

# Interplay Between Coulomb Interaction and Hybridization in Ca and Anomalous Pressure Dependence of Resistivity

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Increasing 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 structure, i.e., the formation of an electride. The corresponding electronic states are partially filled and localized and, hence, 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 site. 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 increase of resistivity of the simple cubic phase of calcium under pressure.

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Ca metal exhibits unusual increase of electrical resistivity with increasing pressure [1]. Moreover, Ca has a very complex phase diagram and in the high-pressure phase it is superconducting with critical temperature of 25 K, the highest among all elements [2]. X-Ray diffraction reveals that at low temperature Ca undergoes series of phase transition: it has  $bcc$  structure below 32 GPa; it possesses  $\beta$ -tin ( $I4_1/amd$ ) tetragonal structure in pressure range 32–40 GPa; then it undergoes a phase transition into the  $Cmmm$  structure which is a distorted cubic structure; above 47 GPa Ca has simple cubic (SC) structure [3, 4]. The existence of the  $I4_1/amd$  structure was predicted in DFT (Density Functional Theory) calculations [3] at first and then it was confirmed to be stable below 7 K in the experiment [4]. Nevertheless, despite large effort achieved recently in developing computational methods based on DFT, within DFT it is not possible to reproduce fully the phase diagram of Ca. In particular, the SC phase always has higher enthalpy in DFT calculations [3, 5]. The explanation of all these puzzles can originate from a specific electronic structure which appears under high pressure.

The idea of the relationship between possible  $s$ - $d$  electron transfer and anomalous increase of resistivity

with pressure in a wide pressure range from 32 to 109 GPa was proposed in [1]. In particular, it was proposed that the mechanism of bonding [6] can be based on electron transfer from  $s$ - to  $d$ -states which takes place under pressure [7, 8] and effects of strong hybridization and Coulomb correlations can be important for the explanation of intriguing electronic properties [1].

The first theoretical attempt in the description of the phase transition from  $\beta$ -tin to SC phase utilized hybrid functional which partially takes into account interactions between electrons [9]. Although the transition into  $Cmmm$  phase was not reproduced in this calculation, it hints on the importance of Coulomb interactions between electrons in the states that are a mixture of atomic  $s$ - and  $d$ -states for both electronic and structural properties of calcium. However, a systematic picture and microscopic understanding of the relationship between the resistivity anomalies, structural transformations under pressure and interplay between hybridization and Coulomb repulsion in the high-pressure phases of Ca was not studied.

We start with simple DFT calculations, which give the crystal structure with relaxed atomic positions for a series of cell volumes and yield the electronic structure of Ca. The pseudopotential VASP package [10] was used for optimization of crystal structures and band

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structure calculations which are 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 the DFT+U method using the so-called “restricted Hartree–Fock” approach which was successfully applied for description of band-structure in the vicinity of Fermi level of a correlated compound [11].

For further interpretation of the DFT and DFT+U results, we also propose an effective microscopic model which explains the phase transition as a result of interplay between hybridization and correlation effects and reproduces the energy gap opening in SC phase of Ca.

In the [5] the idea of the formation of the electrider in simple cubic phase of Ca under pressure was proposed based on an analysis of the unusual distribution of the electron localization function (ELF) in the simple cubic phase. The ELF had maxima not only at Ca sites, but also in the cubic voids between them. To analyze the changes of the electrider states we have also checked the ELF of the lower-symmetry phases, namely  $\beta$ -tin and  $Cmmm$ . Figure 1 shows the charge density obtained as a result of DFT calculations for SC (a) and

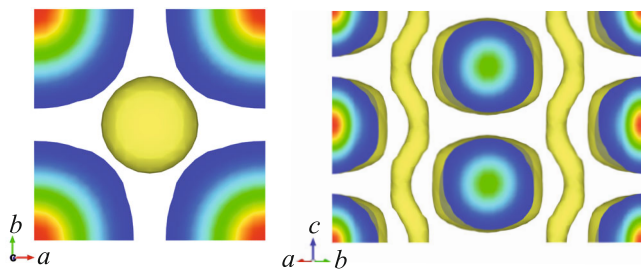


Fig. 1. (Color online) Charge density for SC (left panel) and  $\beta$ -tin (right panel) structures as obtained in the GGA calculation at  $P = 42.6$  GPa

$\beta$ -tin (b) structures. One can see that the charge density behaves completely differently bonding  $s$ -orbital of Ca in SC phase forms a large region which contains 0.66 electrons whereas in  $\beta$ -tin structure there are 0.61 electrons in the small narrow worm-like areas in the interstitial space. In the  $bcc$  structure of calcium there is no obvious empty space in the structure; one can view this structure as derived from the SC structure, with an extra Ca atom filling the cubic void (in the SC structure this void is occupied by the localized electron pair). With pressure increase, calcium goes from  $bcc$  into a strongly distorted  $\beta$ -tin structure in which the Ca atoms are displaced from the ideal positions of the cubic structure alternating along the  $c$  axes, thus forming corrugated planes with different Ca–Ca distances. Under further compression the distance between atoms

decreases, which strengthens hybridization due to increasing overlap of the bonding  $s$ -orbital in the middle of the unit cell and Ca  $d$ -orbitals. At pressures above 42 GPa, the transition to the simple cubic phase takes place, in which the electrider states are formed.

Note, that  $\beta$ -tin structure has narrow channels running along the  $c$ -direction, where accumulation of charge density takes place. This change in charge distribution follows the distortions of the crystal structure.

To investigate the influence of Coulomb interaction we have carried out GGA+U calculations for the SC structure. In Figure 2 we show the number of

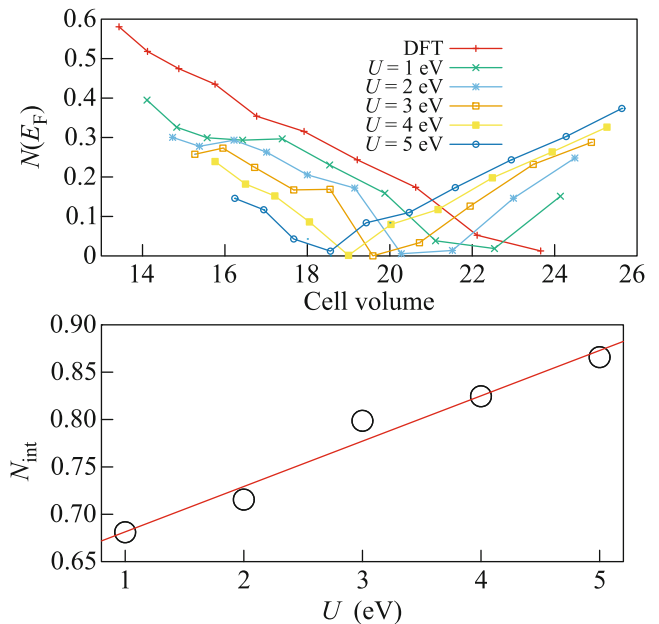


Fig. 2. (Color online) Number of electronic states at the Fermi level  $N(E_F)$  (upper panel) and number of electrons occupying the interstitial site  $N_{\text{int}}$  (lower panel) of SC Ca for different values of the Coulomb parameter  $U$

states at the Fermi level for the SC structure. DFT gives  $N(E_F)$  increasing with decreasing of cell volume. Within DFT+U we obtain a more complicated behavior. There is a critical volume that depends on the Coulomb interaction parameter.  $N(E_F)$  decreases with pressure at volumes larger than the critical one and increases below the critical volume. The critical volume decreases with increasing value of the Coulomb interaction parameter. For values of  $U$  larger than 4 eV,  $N(E_F)$  decreases in a wide range of volumes, which corresponds to the stability of the SC phase.  $U = 4$  and 5 eV are much larger than one can expect for Ca metal. Standard DFT+U codes allow one to apply Coulomb interaction correction to pure atomic states, but not to a molecular orbital. The orbitally resolved band structure

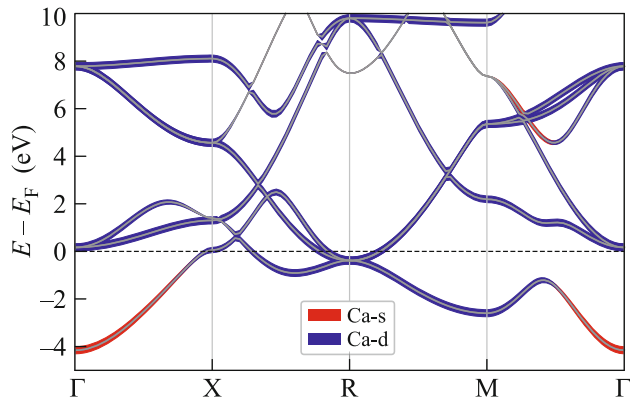


Fig. 3. (Color online) Band structure of SC Ca and contributions of the atomic  $s$ - and  $d$ - states to the energy bands

of Ca shown in Fig. 3 indicates that partially filled energy bands are formed by a mixture of Ca- $s$  and Ca- $d$  states which cross Fermi level. Hence a more sophisticated method should be used in case of Ca.

In order to reveal the mechanism of the pressure-induced phase transition in Ca under pressure we take into account justified microscopic model. For constructing the basis functions for the model we applied Wannier function (WF) projection procedure as implemented in Wannier90 package [12]. Six WFs: one of  $s$ -symmetry centered in the cubic void of the structure and five of  $d$ -symmetry centered on Ca ions, were chosen as the starting point of maximum localization procedure.

Crystal field of Ca ions splits Ca- $d$  states in threefold-degenerate  $t_{2g}$  and twofold-degenerate  $e_g$  orbitals which have higher energy. Thus we focus on  $t_{2g}$  orbitals since they cross Fermi level and are aligned in the directions of body diagonals of the unit cell and hence can hybridize with electrone states. Fig. 4a shows the spatial distribution of the resulting maximally localized WF the first WFs: the with the symmetry of  $s$ -orbital is centered in the interstice, the second WF with the symmetry of  $d_{xy} + d_{yz} + d_{zx}$  orbital is centered on Ca atom. Symmetry decreases with decreasing pressure and in both  $Cmmm$  and  $\beta$ -tin structures all orbitals turn to be inequivalent but we keep the same  $t_{2g}$  and  $e_g$  notation for the sake of simplicity.

We have carried out self-consistent DFT+U calculations using model Hamiltonian in WF-basis transformed in  $k$ -space. The set of Coulomb parameters values  $U = 2$  and  $4\text{eV}$  were chosen to investigate the influence of electron-electron repulsion straight on spectral properties of Ca.

Hund's exchange interaction parameter  $J$  was set to zero in both cases. Upper panels of Fig. 5 show the results of calculation for the SC structure with a cell

volume of  $21.9\text{\AA}^3$  and  $\beta$ -tin phase with a cell volume of  $21.7\text{\AA}^3$  for  $U = 4\text{eV}$ . One can see that while DFT gives a rather good metallic state for both phases, inclusion of the Coulomb interaction affects their electronic structure differently. The  $\beta$ -tin phase remains in the metallic state, although pseudogap at Fermi level becomes more pronounced. Moreover, the band shift is small and band structure in a vicinity of Fermi level is almost unchanged. On the other hand, band structure of the SC phase changes drastically and insulating state with the gap of  $0.3\text{eV}$  emerges. The results for smaller  $U$  value  $2\text{eV}$  are shown in Fig. 5 (lower panels). Both phases possess pseudogap at Fermi level, but while the SC phase is almost an insulator, the  $\beta$ -tin phase has a much higher density of states at Fermi level. Our DFT+U calculations show that Coulomb interaction has a strong influence on electronic properties: it lowers the total energy and opens a band gap in the SC phase, which makes this structure more energetically preferable than  $\beta$ -tin phase at higher pressure even for smaller  $U$  (where SC is a metal with a pseudogap).

We argue that the main cause of the phase transition is the cooperative action of hybridization effects and Coulomb repulsion. In order to illustrate this assumption, we construct an effective microscopic *ad hoc* model with a minimal set of orbitals. The model is a 1-D chain of two atoms with next-nearest neighbor hopping (see Fig. 4b) and can reproduce band structure in the  $\Gamma$ - $R$  direction and gap opening in Ca under pressure. In Figure 4b the green circle corresponds to the WF of  $s$ -symmetry centered in the cubic void in the middle of the cubic primitive cell. The blue circle stands for WF of  $t_{2g}$ -symmetry centered on Ca ions. The model Hamiltonian is given by:

$$H = \begin{pmatrix} e_d - 2t_1 \cos(k) & -2\alpha t_3 \cos(\frac{k}{2}) \\ -2\alpha t_3 \cos(\frac{k}{2}) & e_s - 2t_2 \cos(k) \end{pmatrix}, \quad (1)$$

where  $e_{s,d}$  are energies of WFs with  $s$  and  $d$  symmetry,  $t_1, t_2, t_3$ , are hoppings between WFs,  $\alpha$  stands for hybridization scaling parameter and  $k \in [-\pi, \pi]$ . Then the Coulomb interaction was added into the model in the form:

$$\hat{H}_{\text{int}} = U \cdot \hat{n}^\sigma \hat{n}^{\sigma'}. \quad (2)$$

For the model which has no spin splitting the correlation effects simply shift the occupied states down and empty states up by  $U/2$ . The results of the model simulation are presented in Fig. 5. The width of model bands obtained with the following set of parameters  $t_1 = 3.5\text{eV}$ ,  $t_2 = 1\text{eV}$ ,  $t_3 = -1.5\text{eV}$  and  $U = 4\text{eV}$  reproduces the results of DFT and DFT+U calculations. Scaling of  $\alpha$  corresponds to phase transition from SC ( $\alpha = 1$ ) to

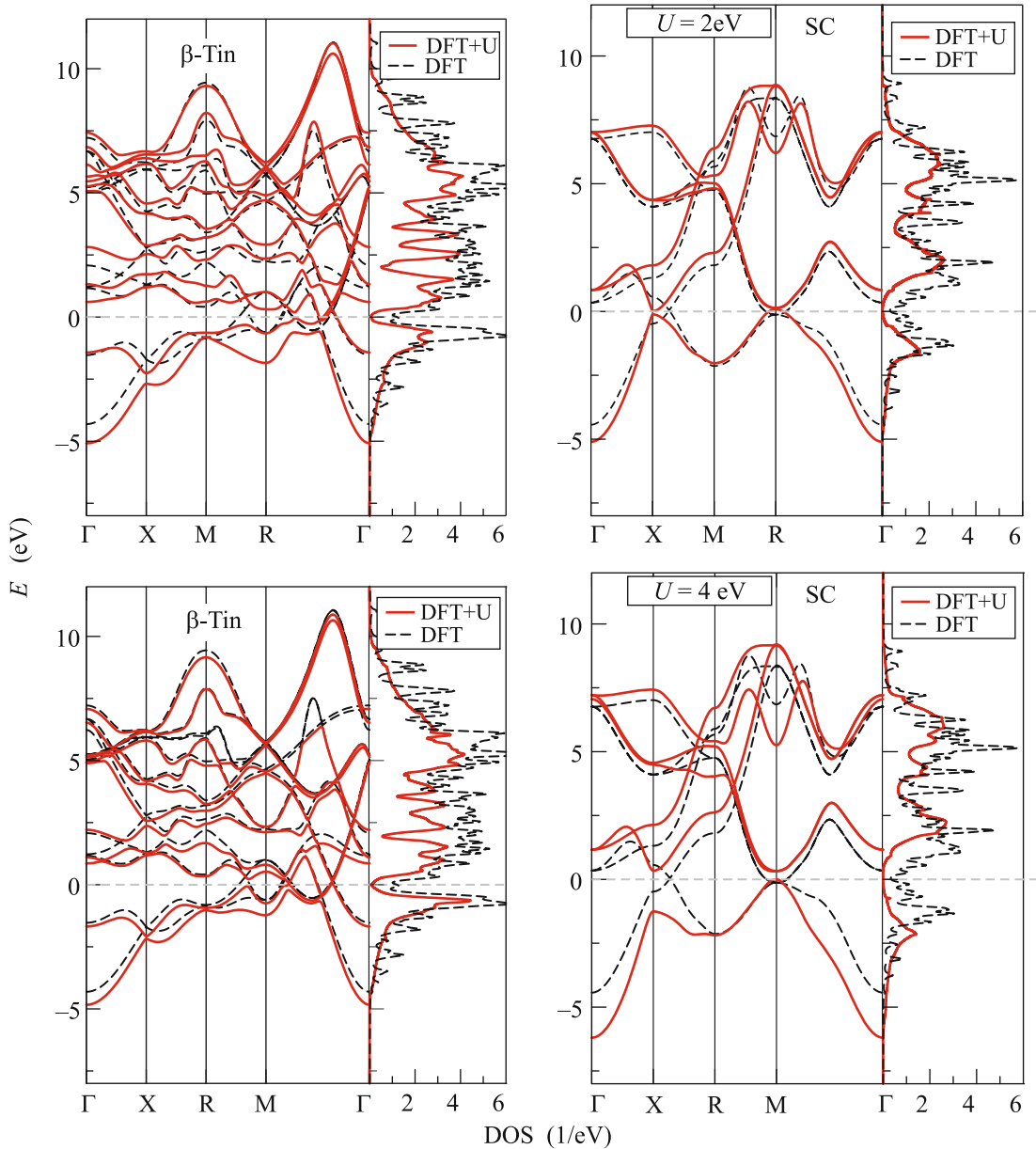


Fig. 4. (Color online) Band structure and DOSs obtained in DFT (black dashed lines) and DFT+U on WFs (red solid lines) for model Hamiltonian in basis of WFs of  $s$ - and  $d$ -symmetry for SC and  $\beta$ -tin phases for  $U = 4$  eV (top panels) and  $U = 2$  eV (lower panels)

$bcc$  structure ( $\alpha = 0$ ). One can see that with increasing of  $\alpha$  parameter the hybridization opens indirect gaps but the model gives metallic solution even for  $\alpha = 1$ . Correlation effects open the gap which was already prepared by hybridization and the model gives bad metal for  $\alpha = 0.5$  and insulating solution for  $\alpha = 1$ , which is reminiscent of the band structure evolution obtained in DFT+U calculation. The same mechanism can be responsible for the anomalous increase of resistivity with pressure [1]: the hybridization strength is inversely proportional to the distance between Ca crite and center of

the cell where bonding  $s$ -orbital is placed, and therefore increases with pressure. Therefore, pressure drives the system closer to the insulating state, which is reflected in the increase of electrical resistivity.

In this paper, we investigated the role of electronic correlations and hybridization in determining the phase diagram of calcium and puzzling increase of resistivity of the simple cubic phase of Ca with pressure. We have obtained that both the transfer of electrons from  $4s$  to  $3d$  states with increasing of pressure and Coulomb correlations play an important role in the formation of the

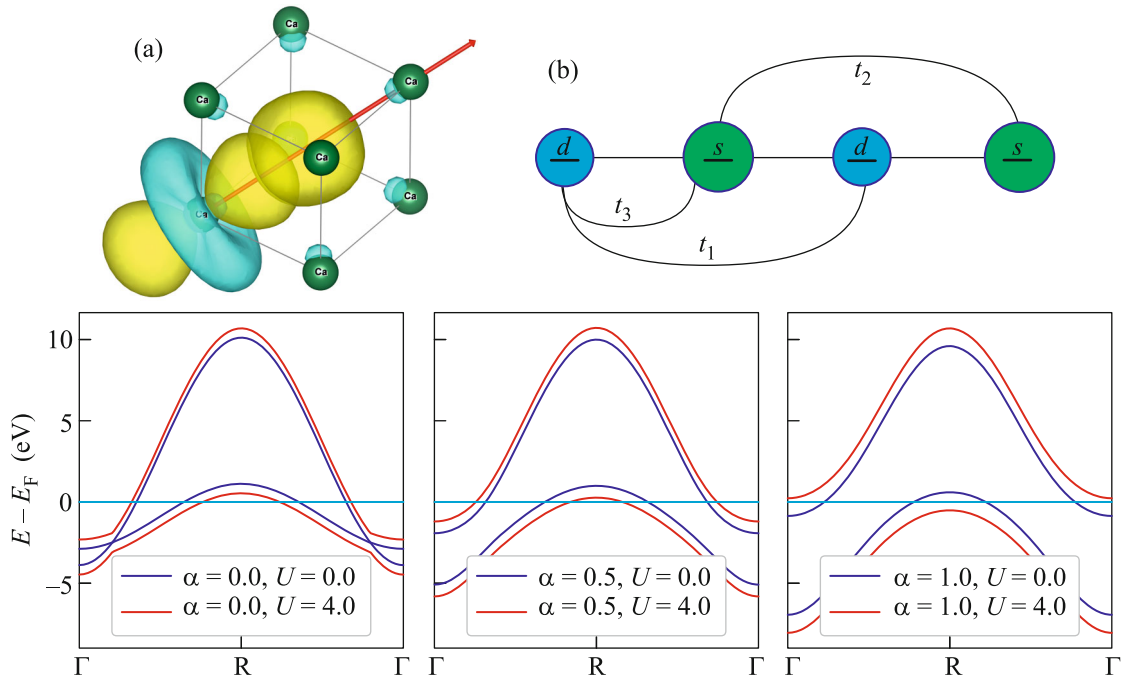


Fig. 5. (Color online) Upper panel: (a) – Spatial distribution of the two Wannier functions in the simple cubic structure where the positive (negative) amplitude is denoted by yellow (blue) color (see text for details). The red arrow shows the [111] direction along that the two WF’s overlap. (b) – One-dimensional effective model (upper panel). Small and large circles correspond to WF’s of  $t_{2g}$ -symmetry centered on atoms (denoted as  $d$ ) and WF of  $s$ -symmetry in central empty space (marked as  $s$ ). Model band structure for the set of parameters corresponding to  $\beta$ -tin (a), bcc (b) and simple structure (c). See text for details

electronic ground state of the system under pressure. The former leads to the localization of the electron density in the interstices and the existence of the partially filled bands, rendering the simple cubic phase of calcium an electrider and opening a pseudogap at the Fermi level.

The idea of taking electronic correlations into account when describing the electrider states allowed us to explain the experimentally observed structural transition to the simple cubic phase, as well as the anomalous behavior of resistivity during 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.

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