Interplay between Coulomb interaction and hybridization in Ca and anomalous pressure dependence of resistivity

D. Y. Novoselov[+*1)], *D. M. Korotin*[+], *A. O. Shorikov*[+*], *A. R. Oganov*[×∘], *V. I. Anisimov*[+*]

[+]*M. N. Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620108 Yekaterinburg, Russia*

[*]*Department of theoretical physics and applied mathematics, Ural Federal University, 620002 Yekaterinburg, Russia*

[×]*Skolkovo Institute of Science and Technology, 143026 Moscow, Russia*

[∘]*Moscow Institute of Physics and Technology, 141701 Dolgoprudny, Russia*

Submitted 30 November 2018
Resubmitted 25 December 2018
Accepted 26 December 2018

DOI: 10.1134/S0370274X19060092

Metallic Ca exhibits unusual growth of electrical resistivity with an increase of pressure [1]. Moreover Ca has a very complex phase diagram and in the high-pressure phase it has the superconductivity with critical temperature of 25 K, the highest among all chemical elements [2]. The explanation of all this behavior can originate from a specific electronic structure characteristic of the high-pressure phase(s). Despite large effort achieved recently in developing computational methods based on DFT (Density Functional Theory), researchers failed to reproduce the full phase diagram of Ca.

We start with DFT calculations, which give the crystal structure with relaxed atomic positions for a series of cell volumes and provide the electronic structure of Ca. The pseudopotential VASP package [3] was used for optimization of crystal structures and band structure calculations which was used as the starting point for construction of a correlated states Hamiltonian in Wannier function (WF) basis. For the constructed Hamiltonian the Coulomb correlations were taken into account within DFT + U method using so-called "restricted Hartree–Fock" approach.

An increase of external pressure gives rise to s-d electron transfer in calcium that results in the localization of the charge density in the interstices of the crystal cell, i.e., the formation of an electride. The corresponding electronic states are partially filled and localized and, hence, strong electronic correlations could arise. We have carried out theoretical calculations for the high-pressure phases of Ca taking into account the Coulomb interactions between the electronic states centered on the interstitial sites. The results of our calculations and proposed microscopic model showed that the structural phase transition under high pressure is due to an interplay of hybridization and correlation effects. Furthermore, it was found that the Coulomb repulsion can explain the experimentally observed anomalous growth of the resistivity with pressure in the simple cubic phase of calcium.

We have found that both the transfer of electrons from $4s$ to $3d$ states with increasing pressure and Coulomb correlations play an important role in the formation of the ground electronic state of the system under pressure. The former leads to the localization of the electron density in the interstices and the existence of partially filled bands, rendering the cubic phase of calcium an electride and the latter is responsible for the opening of the energy gap.

The idea of taking electronic correlations into account for electride states allowed us to describe and explain the experimentally observed structural transition to the simple cubic phase, as well as the anomalous behavior of resistivity as a function of compression. Quantitative description of this transition requires more accurate charge self-consistent theoretical techniques such as dynamical mean-field theory (DFT + DMFT) or DFT + U.

Authors thank M. A. Korotin for his CPA (Coherent-Potential Approximation) computer code used in our calculations.

This work was supported by Russian Science Foundation (Project 19-72-30043).

Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S0021364019060043

1. T. Yabuuchi, Y. Nakamoto, K. Shimizu, and T. Kikegawa, J. Phys. Soc. Jpn. **74**, 2391 (2005).
2. H. Fujihisa, Y. Nakamoto, K. Shimizu, T. Yabuuchi, and Y. Gotoh, Phys. Rev. Lett. **101**, 095503 (2008).
3. G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).

1)e-mail: novoselov@imp.uran.ru