Structural phase transition in NdAs

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Abstract. A consistent calculation has been performed to describe the structural phase transition of NdAs using a well known three-body interaction potential model (TBIPA). Phase transition pressure is associated with a sudden collapse in the volume. The computed results on the phase transition pressure, volume collapse and pressure derivative of bulk modulus have shown a reasonably good agreement with their accurately measured data. In view of its overall success TBIPM has been regarded an adequate and appropriate model suitable for high-pressure studies.

1. Introduction

In recent studies, the high pressure structural behaviour of binary AB compounds with NaCl type structure has been a popular topic in condensed matter research. The high pressure structural behaviour of the rare-earth monopnictides contains to be a vivid research area both theoretically and experimentally, because of the diversity in their electronic, magnetic and structural properties. Out of numerous rare earth elements which are trivalent and their corresponding monopnictide compounds show the lanthanide contraction and exhibit metallic properties. Rare-earth monopnictides are generally semiconductors and semimetals. Despite their simple rock salt structure, they demonstrate various types of magnetic ordering generally with low transition temperature. Their electronic structures and magnetic properties are sensitive to temperature, pressure and impurity effects. The rare-earth 4f-5d interactions and the hybridization between the rare-earth non-4f and pnictogen p states are responsible for many fascinating phenomena that occur in rare-earth monopnictides [1]. Most of the rare earth monopnictides compounds crystallize in cubic NaCl (B1) type structure at ambient pressure but undergo a phase transition either to a CsCl (B2) or a body centered tetragonal phase under high pressure [2]. These transitions result in the increase in coordination number from 6 to 8. The B1→B2 transition is of considerable importance as a model for other structural phase transitions. It is one of the simplest first order transition. The salient features of NdAs experimentally observed by Shirotani et al. [2] from their high-pressure X-ray diffraction experiments. They reported phase transition in NdAs a B1→B2 transition at 24.2 GPa.

In the present paper, we aim to investigate the phase transition pressure, relative volume changes and pressure derivative of bulk modulus of NdAs. For this purpose we have used three body interaction potential approach (TBIPA) [3]. A brief account of the theoretical approach is presented in section 2; the results are discussed in section 3.
2. Method of Calculations

The important ionic solids crystallize in either rock salt (B1) or cesium chloride (B2) structure. An isolated phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As the temperature or pressure or any variable acting on the systems is altered, the free energy changes smoothly and continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy. It is well known that the pressure on crystals results in change its volume, which leads to an increased charge transfer (or three-body interaction effects) due to the deformation of the overlapping electron shells of the adjacent ions. The three body interaction arises during lattice vibrations when electron shells of neighbouring ions overlap. This overlapping leads to the transfer of charge which interacts with other charge, many body interactions (MBI) take place, the dominant part of MBI is three body interactions[4,5]. These interactions becomes more important to consider due to the decreases in interionic spacing of the lattice crystal when pressure is increased and when ions experience sufficient overlap. Besides, enhance in overlap energy, the transferred charge due to the overlap in electron shells, modify the ionic charge which in turns modify the coulomb energy.

\[ \phi_{n2}(r) = \phi + \Phi \]  
\[ \phi_{n2}(r) = \left[ -\frac{2n^2 \pi^2 \alpha^2}{r} \right] \left[ 1 + \frac{2}{\Delta} f(r) \right] \]  

Here \( \alpha_{2n} \) is the Madelung constants, which is 1.7476 (1.7629) for NaCl (CsCl) structure solids and \( r \) is the equilibrium nearest neighbour (nn) ion separation, \( n \) is the number of nearest neighbours and \( f(r) \) is the TBI parameter and is independent on the nearest neighbour distance \( (r^2) \) as

\[ f(r) = f_{2n} \alpha_{2n} \left( \frac{-n}{\rho} \right) \]  

The NdAs transforms from their initial B1 to B2 structure under pressure. The stability of a particular structure is decided by the minima of Gibbs free energy,

\[ G = U + PV - TS \]  

Where U is the internal energy, which at 0 K corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature \( T \), pressure \( P \) and volume \( V \).

The Gibbs free energies

\[ G_{B1}(r) = U_{B1} + 2Pr^3 \]  

for NaCl (B1) phase and

\[ G_{B2}(r) = U_{B2} + 1.51Pr^3 \]  

for CsCl (B2) phase become equal at the phase transition pressure \( P \) and temperature 0 K. Here the abbreviations

\[ H_{B1}(r) = -\frac{2n^2 \pi^2 \alpha^2}{r} \left( \frac{H_{B1}(r^2/2)}{r} \right) + \beta_1 \beta_2 \beta_3 \frac{\beta_2}{\beta_1} \frac{r}{\rho} \]
and

\[ U_{B2}(r) = -\frac{a_1}{\rho} + \frac{B_{12} Z_1^2 Z_2^2 f(r)}{\rho} + 4b^1_1 \rho \exp \left( \frac{r_{12} - r}{\rho} \right) \]  

(8)

represent cohesive energies for B1 and B2 phases, respectively. Here, the first term in the above equations (7) and (8) is a long range Coulomb energy and the second term is due to three–body interactions corresponding to the nearest neighbour separation \( r(r') \). \( a_1 \) and \( a_2 \) are the Madelung constants for B1 (B2) phases. The remaining term corresponds to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second –neighbor ion, with \( b^1 \) (\( b^2 \)) are the hardness parameters for B1 (B2) phases and \( \rho \) is the range parameter for both the phases, \( \beta_{ij}(l,j = 1,2) \) are the Pauling coefficients defined as \( \beta_{ij} = 1 + (Z_i/n_i) + (Z_j/n_j) \) with \( Z_i(n_i) \) and \( n_i(n_j) \) are the valence and the number of electrons of the \( i(j) \) th ion. The cation (anion) radii are given by \( r_i(r_j) \). \( Z_e \) is the ionic charge.

There are three model parameters \( (\beta, \rho, f(r)) \) involved in the present TBP. The hardness \( (\beta) \) parameter for B1 (B2) structures and range \( (\rho) \) parameter for both the structures have been determined from the equilibrium conditions

\[ \frac{d\rho}{dr} \bigg|_{r=r_0} = 0 \quad \text{and} \quad \frac{d^2\rho}{dr^2} \bigg|_{r=r_0} = 9k_0 B_T \]  

(9)

Here, \( B_T \) is isothermal bulk modulus and \( k=2 \) for B1 phase. Accordingly, the value of hardness parameter increases by the ratio \( \frac{8}{6} \) for B1 phase as

\[ b' = \frac{8}{6} b \]  

(10)

Here, number 8 and 6 are the coordinate number for B1 and B2 structures respectively. Using model parameter \( (\beta, \rho, f(r)) \), pressure derivative of bulk modulus has been computed whose expressions [6] are as follows:

\[ \frac{dB_T}{d\rho} = \left( \frac{dB_T}{d\rho} \right) \bigg|_{T=1} \frac{13.980}{10^5} \left( Z + 12f(r) \right) + C_1 - 3A_1 + C_2 - 3A_2 \]

\[ -167.764 \times 10^5 \left( Z + 12f(r) \right) + 413.420 \times 10^3 \left( Z + 12f(r) \right) \]

(11)

Where,

\[ \Omega = -1.393 \times 10^5 \left( Z + 12f(r) \right) + A_2 + A_4 + 21.96 \times 10^3 \left( Z + 12f(r) \right) \]  

(12)

Here, \( \rho \) is the range, \( \beta \) is the hardness, and \( (A_1 \ B_1) \) and \( (A_2 \ B_2) \) are the short range parameters which can be obtained from differentiate the short range repulsive interaction.
Table 1. Input crystal data and model parameters of NdAs.

| compound | input data | | | model parameters |
| - | - | - | - | - |
| NdAs | 0.98 | 1.20 | 2.985 | 83.9 \( \pm 4.6 \) | 48.0531 | 64.0531 | 0.426 | 0.047 |

* Ref. [2]

Table 2. Phase transition properties of NdAs.

| compound | phase transition pressure (GPa) | relative volume collapse (%) | pressure derivative of bulk modulus |
| - | - | - | - |
| NdAs | present | 25.2 | 7.3 | 3.3 |
| | expt. | 24.2 | 10 | 4.3 \( \pm 5 \) |

* Ref. [2]

3. Results and Discussion

Using the values of input data we have calculated the model parameters given in table 1. In order to predict the transition pressure, we have minimized the Gibbs free energy with respect to interionic separations and calculated \( \Delta G \) for various pressures. As the pressure is increased, these values of \( \Delta G \) decreases and approach zero at the transition pressure. Beyond this pressure \( \Delta G \) becomes negative as the phase B\textsubscript{2} become more stable. The variation of \( \Delta G \) with pressure for NdAs has been plotted in figure 1. The phase-transition pressure obtained from these calculations is presented in table 2 and compared with other experimental result.

The first-order phase transition involving a discontinuity in volume indicating a drastic structural change at the phase-transition pressure obtained at a point, where \( \Delta G = 0 \). The relative volumes, \( V(P)/V(0) \) (Here, \( V(P) \) is the volume of the material at applied pressure \( P \) in NaCl/CsCl phase and \( V(0) \) is the volume at \( P = 0 \) i.e. in NaCl phase) have been computed and plotted against the pressure in figure 2 to get the phase diagrams and volume collapse, \( V(P_0)/V(0) \) (Here, \( V(P_0) \) is the difference in volumes of two phases at \( P_0 \)), associated with the phase transition. The present values (solid line) are compared with experimental results (solid squares) reported by Shirotani et al [2]. It is clear from this figure that results from present model are in good agreement with experimental results and the trend of curves is also same. The value of the volume collapse along with their experimental result is listed in table 2 for NdAs. The magnitude of relative volume change at the transition pressure for NdAs is 7.3% which is also in good agreement with those from experimental approach which is
given in table 2 and figure 2. The pressure derivative of bulk modulus of NdAs is also given in table 2. It is clear from table 2 that our calculated value of pressure derivative of bulk modulus of NdAs is in good agreement with the experimental value.

On the basis of above work we conclude that the TBIPA approach is adequately suitable for the prediction of B1 → B2 phase transition pressure and associated volume collapse in NdAs. This approach may be applied to other lanthanide monopnictides for the study of phase transition phenomenon.

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