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High-pressure phase transitions in NiAs-type compounds from first-principles calculations

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We have extensively explored the structural stability and high pressure phase transitions of NiAs-type compounds (AlP, AlAs, BeS, BeSe, BaO, TiS, and CrTe) by using *ab initio* lattice dynamics calculation. We have identified a pressure-induced unstable transverse acoustic phonon mode in AlP and AlAs and proposed a post-NiAs high pressure orthorhombic structure for these two compounds. No lattice dynamical instability was found in BeS, BeSe, and TiS upon compression, which can naturally explain the experimental observation of ultrastability of these compounds up to very high pressure. Systematic analysis suggested that high pressure phase transitions in NiAs-type compounds are intimately related to the c/a ratio, where an ideal value of 1.633 is critical to determine the structural stability.

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I. INTRODUCTION

The hexagonal NiAs phase ($P6_3/mmc$, $Z=2$) is one of the most common AB-type structures. In this phase, each cation has the same octahedral environment as it is in NaCl structure, but the anions have their six neighbors hexagonally arranged. The sites of the two atomic species are not equivalent and hence there exists an anti-NiAs structure where cations and anions have positions interchanged in comparison to the NiAs phase. This structure has a unique position in crystal chemistry, being intermediate between predominantly ionic compounds with NaCl structure and intermetallic compounds having the CsCl structure.[1] In crystal chemistry the NiAs phase is of fundamental importance in ordering the wealth of known structures and in helping to elucidate structural principles. The graphical connection of topologically related structures can be represented as a hierarchic ordering in the form of a family tree,[2] the NiAs structure as a high symmetry parent structure being a so-called aristotype.[3] Therefore, general inspection of the phase transition in the NiAs compounds seems more or less complicated but very interesting.

Pearson in 1972 noted that 55 binary compounds known to have the NiAs structure all contain a transition-metal (TM) ion, with only one exception, AuSn.[4] Recent experiments at high pressures have revealed more exceptions without any TM ion involved: BeS,[5] BeSe,[6] BaO,[7] and MgTe (Ref. 8) among the II-VI compounds, and AlAs (Ref. 9) and AlP (Ref. 10) among the III-V compounds stabilize in NiAs phase upon compression. Higher pressure experiments demonstrated that NiAs phase remains stable up to 43 and 39 GPa for AlP and AlAs, while much higher pressures of 96 and 72 GPa for BeS and BeSe, respectively.

For some NiAs-type TM compounds [MnAs,[11] CrTe,[12] MnTe,[13] and CrSb (Ref. 14)], a pressure-induced phase transition to an orthorhombic MnP type structure ($Pnma$, $Z=4$) is observed experimentally. However, the phase transition sequence in non-TM compounds remains unclear though our previous work has predicted that NiAs-type MgTe also transforms to the MnP structure under compression.[15] Instead, both experiment and theory[16] suggested that NiAs-type BaO (phase-II) transforms to a tetragonal phase (phase-III). It is greatly desirable to explore the high pressure phase transitions and the corresponding transition mechanism for non-TM NiAs-type compounds (e.g., AlAs, AlP, BeS and BeSe). It is well known that lattice dynamic instabilities are often responsible for phase transitions under pressure,[17] while the phonon dispersion curves are frequently explored in search of dynamical precursor effects of lattice instabilities. Consequently, by freezing the unstable mode, one can search for a local energy minimum and predict a high pressure phase.[18] In the present study, we have used this method to extensively explore the post-NiAs phase in these non-TM compounds (BeS, BeSe, AlAs, AlP, and BaO). Based on the current research and earlier experimental and theoretical knowledge, we have proposed an empirical rule to predict the high pressure transitions on NiAs-type compounds.

The phonon calculations have been carried out using a plane-wave pseudopotential scheme within linear response density-functional theory (DFT) (Ref. 19) as implemented in the QUANTUM-ESPRESSO package.[20] *Ab initio* electronic-structure calculations are based on the generalized gradient approximation (GGA) (Ref. 21) for the exchange-correlation energy in the density-functional theory.[22] The electronic wave functions and the electron density are expanded by the plane-wave basis sets to ensure convergence of total energy within the desired accuracy (~2 meV/atom).[23] The current calculation results are in good agreement with the experiment on the structural parameters, pressure-volume curves and the transition pressures from ground state to NiAs phase. These results prove that our calculation parameters and the pseudopotentials adopted are suitable for the high pressure study of the materials.

The lattice dynamics calculations reveal that NiAs-type BeS and BeSe do not show any dynamical instability up to 200 GPa. This is consistent with the experimental observation that these two compounds remain stable up to very high pressures 96 GPa and 72 GPa, respectively.[5,6] However, for NiAs-type AlP and AlAs, pressure-induced phonon instability of acoustic M_4^- mode (an irreducible representation of D_{6h}^4 at the M point) is predicted, leading to the structural collapse under pressure. We plot out the square of the M_4^- mode frequency versus pressure in Figs. 1(a) and 1(b), where a critical pressure P_c at which ν^2 becomes zero, signaling the

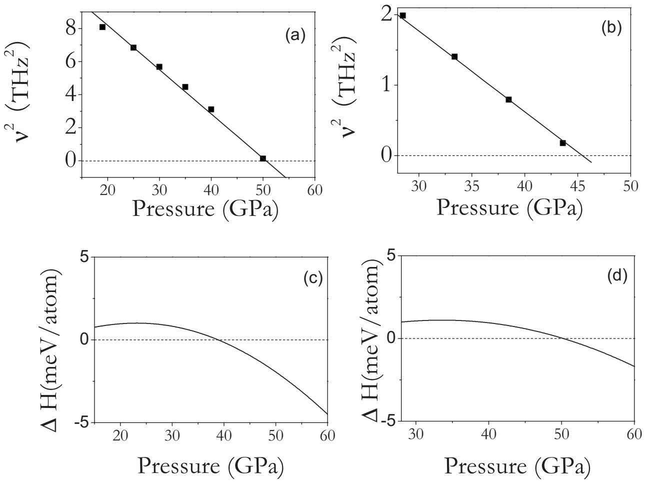

FIG. 1. The variations of the frequency square of M_4^- mode with pressure for NiAs-type AlP (a) and AlAs (b), respectively. The enthalpy curves of predicted *Pbcm* phase with respect to NiAs structure as a function of pressure for AlP (c) and AlAs (d), respectively.

structural instability, is calculated to be 51 and 45 GPa for AlP and AlAs, respectively. Taking AlAs as an example in the subsequent paragraph, we predict the post-NiAs phase in terms of the softened M_4^- mode.

The basis functions of the unstable mode are shown along the *c* direction of the three adjacent layers in NiAs phase for each compound [Fig. 2(a)] and all the atoms moved in ***a*-*b*** plane. The distortions corresponding to the basis functions lead to a new stable high pressure structure. At the transition, each atom shifts slightly from its original equilibrium position in the NiAs type structure shown in Fig. 2(a). A phonon frequency is the second-order derivative of the total energy with respect to a vibration eigenvector; therefore, an imaginary phonon ($\nu^2 < 0$) corresponds to the saddle point in the multidimensional energy surface and atomic displacement along the vibration eigenvector should lead to the true energy minimum. This can be expressed by the following simplified equation: $\Delta E = (1/2) m \nu^2 \Delta u^2$, where E is the static total energy, ν is the phonon frequency, u is the displacement along the vibration eigenvector, and Δ indicates the corresponding small variation of E and u. Energy evolution curves in Fig. 2(b) are thus derived from distortions along the eigenfunctions of the M_4^- phonon mode at selected pressures. It is evident that at high pressures of 50 and 60 GPa the energy minima lie in the distortion path and, therefore, a lower-energy structure is formed. The predicted post-NiAs phase has an orthorhombic lattice with space group *Pbcm* ($Z=4$). Note that since the eigenfunctions of the M_4^- phonon mode in AlP are identical to those in AlAs, the same post-NiAs phase applies also to AlP. This phase transition is accompanied by a continuous volume change at the transition signifying the second-order transition nature. Landau phase transition theory suggests that the space group symmetries of the initial and final structures in the displacive phase transition satisfy the group-subgroup relations. Here, we point out that $P6_3/mmc$ is a supergroup of *Pbcm*.

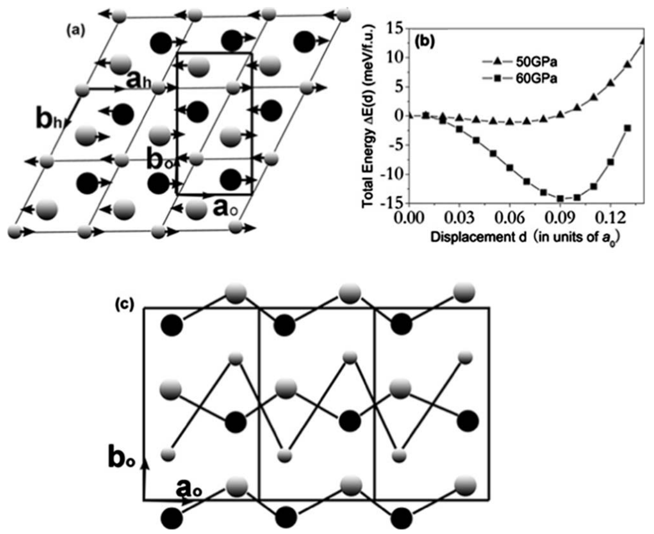

FIG. 2. (a) The distortions corresponding to M_4^- mode in the NiAs phase projected along the ***c*** axis. All the movements of the cations and anions are paralleled or anti paralleled with the ***a*** axis in ***ab*** plane indicated by arrows. Small spheres are metal atoms and large spheres are nonmetal atoms. The gray (black) spheres represent their positions above (below) the plane. (b) Total energies with atomic displacements along the eigenvectors of M_4^- mode at different pressures. (c) The Al-As and P-P (As-As) zigzag chains along the [100] direction in AlP (AlAs). At 60 GPa, the lattice parameters of *Pbcm* phase for AlP are $a=3.236$ Å, $b=5.639$ Å, $c=5.227$ Å and the Wyckoff 4*c* sites are Al: 4c (0.737, 0.25, 0) and P: 4*d* (0.761, 0.917, 0.25); At 50 GPa, the lattice parameters of *Pbcm* phase for AlAs are $a=3.545$ Å, $b=6.050$ Å, $c=5.571$ Å and the Wyckoff 4*c* sites are Al: 4*c* (0.754,0.25,0); As: 4*d* (0.747, 0.918, 0.25).

One finds zigzag chains of cation and anion atoms running in the [100] direction of *Pbcm* structure [Fig. 2(c)]. Therefore, *Pbcm* structure is morphologically in close relation with MnP-type structure. However, in the [001] direction of *Pbcm* structure cation atoms align linearly, in clearly different from that of MnP-type structure. We thus call *Pbcm* structure as quasi-MnP type. In the NiAs phase, each cation has two close metal-metal contacts, while after the transition, it adds another two with similar metal-metal distances in the *Pbcm* structure but larger distances in the MnP-type phase. Analysis of geometrical relations between the post-NiAs and NiAs structures also elucidates the subtle difference between the *Pbcm* and MnP-type structures. At the transition, the orthorhombic *Pbcm* structure can be represented by the parent hexagonal NiAs phase as $\boldsymbol{a}_\mathrm{o}=\boldsymbol{a}_\mathrm{h}$, $\boldsymbol{b}_\mathrm{o}=3^{1/2}\boldsymbol{a}_\mathrm{h}$, and $\boldsymbol{c}_\mathrm{o}=\boldsymbol{c}_\mathrm{h}$ [Fig. 2(a)], while in the MnP-type structure, it is $\boldsymbol{a}_\mathrm{o}=\boldsymbol{c}_\mathrm{h}$, $\boldsymbol{b}_\mathrm{o}=\boldsymbol{a}_\mathrm{h}$, and $\boldsymbol{c}_\mathrm{o}=3^{1/2}\boldsymbol{a}_\mathrm{h}$.

The predicted phase transitions in AlP and AlAs are further confirmed by the enthalpy calculation (relative to NiAs structure) shown in Figs. 1(c) and 1(d). It can be clearly seen that the *Pbcm* structure starts to be stable at 39 GPa and 50 GPa for AlP and AlAs, respectively. However, the enthalpy difference between NiAs and *Pbcm* phases around 40–60 GPa is too small to be clearly distinguishable. In fact, a small variation of 2 meV/atom (within our calculation accuracy) on the enthalpy difference leads to a transition pressure change of 11 GPa. Therefore, the transition pressures obtained from phonon softening calculations (51 GPa for AlP

TABLE I. The structural transition behaviors of some NiAs-type compounds associated with c/a ratio under pressure. The third column present the c/a range of the observed/calculated (Expt./Theo.) at different pressure ranges (in brackets), where A means ambient pressure. “+” or “−“ in the Δ column represents that c/a ratio is larger or smaller than 1.633, respectively. “Tran.” indicates whether (Yes or No) the selected NiAs-type compounds have the transition to the orthorhombic structure. “Confirmed” means that the transformation has been confirmed by experiment (Expt.) or theory (Theo.).

		c/a (pressure) (GPa)				Confirmed	
		Expt.	Theo.	Δ	Tran.	Expt.	Theo.
Nonmetal	BeS	1.586(66)[a]	1.566 ~ 1.554(66 ~ 200)[b]	−	No	√	√
	BeSe	1.587(72)[c]	1.564 ~ 1.568(70–200)[b]	−	No	√	√
	Na-hP4		1.566 ~ 1.327(180 ~ 600)[d]	−	No	√	√
	MgTe	1.634(0 ~ 12)[e]	1.641 ~ 1.652(30 ~ 60)[b]	+	Yes		√
Metal	MnTe	1.618 ~ 1.559(2.5 ~ 27)[f]		−	Yes	√	
	MnAs	1.541(A)[g]		−	Yes	√	
	CrSb	1.322 ~ 1.274(0 ~ 17)[f]		−	Yes	√	
	AlP	1.607(19)[h]	1.595 ~ 1.593(19 ~ 50)[b]	−	Yes		√
	AlAs	1.578 ~ 1.542(20 ~ 38)[f]	1.609 ~ 1.613(30 ~ 40)[b]	−	Yes		√
	CrTe	1.557 ~ 1.530(A ~ 10.5)[f]	1.547 ~ 1.543(6.6 ~ 20)[b]	−	Yes	√	√
	TiS	1.953 ~ 2.021(A ~ 41)[f]	2.058 ~ 2.122(37 ~ 80)[b]	+	No	√	√

[a] Reference 5.
[b] Present study.
[c] Reference 6.
[d] Reference 24.
[e] Reference 8.
[f] Reference 14.
[g] Reference 11.
[h] Reference 10.

and 45 GPa for AlAs) are in reasonable agreement with these deduced from the enthalpy calculations. In addition, we have performed the lattice dynamics calculation and found no imaginary phonons for the *Pbcm* phase in AlP and AlAs above the transition pressures, indicating that the predicted phases are dynamically stable. Since *Pbcm* structure is a small distortion of NiAs structure at the transition, it might be difficult to identify the new phase by sole x-ray diffraction pattern[5,6] unless one goes up to very high pressure. We here analyze the theoretical Raman spectrum which might help the future verification of the predicted phase by experiment. Based on the group-theoretical analysis, one obtains only one Raman active E_{2g} mode out of the total 9 optical modes in NiAs phase. While in *Pbcm* phase, 12 Raman active modes of $2(2A_g+B_{1g}+2B_{2g}+B_{3g})$ from the 21 optical modes can be observable. It is gratifying to confirm that the Raman spectrum is a good measure to clearly resolve the structural changes at the transition.

It is interesting to note that the calculation of phonon dispersion curves on BaO-II does not reveal any softening phonon modes to drive the structural transition into the experimentally observed tetragonal phase. Inspection of BaO-II structure reveals an anti-NiAs structure with the anions and cations sitting at (0,0,0) and (1/3, 2/3, 1/4), respectively, which are opposite to the atomic positions in NiAs structure. Therefore, the high pressure behaviors of anti-NiAs structure are fundamentally contrasted to those in NiAs structure.

In survey of literatures on NiAs-type TM containing compounds, the transition sequence of NiAs → MnP has been experimentally observed in MnTe, MnAs, CrSb and CrTe while no such phase transition was found in TiS. We then selected the representative CrTe and TiS as examples and identified a pressure-induced phonon softening behavior in CrTe identical to those in AlP and AlAs while no soft mode was found in TiS. This clearly classifies the NiAs-type compounds into two groups (i) with structural instability (e.g., MgTe, AlP, AlAs and CrTe, etc.) driven by the soft phonons and (ii) with structural stability (e.g., BeS, BeSe, NiTe and TiS, etc.) without phonon instability under high pressure. It is greatly desirable to dig out a general rule to judge the pressure-induced phase transition to an orthorhombic structure on the selected NiAs compounds. Remarkably, we found that the c/a ratio, one of the major structural factors for NiAs compounds, is intimately related to the phase transition. In Table I, we have summarized the experimentally observed or theoretically predicted phase transitions associated with c/a ratio for some NiAs compounds. It can be clearly seen that there is a systematic emergence of structural transition for metallic (nonmetallic) compounds with c/a ratio below (above) the ideal value 1.633. Specifically, upon compression (i) for nometals, MgTe with c/a ratio (e.g., 1.650 at 50 GPa) larger than 1.633 undergoes the phase transition while the ones (BeS, BeSe and Na-hP4[24]) with c/a (e.g, 1.568 for BeS and 1.563 for BeSe at 50 GPa, 1.391 for Na-hP4 at 390 GPa) smaller than 1.633 remain stable; (ii) for metallic compounds, AlP, AlAs, MnAs,[11] CrTe,[12] MnTe,[13] and CrSb (Ref. 14) with c/a smaller than 1.633 are unstable, while TiS with c/a larger than 1.633 remains stable. It is known that c/a ratio normally changes with pressure. Here, we note that this does not affect our above conclusion. Onodera *et al.* demonstrated that c/a ratio increases (decreases) with pressure, depending on whether the initial c/a ratio is larger (smaller) than the ideal value 1.633, supported also by our recent results on the transparent sodium.[24] We have performed additional calculations on variation of c/a ratio with pressure for MgTe, AlP, AlAs, BeS, BeSe, CrTe, and TiS and found the same trend.

We note that since experimental and theoretical data on the structural stability of NiAs compounds are far from complete, our current theoretical model still need more testimony. Nevertheless, we are satisfied with such empirical rule to determine the phase transition although it still remains a challenge to understand why c/a ratio has such close correlation with the structural stability in NiAs compounds. It is quite clear that much experimental and theoretical effort is needed to clarify this issue. Anyhow, one might expect the high pressure phase transitions in NiAs-type NiTe, CrSe, VSe, CrS, CoTe, and PdSb ($c/a < 1.633$) based on this rule.

The present study on NiAs-type compounds in VIA-IIA and VA-IIIA compounds (AlP, AlAs BeS, BeSe, and BaO) and in transition-metal compounds (CrTe and TiS) is devoted to understanding high pressure structural transitions. We found the lattice dynamical instabilities in MgTe, AlAs, AlP, and CrTe, leading to structural transition from NiAs-type to the orthorhombic type. However, no such phase transition is found in NiAs-type BeS, BeSe and TiS up to 200 and 80 GPa, respectively. Together with the experimental results on other NiAs compounds, we here proposed an empirical rule for the pressure-induced phase transition in NiAs compounds, i.e., nonmetals (or metals) with c/a ratio larger (smaller) than 1.633 will undergo a phase transition to the orthorhombic type structure under high pressure driven by the soft modes.

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