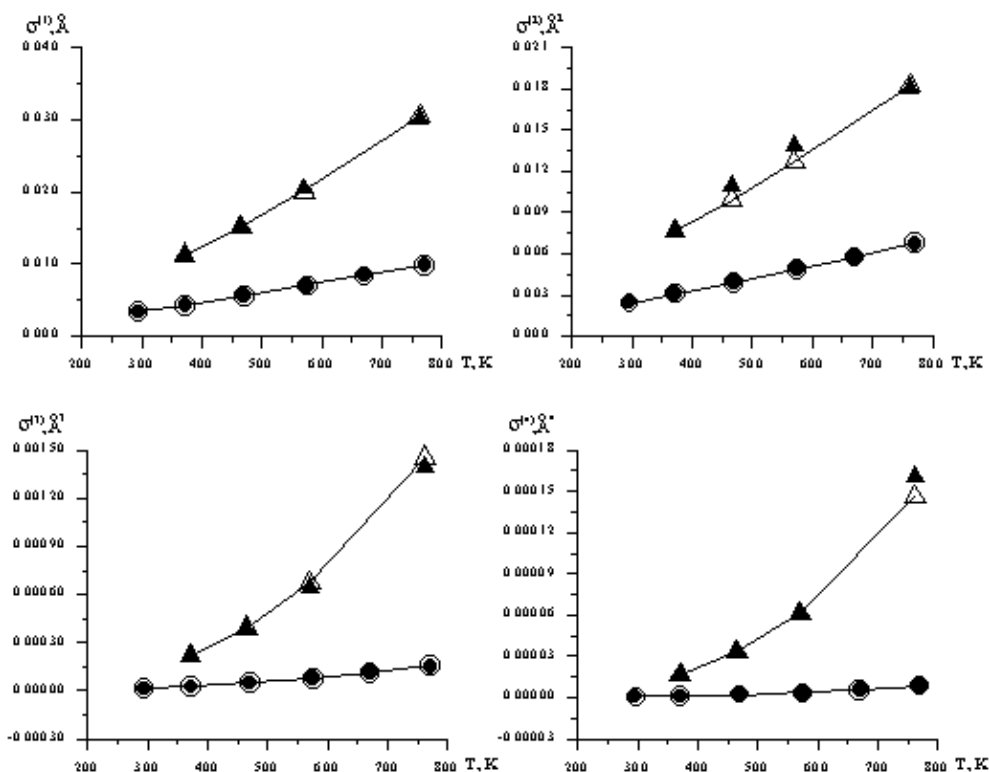


Figure 3. Temperature dependence of the cumulants for ZnO (circles) and for Zn_{0.1}Mg_{0.9}O (triangles). Experimental data are given by open symbols; full symbols correspond to the calculated ones with formulas (1).

3. Results and discussion

The best-fit force constants are $a = 10.82 \pm 0.30 \text{ eV } \text{Å}^{-2}$, $b = -4.98 \pm 0.15 \text{ eV } \text{Å}^{-3}$, $c = -7.7 \pm 0.2 \text{ eV } \text{Å}^{-4}$ for ZnO and $a = 4.93 \pm 0.15 \text{ eV } \text{Å}^{-2}$, $b = -2.01 \pm 0.06 \text{ eV } \text{Å}^{-3}$, $c = -9.0 \pm 0.3 \text{ eV } \text{Å}^{-4}$ for Zn_{0.1}Mg_{0.9}O. Thus, the pair potentials of the Zn–O bond significantly change as the bond length increases from 1.98 to 2.08 Å and the coordination number increases from 4 to 6. The anharmonic effective pair potentials for both the Zn–O bonds are shown in figure 4.

The values of the force constants, which have been found by the XAFS analysis, were then used to calculate local thermodynamic properties [1, 4]. We calculate local thermodynamic properties of ZnO. The linear coefficient of a thermal expansion was determined using the expression:

$$\alpha(T) = \frac{\Delta R}{R_0 T} = -\frac{3bk_B}{a^2 R_0} \left[1 + \frac{k_B T}{a^2} \left(45 \frac{b^2}{a} - 32c \right) \right]. \quad (2)$$

This gives $\alpha = 6.0 \pm 0.5 \times 10^{-6} \text{ K}^{-1}$ in the temperature range 300–673 K, while the known bulk value in this range is $\alpha = 5.5 \times 10^{-6} \text{ K}^{-1}$ [11]. Such a good agreement is especially encouraging if one takes into account that no bulk properties were used in the XAFS measurements of α .

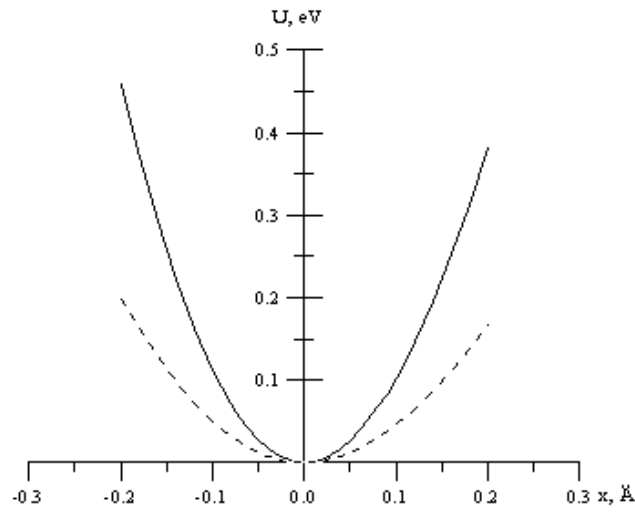


Figure 4. Anharmonic effective pair potential for the Zn–O bond in ZnO (solid line) and Zn_{0.1}Mg_{0.9}O (dashed line).

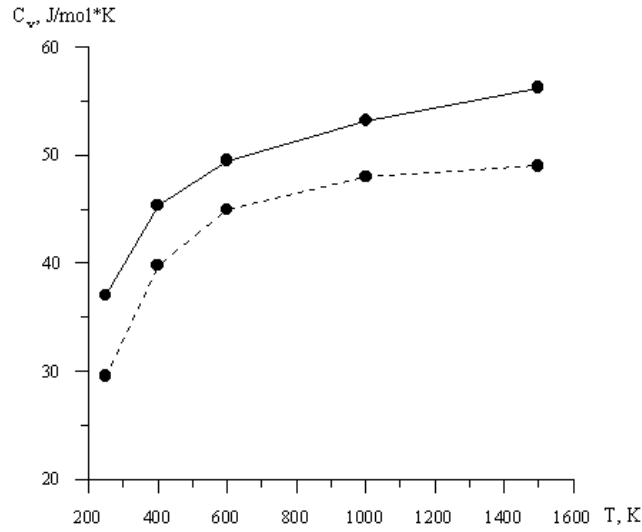


Figure 5. Calculated specific heat against *T* (dashed line) and thermodynamic measurements [11] (solid line).

Next, the Einstein temperature was calculated as

$$\Theta_E = \frac{\hbar}{k_B} \sqrt{\frac{a}{M_R}} \tag{3}$$

where M_R is the reduced mass.

The result is $\Theta_E = 686 \pm 10$ K. Using the ratio $\Theta_D/\Theta_E \approx 1.27$ suggested by Lottici [12], we have obtained the Debye temperature $\Theta_D = 871 \pm 16$ K. To the knowledge of the authors there are no experimental data on Θ_D for ZnO in the literature.

Finally, the specific heat within the Debye model may be calculated using the Debye temperature according to

$$C_V(T) = 18k_B N_A \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{e^z z^4 dz}{(e^z - 1)^2} \quad (4)$$

where $z = \Theta_D/T$. Our results and the values taken from [11] are shown in figure 5. One can see that both functions agree reasonably well. An available difference, averaged over the temperature range 250–1500 K, is 12%.

Thus it has been shown in this paper that structural parameters significantly influence on the force constants. The thermodynamic characteristics obtained by XAFS for ZnO agree well with thermodynamic measurements.

Acknowledgments

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