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ORIGINAL PAPER

First-principles study of the elastic tensor of GaP at high electronic temperature

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Abstract
Gallium phosphide (GaP) in the cubic zinc-blende structure is a wide bandgap III-V semiconductor used in electronic devices due to its electroluminescent properties. Despite this importance for optoelectronics, the response of its three-element elastic tensor to illumination is unknown. We use density functional theory to investigate changes in the elastic moduli under photoexcitation. We assume a thermalized photoexcited state represented using hot-electron Fermi distributions of Kohn-Sham occupation numbers, with electronic temperatures between 0.1 eV to 1.0 eV, corresponding to 1.2 to 11,606 K and excited-carrier densities of up to 10^{22} cm^{-3}. Ground-state elastic constants computed in this work agree with prior experimental and simulation results. When computing the elastic moduli for increasing electronic temperatures, the elements of the elastic tensors change by up to 61% and approach each other. Based on the Born stability criteria the material remains stable under all electronic temperatures.

Introduction

For several wide bandgap semiconductors including ZnO, ZnS, and CdS a modification of their elastic properties was reported under illumination, see e.g., Ref. [1] and references therein. Stiffness increases of up to 40% were discussed for ZnO in that reference and these optomechanical effects were attributed to the influence of defects in the material. At the same time, such a strong change of the elastic properties of a material opens the possibility of interesting applications of these effects and renders tuning the magnitude of the response through defect or materials engineering an interesting research endeavor.

Unfortunately, effects of illumination on elastic properties are poorly understood and their detailed study using accurate electronic-structure theory is largely absent. In particular, better understanding is needed regarding the origin of modifications of the elastic properties. Here, we use first-principles quantum-mechanical simulations based on density functional theory to study the influence of intermediate to high *electronic* temperature on the elastic tensor of gallium phosphide (GaP). This material is a wide band gap III-V semiconductor that is widely used in electronic devices due to its electroluminescent properties.

With the goal of eventual materials design in mind, carefully disentangling different possible origins of optomechanical effects is critical to build intuition that is necessary for future selection of the most promising materials for applications. While achieving this using computational work may save resources and time, it also is a route to unequivocally determine the magnitude of the different contributions to optomechanical properties when investigating new materials [2]. In this work, our main motivation is to quantify

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electronic effects on the elastic tensor, independently of any lattice temperature effects. High electronic temperatures are particularly relevant in the ultrafast excitation regime that becomes accessible experimentally via pump-probe techniques using ultrashort pulsed laser [3] or ion beams [4]. In this work we briefly report the outcomes of a Research Experiences for Undergraduates (REU) summer project that we accomplished within the PREM seed collaboration of the Illinois MRSEC, Tennessee State University, and Fisk University.

Materials and methods

We used density functional theory (DFT), as implemented in the Vienna *Ab-Initio* Simulation Package [5, 6] (VASP), to calculate the elastic constants of ground-state GaP as well as several non-zero electronic temperatures. The zinc-blende structure of GaP is used, where each gallium (Ga) atom is at the center of the cubic structure and the phosphide atoms (P) are at the four corners. In our simulations, the exchange-correlation functional is described by the generalized-gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE) [7]. A 6×6×6 Monkhorst-pack **k**-point grid [8] is used to sample the Brillouin zone and Kohn-Sham states are expanded into a plane-wave basis up to a kinetic-energy cutoff of 500 eV. This leads to a total energy convergence of about 0.25 meV for the entire simulation cell and we relaxed forces on all atoms for T = 0 K electronic temperature to less than 5 meV/atom. Elastic constants are derived from the strain-stress relationship using values determined from six finite distortions of the lattice. For this, we compare the VASP internal method for computing the stress tensor [9] and a manual displacement approach implemented in the Atomic Simulation Environment (ASE) [10] and its extension module 'Elastic' [11, 12].

To model the photoexcited state, we assume a fully thermalized electronic system which is a good approximation for semiconductors about a picosecond after the excitation or even earlier, as illustrated e.g., in Ref. [13] for GaN. The corresponding hot-electron temperatures are simulated within Mermin DFT [14] using a range of smearing values $\sigma = k_B T$ from 0.1 eV to 1.0 eV, that enter the Fermi distribution of electron and hole occupation numbers,

$$f(E) = \frac{1}{e^{(E-E_F)/\sigma} + 1}.$$

For these occupations we compute the corresponding excited electron-hole pair densities using

$$n = \int \frac{1}{e^{\frac{E-E_F}{\sigma}} + 1} g(E)\, dE,$$

leading to values of up to $n = 10^{22}$ cm^{-3} (see right panel of Fig. 1). The influence of these smearing parameters on the occupation numbers of Kohn-Sham states is illustrated in the left panel of Fig. 1 and we subsequently compute the elastic tensors of the material in this work. Thermalization of these excited electronic states with the lattice occurs on the several tens of pico-second time scale and is not the subject of this work. We did, however, simulate the change of

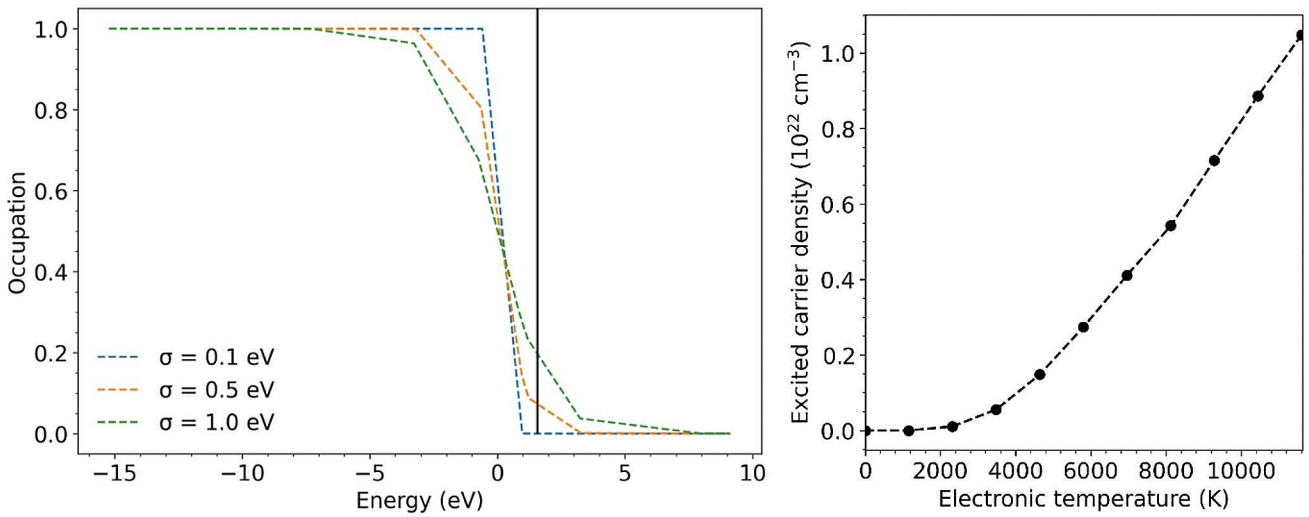

Fig. 1 (left) Kohn-Sham occupation numbers for different band energies at the Gamma point of the Brillouin zone, for different electronic temperatures, expressed via the Fermi smearing parameter Sigma. Occupations are shown for Sigma = 0.1 eV, 0.5 eV, and 1.0 eV. The solid vertical line is the conduction band minimum at 1.57 eV at the Gamma point in our DFT-PBE simulations for the smallest smearing. This is similar to the lowest indirect and direct gaps of 1.59 eV reported on Materials Project [15–17]. (right) Excited electron-hole pair densities at electronic temperatures covered in this work, corresponding to smearing values ranging from 0 to 1.0 eV

the lattice parameter upon increasing the electronic temperature and observe a reduction from 5.506 Å to 5.485 Å when the temperature is increased to σ=0.8 eV. The band gap at the Gamma point increases from 1.57 eV to 1.68 eV for the same change in electronic temperature.

Results and discussion

First, we verify the crystal structure by computing the equilibrium lattice constant of the cubic zinc-blende eight-atom conventional unit cell. For this, we vary the volume between 157.13 $Å^3$ and 177.17 $Å^3$ and compute the total energies from ground-state density functional theory simulations. We perform this procedure at T = 0 K electronic temperature and fit the Birch-Murnaghan equation of state to this data. This yields a lowest total energy of -36.503 eV at the minimum of the E(V) curve and a corresponding unit-cell volume of about 166.94 $Å^3$. Our result agrees very well with the value reported on Materials Project [15–17] of 41.737 $Å^3$ for a two-atom primitive unit cell, corresponding to 166.95 $Å^3$ when multiplied by four to match the 8-atom conventional cell used in this work.

There are three independent elements of the elastic tensor for the cubic zinc-blende structure used here to describe GaP [18]. We use the normalized Voigt notation for cubic symmetry to describe these: C11, C12, C44. First, we compute all three using the ASE 'Elastic' implementation at T = 0 K of electronic temperature and compare the results to the tensor elements computed using the VASP internal routines (see Table 1). We find that the values for C11 and C12 from both methods agree very well, but C44 differs by about 33%. The origin of this deviation is not entirely clear, but we note that the ASE Elastic method used structures with strain magnitudes of ± 1% and ± 2%, whereas the VASP internal routine uses finite displacements of ± 1.5%.

Next, we compare these results to previously published theoretical and experimental data. Relative to computational data from the Materials Project [15–17], where ± 0.5% and ± 0.1% displacements were used, our values from the VASP internal routine agree very well for all tensor elements. Consequently, our ASE 'Elastic' results for C11 and C12 agree well with the Materials Project data, but the disagreement is significant for C44, as discussed above. Relative to the experimental data from Raoul Weil and Warren O. Groves [19], our values from the VASP internal routines agree within about 15% or better. Also, the trend C11 > C44 > C12 between the elastic constants captured in the experiment is reflected in our results. The difference of elastic constant values from experiment and DFT simulations for another cubic semiconductor, GaAs [9], show the largest deviation of about 9% also for C44. In summary, we conclude that the elastic constants computed with the VASP internal routine constitute a reliable starting point for temperature dependent simulations in this work.

Table 1 Elastic tensor elements C11, C12, and C44 of GaP at T = 0 K from our simulations, compared to prior experimental and computational literature

	Elastic Moduli (GPa)		
	C11	C12	C44
This work (VASP routine)	126.79	53.23	64.50
This work (ASE Elastic)	125.13	51.73	82.72
Materials Project [15–17]	125.00	52.00	65.00
Weil & Groves [Exp., Ref. 18]	141.20	62.50	70.40

We then use the VASP internal routines to account for non-zero electronic temperature in computing the components of the elastic tensor and visualize our results in Fig. 2. This data shows that C11 and C44 decrease by about 36.33% and 61.88%, respectively, and C12 increases slightly by 2.54% as we increase the electronic temperature up to 11,606 K. We considered electronic temperatures up to 11,606 K, which are reachable on a femto- to picosecond time scale after photoexcitation. For instance, 1 ps after laser irradiation the electronic temperature in a gold thin film can reach up to 1.96×10^4 K, based on an ultrashort laser metal heating model [20]. As a result of the sharp decrease of C11 and C44, and slight increase of C12 from their starting values, these elastic constants reach values closer to each other at the highest electronic temperature studied in our calculation. This is a similar trend as the one reported in another computational study of silicon, which also shows three independent elastic constants and investigated a broader electronic temperature range up to 25,000 K [21]. Their reported temperature dependence of C11, C12, and C44 shows the same behavior as our calculation up to 11,606 K by having C11 decreased by 37.5%, C44 by 60% and C12 increased by 3%. C12 begins to decrease after 12,500 K and all C11, C12, and C44 converge near 0. We also note that our results for C11, C12, and C44 indicate stability of the material by means of the three Born stability criteria for cubic systems [22] across all electronic temperatures studied here.

Conclusions

We studied the ground-state lattice structure of GaP and computed all three independent elements of the elastic tensor using first-principles density functional theory simulations. Our results for the electronic ground state are in agreement with prior computational and experimental data. Accounting for non-zero electronic temperature, to represent thermalized excited states after photoexcitation, leads to significant changes of the tensor elements. We find that C11 and C44 decrease by about 36.33% and 61.88%,

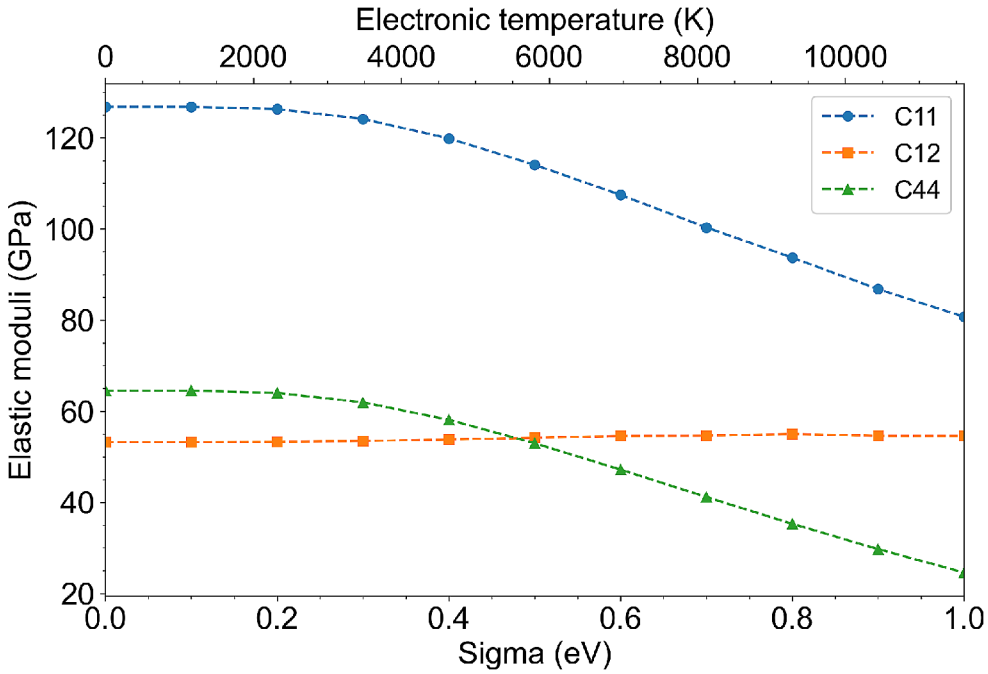

Fig. 2 Elements of the elastic tensor, C11 (blue), C12 (orange), and C44 (green), of GaP for different electronic temperatures up to 1.0 eV

respectively, and C12 increases by 2.54%. Direct comparison to experiment is currently outstanding. The effect of high lattice temperature and of defects in the materials on the elastic tensor remains to be studied in future work.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1557/s43580-024-00825-0.

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Author contributions Ethiopine Choping, Junehu Park, Cindy Wong contributed to the simulations and data collection. All authors contributed to data analysis, scientific discussions, and manuscript preparation. The final manuscript has been read and approved by all authors.

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Data availability The data used to support findings in this study are included and additional input and output files of all simulations are available upon request.

Declarations

Ethical approval No human participants were involved in this study and no ethics approval is required.

Consent to participate No human participants were involved in this study.

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

References

1. J. Dong, Y. Li, Y. Zhou, A. Schwartzman, H. Xu, B. Azhar, R. Jaramillo, Giant and controllable photoplasticity and photoelasticity in compound semiconductors. Phys. Rev. Lett. **129**(6), 065501 (2022). https://doi.org/10.1103/physrevlett.129.065501
2. D.K. *Ferry: Semiconductors* (Macmillan, New York 1991)
3. J. Lloyd-Hughes et al., J. Phys.: Condens. Matter. **33**, 353001 (2021). https://doi.org/10.1088/1361-648X/abfe21
4. L. Kalkhoff, A. Golombek, M. Schleberger, K. Sokolowski-Tinten, A. Wucher, L. Breuer, Phys. Rev. Res. **5**, 033106 (2023), https://doi.org/10.1103/PhysRevResearch.5.033106
5. G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B **54**(16), 11169 (1996). https://doi.org/10.1103/PhysRevB.54.11169
6. G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B **59**(3), 1758 (1999). https://doi.org/10.1103/PhysRevB.59.1758
7. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. **77**(18), 3865 (1996). https://doi.org/10.1103/PhysRevLett.77.3865
8. H.J. Monkhorst, J.D. Pack, Special points for Brillouin-Zone integrations. Phys. Rev. B **13**(12), 5188 (1976). https://doi.org/10.1103/PhysRevB.13.5188

9. Le Y. Page, P. Saxe, Symmetry-general least-squares extraction of elastic data for strained materials from ab initio calculations of stress. Phys. Rev. B **65**(10), 104104 (2002). https://doi.org/10.1103/PhysRevB.65.104104
10. A.H. Larsen, J.J. Mortensen, J. Blomqvist, I.E. Castelli, R. Christensen, M. Dułak, K.W. Jacobsen, The atomic simulation environment—a Python library for working with atoms. J. Phys.: Condens. Matter. **29**(27), 273002 (2017). https://doi.org/10.1088/1361-648X/aa680e
11. P.T. Jochym, Module for calculating elastic tensor of crystals, software, https://github.com/jochym/Elastic/, https://doi.org/10.5281/zenodo.593721
12. P.T. Jochym, K. Parlinski, M. Sternik, TiC lattice dynamics from ab initio calculations. Eur. Phys. J. B-Condensed Matter Complex. Syst. **10**, 9–13 (1999). https://doi.org/10.1007/s100510050823
13. V.A. Jhalani, J.J. Zhou, M. Bernardi, Ultrafast hot carrier dynamics in GaN and its impact on the efficiency droop. Nano Lett. **17**(8), 5012–5019 (2017). https://doi.org/10.1021/acs.nanolett.7b02212
14. N.D. Mermin, Thermal properties of the inhomogeneous electron gas. Phys. Rev. **137**(5A), A1441 (1965). https://doi.org/10.1103/PhysRev.137.A1441
15. A. Merchant, S. Batzner, S.S. Schoenholz et al., Scaling deep learning for materials discovery. Nature. **624**, 80–85 (2023). https://doi.org/10.1038/s41586-023-06735-9
16. de M. Jong, W. Chen, T. Angsten et al., Charting the complete elastic properties of inorganic crystalline compounds. Sci. Data. **2**, 150009 (2015). https://doi.org/10.1038/sdata.2015.9
17. The Materials Project, Materials data on GaP by materials Project. United States: N p 2020 Web https://doi.org/10.17188/1200314
18. N.W. Ashcroft, N.D. Mermin, *Solid State. Physics* (Holt, Rinehart and Winston) Appendix C, New York, 1976)
19. R. Weil, W.O. Groves, The elastic constants of gallium phosphide. J. Appl. Phys. **39**(9), 4049–4051 (1968). https://doi.org/10.1063/1.1656922
20. H.L. Tsai, L. Jiang, (2005, April). Fundamentals of energy cascade during ultrashort laser-material interactions. *In Photon Processing in Microelectronics and Photonics IV* (Vol. 5713, pp. 343–357). SPIE. https://doi.org/10.1117/12.589461
21. P. Brommer, A. Kiselev, D. Schopf, P. Beck, J. Roth, H.R. Trebin, Classical interaction potentials for diverse materials from ab initio data: a review of potfit. Modelling Simul. Mater. Sci. Eng. **23**, 074002 (2015). https://doi.org/10.1088/0965-0393/23/7/074002
22. Félix, Mouhat, F.-X. Coudert, Necessary and sufficient elastic stability conditions in various crystal systems. Phys. Rev. B **90**, 224104 (2014). https://doi.org/10.1103/PhysRevB.90.224104