On temperature effects on the structural phase transitions of GaP

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Abstract. In this presentation by employing a combination of calculations based on Density Functional Theory (DFT) and Molecular Dynamics simulations (MD), we show that temperature has an unquestionable role in the behavior of Gallium Phosphide under pressure, shedding a new light in the controversial interpretation of experimental results. For example, we justify the absence of some structures predicted by early theoretical works, which remained up to now misunderstood. Moreover, we predict transitions to new structures at high temperature that may encourage new experiments. The differences in the observed transition sequences at low and high temperatures indicate that the vibrational corrections we included in the DFT calculations are fundamental to the description of the stability of higher pressure structures, and may be employed on other materials. Additionally, the good agreement between DFT and MD shows the suitability of the classical effective many-body interaction potential used to describe the different high-pressure phases of GaP in the Molecular Dynamics simulations. Finally, we discuss the behavior of GaP under extreme conditions for temperatures up to 1400 K and pressures up to 50 GPa, predicting new phases.

1. Introduction

Materials subjected to high pressure may exhibit utterly different properties when compared to their behavior at normal conditions. In most cases a phase transition accompanied by the changes in the coordination of chemical elements may occur, which is associated with drastic changes of their physicals properties. Among the high-pressure studies, semiconductors have particular interest due their well known technological applications\cite{1}. In particular, gallium phosphide (GaP) is a III-V semiconductor, which has a zinc blend (ZB) structure (B3, space group \textit{F}4\textit{3}m) at ambient conditions and several phase transitions at high pressure have been reported in the literature. Early studies on resistivity measurements of GaP found a transition to a metallic phase that was thought to have \textit{\beta}-tin-type symmetry\cite{2, 3}. A few years later Yu et al.\cite{4} carried out diffraction studies and reported that the phase obtained above 22.0(5) GPa was not compatible with neither cubic nor the \textit{\beta}-tin structures. Baublitz and Ruoff\cite{5} reexamined these results with a more detailed diffraction study using energy dispersive X-ray spectroscopy(EDX) and found that the transition at 21.5(8) GPa was indeed to a \textit{\beta}-tin. Hu et al\cite{6} partially endorsed this result, by concluding that this phase is in fact a mixture of the
ZB and \( \beta \)-tin phases to allow extra reflections and shoulders on the low-angle side of the 200 and 220 peaks. The controversial study of GaP at high pressure was accentuated by Nelmes et al, using x-ray absorption (ADXR)[7], that found a diffraction profile similar to the obtained by Baublitz and Ruoff and concluded that the transition was found at 24(2) GPa and that the profile that gives a good fit to the data was consistent with a site-disordered Cmcm structure with \( a = 4.707(2) \) Å, \( b = 4.949(1) \) Å, \( c = 4.701(3) \) Å, \( y(Ga/P) = 0.647(3) \), and \( y(Ga/P) = 0.159(3) \).

The Cmcm structure can be regarded as a distortion of the rock salt (NaCl) structure and it has been observed in several III-V and II-VI compounds[8, 9].

With the advent of high performance multiple CPU computers associated with massive parallel processing, interconnecting thousands of processors, studies based on computer simulation have been particularly valuables in complementing the experimental data, helping in their interpretation and in predicting new thermodynamically stable phases. In this scenario, molecular dynamics simulations (MD) and density functional theory (DFT) are two of the most prominent frameworks for materials computational simulations. Several works involving either MD or DFT[10, 11, 12, 13, 14] separately have been performed in the past few decades. However, these methods can actually be combined to provide a more complete description of the temperature effects on the phase transition of materials submitted to high pressure.

While DFT succeeds at low temperatures, where quantum effects are very important and vibrational corrections can be included within the harmonic approximation, MD shines at higher temperatures, where anharmonic effects become relevant. Still, even MD can provide reliable results at low temperatures, such as the crystal structures and several mechanical properties. Therefore, both methods should display similar trends at intermediate temperatures and complement each other at low and high temperatures.

In this work, we revisit the problem of high-pressure phases of GaP by adding finite-temperature effects to DFT via vibrational corrections within the harmonic approximation and atomistic molecular dynamics (MD) simulations based on an effective many-body interaction potential proposed by Ribeiro-Silva et al.[15]. By examining the phase diagram of GaP at extreme conditions, this work summarizes and complements our published work[16].

\textit{Ab-initio} calculations based on Density Functional Theory (DFT) were performed using the Quantum Espresso package [17, 18, 19] together with LDA and GGA exchange-correlation functionals for electron-electron interactions. For the calculation of the vibrational free energy we use the harmonic approximation and calculate the Gibbs free energy of the structures at different pressures and temperatures. We assume that the equilibrium positions of the atoms in each structure remain unchanged with temperature (thermal expansion effects are not included), so the thermal contributions come only from the vibrational free energy. With that assumption, the Gibbs energy is given by:

\[
g(P, T) = h_{eq}(P, 0) + f_{ph}(P, T),
\]

where \( h_{eq}(P, 0) \) is the zero temperature enthalpy per atom, given by ground state DFT calculations, and \( f_{ph}(P, T) \) is the finite temperature vibrational free energy per atom. On the other hand, the MD simulations use the Vashishta et al[20] effective many-body interaction potential, which have proven to be very efficient in the study of physical properties of several materials under extreme conditions such as the high-pressure phases of semiconductors and under highly extreme conditions such as the damage mechanism during projectile impact[21]. For more details about the parameters used in the potential, see Ref.[16]. Those parameters were chosen in order to reproduce the elastic constant \( C_{11} \), the bulk modulus \( B \), and the cohesive energy per atom. In order to validate this choice, other properties which were not used as input were calculated, such as the melting temperature, vibrational density of states, specific heat, Young’s modulus, shear modulus, Poison ratio, radial distribution function for crystalline,
amorphous, recrystallized and liquid GaP, coordination numbers and the possible high-pressure phases.

2. Results
To shed a light on some discrepancies between controversial experimental results and zero temperature DFT, which predicts some phases not found in experimental results, we now discuss the role of temperature in the phase transitions of gallium phosphide under pressure. The methodology is quite different for DFT and MD calculations.

![Figure 1. Phase diagram of GaP for (a) MD calculation (b) GGA and (c) LDA calculation.](image)

For MD we set the initial configuration to a Zinc Blend (ZB) structure at a very low temperature (1 K) and atmospheric pressure and then the system was heated at constant pressure in steps of 10 K up to 1400 K. At each temperature, the system is allowed to run for 5000 time steps (one time step is about 2.0 fs) in the NPT ensemble. Finally, with the system at \( T = 300, 1000 \) and 1400 K we increase the pressure up to 250 GPa at a rate of 0.5 GPa/2 Kps in the NPT ensemble. As the pressure increases the system may spontaneously go to other phases. The structures that emerge from the pressure increase are characterized by examining the coordination number, bond angles and the radial distribution functions. For DFT, we performed variable-cell calculations in which the unit cell parameters and atomic coordinates were relaxed to a target pressure with a tolerance of 0.05 GPa. Energies and interatomic forces were relaxed to tolerances of \( 10^{-4} \) Ry and \( 10^{-5} \) Ry/Bohr, respectively. Fig 1 shows the phase
diagrams for each calculation: MD (a), DFT-GGA (b) and DFT-LDA (c). The main difference among the graphics is that DFT displays Sc16 phase for both GGA and LDA, while MD does not show a stability region for this phase. The absence of the Sc16 structure in MD calculations may be related to limitations of the effective interatomic potential used in this work. It is worth to stress that the results obtained with MD are dynamical and, even if Sc16 had a region of stability, a transition to this phase could be prohibited due to a large energy barrier. Moreover, one can see in the phase diagram for the DFT calculations that the region corresponding to the Sc16 phase narrows down as temperature increases while the curves for the Cmcn, NaCl, β-Sn and Immm structures shift towards lower pressures. The region of stability for the Sc16 phase, if present, becomes extremely narrow at \( T = 1400 \) K and the structure is completely unstable at higher temperatures, which could explain its absence in experimental measurements. The transition sequence we observe at intermediate temperatures depends on the temperature itself, but it also depends on the functional used in the DFT calculations. For example, at \( T = 1400 \) K, we see the sequence ZB \( \rightarrow \) Sc16 (narrow) \( \rightarrow \) β-Sn \( \rightarrow \) NaCl in LDA and ZB \( \rightarrow \) Sc16 (narrow) \( \rightarrow \) Cmcn\( \rightarrow \) β-Sn \( \rightarrow \) Immm in GGA. Moreover, the calculations indicate that the Immm becomes the most stable at higher pressures, regardless of temperature and functional choice, and that the transition pressure decreases with increasing temperature in the observed range. At higher temperatures, both functionals also show a region of stability for the NaCl structure at intermediate pressures (15–20 GPa), a feature also observed in the MD simulations. In our MD calculations, the transition sequence at room temperature is also the same as the zero temperature case. As temperature increases, the transition sequence becomes ZB \( \rightarrow \) β-tin \( \rightarrow \) NaCl for temperatures around 1000 K and ZB \( \rightarrow \) NaCl for temperatures above 1400 K.

3. Conclusion
We have studied the high pressure phases of gallium phosphide by a combination of DFT calculations with vibrational corrections within the harmonic approximation and MD simulations based on an effective many-body potential which reproduces various properties of GaP. We have found that a good agreement between MD and DFT phase diagrams can only be achieved when vibrational corrections are included in the Gibbs free energy obtained in DFT. We have also justified the absence of the Sc16 structure, in experimental results, predicted by early theoretical works. Both calculations indicate that, as temperature is increased, the β-tin and Cmcn structures become stable for a wider range of pressures and the Sc16 structure becomes less stable. At room temperature, the NaCl phases is not found to be stable, but our calculations at \( T = 1400 \) K indicate that it becomes stable at higher temperatures. We also show that ground state DFT calculations do not capture the correct transition picture at high temperatures, indicating the need of inclusion of vibrational corrections. Even at the level of harmonic approximation, such corrections already lead to closer agreement between DFT and MD, which includes anharmonic effects. Moreover, the good agreement between \textit{ab-initio} and semi empirical calculations indicate that the classical potentials used in MD can be adapted and employed in related materials.

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