

Pressure-induced semiconducting behavior of calcium from *ab initio* calculations

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Pressure-induced dielectrization (full or partial) of fcc alkaline-earth metals Ca and Sr, as well as chemically similar to them rare-earth element Yb, has long attracted attention of both theoretical and experimental physicists. The resistivity measurements demonstrate that in a certain pressure range, each of these elements exhibits a semiconducting (or, perhaps, semimetallic) behavior, most pronounced in case of Yb (see [1] and references therein). In addition, at these pressures a thermopower anomaly is observed [2, 3]. Upon further compression, a re-entrance of metallic conductivity occurs, as the fcc→bcc structural transition takes place. Theoretically, the electronic spectrum of fcc alkaline-earth elements calculated within density functional theory (DFT) [4] is characterized by a hybridization gap which develops into a real gap upon compression and closes at the transition to a metallic bcc phase [5].

However, there are quantitative discrepancies between theory and experiment regarding both the width of energy gap and the pressure interval where it opens. On the one hand, the discrepancies can be attributed to inaccuracies in the transport measurements under pressure. On the other hand, this situation is certainly related to the well-known problem — incorrect estimation of band gaps within DFT. In order to obtain more accurate electron excitation spectra of semiconductors and insulators, the quasiparticle GW approximation is usually employed [6]. However, this method is notoriously complicated and computationally expensive. An alternative approach is to use hybrid functionals [7] that are superior to the DFT in reproducing the experimental gap values, at the same time allowing one to considerably reduce the computational cost as compared to the GW method.

We present *ab initio* calculations of the electronic structure of calcium in the pressure range up to ~20 GPa, where the fcc phase is stable. The initial calculations were done within DFT and then the GW method was applied. The comparison of obtained results demonstrates that with the GW method, the gap is wider and the pressure interval where it exists is smaller than in our DFT calculations. We also checked the applicability of the hybrid functional approach in the situation of variable compression. A value of mixing parameter α at various pressures was determined from comparison with our GW results. The obtained electronic spectra are relatively insensitive to small variations in α value.

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1. E.G. Maksimov, M.V. Magnitskaya, V.E. Fortov *Phys. Usp.* **48**, 761 (2005)
 2. C. Divakar, M. Mohan, A.K. Singh *Solid State Commun.* **41**, 833 (1982)
 3. V.V. Brazhkin, O.B. Tsiok, M.V. Magnitskaya *JETP Lett.* **97**, 490 (2013)
 4. W. Kohn, L.J. Sham *Phys. Rev.* **140**, A1133 (1965)
 5. H.L. Skriver *Phys. Rev. B* **31**, 1909 (1985)
 6. F. Aryasetiawan, O. Gunnarson *Rep. Prog. Phys.* **61**, 237 (1998)
 7. A.D. Becke *J. Chem. Phys.* **98**, 1372 (1993)