Electronic correlations in the ultranarrow energy band compound
Pb$_9$Cu(PO$_4$)$_6$O: A DFT+DMFT study

Dmitry M. Korotin$^{1,2,4}$, Dmitry Y. Novoselov$^{1,2,3}$, Alexey O. Shorikov$^{1,2,3}$,
Vladimir I. Anisimov$^{1,2,3}$ and Artem R. Oganov$^{2,4}$

$^1$M. N. Mikheev Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences, 18 S. Kovalevskaya Street, Yekaterinburg 620108, Russia
$^2$Skolkovo Institute of Science and Technology, 30 Bolshoy Boulevard, Building 1, Moscow 121205, Russia
$^3$Department of Theoretical Physics and Applied Mathematics, Ural Federal University, 19 Mira Street, Yekaterinburg 620002, Russia
$^4$Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny, Moscow Region 141701, Russia

(Received 10 August 2023; revised 13 November 2023; accepted 27 November 2023; published 15 December 2023)

We present results of investigations on the correlated nature of electronic states crossing the Fermi level in Pb$_9$Cu(PO$_4$)$_6$O (also referred to as LK-99) obtained within the DFT+DMFT approach. We found that the band structure in the vicinity of the Fermi level is formed by extremely narrow Cu $d$ states and $p$ states of extra O weakly hybridized with each other. Coulomb correlations between Cu $d$ electrons open the band gap between Cu $d_{xy}/d_{yz}$ and the extra-O $p$ states that form the top of the valence band. Our conclusion is that the extra-oxygen $p$ states play a significant role in the electronic properties and LK-99 cannot be mapped onto a two-band Hubbard model. We also conclude that doping with electrons will turn the stoichiometric Pb$_9$Cu(PO$_4$)$_6$O into a metal, whereas the result of doping with holes is less certain.

DOI: 10.1103/PhysRevB.108.L241111

Introduction. Starting from the first report on the existence of room-temperature superconductivity in Pb$_9$Cu(PO$_4$)$_6$O [1] (“LK-99”), there have been continued attempts to clarify which characteristics of the electronic structure could generate the reported compound properties [2–5]. It is obvious to suggest that the $d$ states of the Cu ion in the formal $d^9$ electronic configuration are on the Fermi level and the supposed superconductivity is interconnected with them. The crystal structure of Pb$_9$Cu(PO$_4$)$_6$O resembles the most well-known high-$T_c$ superconducting cuprates (HTSC) which have similar Cu-O$_2$ planes containing Cu$^{2+}$ ions with a $d^9$ configuration. Hence by analogy with HTSC cuprates, one can assume that LK-99 is a system with strong electron-electron correlations, and density functional theory (DFT) will fail to describe its properties. DFT+$U$ calculations were already presented in Refs. [2–4]. The insulating band structure was obtained in all three works with the existence of long-range ferromagnetic ordering (the long-range magnetic ordering is an artifact of the DFT + $U$ method). The importance of accounting for correlation effects was reported for many high-$T_c$ superconductors with $d$ or $f$ atoms [6–9].

For this study, we have employed the features of the DFT plus dynamical mean-field theory (DFT+DMFT) method to describe the electronic structure of strongly correlated paramagnetic systems, taking into account also a finite electronic temperature.

Methods. We performed DFT+DMFT [10] calculations following the procedure described in Ref. [11]. As a first step, DFT calculations using the QUANTUM ESPRESSO [12] package with pseudopotentials from the standard solid-state pseudopotential library set [13] were performed. The exchange-correlation functional was chosen to be in the Perdew-Burke-Ernzerhof functional adapted for solids (PBEsol) form. The energy cutoff for the plane-wave function and charge density expansion has been set to 50 and 400 Ry, respectively. The convergence criteria used for crystal structure relaxation within DFT are as follows: total energy $<10^{-8}$ Ry, total force $<10^{-4}$ Ry/bohrs, pressure $<0.2$ kbar.

The Wannier functions $|W_n\rangle$ were utilized for a description of the Cu $d$ and O $p$ states. In the reciprocal space $|W_{n\mathbf{k}}\rangle$ are calculated as a projection of the pseudoatomic orbitals $|\phi_{n\mathbf{k}}\rangle$ onto a subspace of Bloch functions that is defined by setting an energy interval $E_{1} \leq E_{i}(k) \leq E_{2}$:

$$|W_{n\mathbf{k}}\rangle \equiv \sum_{E_{1} \leq E_{i}(k) \leq E_{2}} |\Psi_{i}(k)\rangle \langle \Psi_{i} |\phi_{n\mathbf{k}}\rangle.$$  

Then the obtained Wannier functions were orthogonalized with the Löwdin symmetric orthogonalization approach [14].

Next, to take into account Coulomb correlations and many-body effects for the constructed small Hamiltonian, the DFT+DMFT approach [10,15] was utilized to solve the Hubbard model (in a density-density approximation). The Coulomb repulsion parameter $U$ which is equal to the $F_0$ Slater integral and the Hund exchange parameter $J$ are set to 1.8 eV and 0.7 eV, correspondingly. DFT+DMFT calculations were performed at an electronic inverse temperature $\beta = 1/k_{B}T = 40$ eV$^{-1}$, where $k_{B}$ is the Boltzmann constant.
and $T$ is the absolute temperature, which corresponds to 290 K. An effective DMFT quantum impurity problem [16] was solved using the continuous-time quantum Monte Carlo method with the hybridization expansion algorithm [17] as implemented in the package AMULET [18]. We used the maximum entropy method [19] to perform an analytic continuation from imaginary to real frequencies for the single-particle Green’s function to obtain spectral functions.

Results. We are still lacking sufficient data regarding the detailed crystal structure of the LK-99 [1] compound. It is known that it was identified as lead apatite Pb10(PO4)6O with the P63/m space group, wherein a copper ion substitutes one of the Pb ions at position 4f. Consequently, selecting an appropriate crystal structure for electronic structure calculations is not straightforward.

We started our investigation using the Pb10(PO4)6O crystal structure [20], as illustrated in Fig. 1. Importantly, the oxygen ion, which is not part of the PO4 octahedra, is located at the Wyckoff site 4e with a partial occupation of 0.25. In our analysis, we refer to this oxygen ion as “extra O” throughout the text.

The problem of dealing with partial occupation sites (or impurity sites) can be approached in two ways: (1) by calculating large supercells with randomly occupied 4e sites by oxygen ions, or (2) by staying within a single cell and avoiding relaxation of the internal atomic positions of the extra-O ion. Avoiding atomic position relaxation in small cells prevents undesirable local distortions that would propagate throughout the crystal due to translation symmetry.

The full band structure and partial densities of states for the extra-O ion for the parent lead apatite compound are shown in Fig. 2. Calculations were done for the experimental crystal structure with only one extra-O ion in the cell. The left panel of Fig. 2 illustrates the presence of narrow energy bands, with a width of approximately 400 meV, situated just below the Fermi level in Pb10(PO4)6O. These three bands arise from the $p$ states of the extra-O ion. The figure provides evidence that the extra-O ion in the lead apatite can be treated as an impurity, exhibiting minimal interaction with the surrounding ions. Consequently, it forms a distinct set of narrow energy bands.

The same rationale was used for a copper ion substitution in LK-99, replacing one of the ten Pb ions. The copper ion acts as an impurity that exerts a negligible influence on the average positions of the Pb ions. Consequently, to obtain the structure representing Pb10-xCu_x(PO4)6O ($x = 1$), we substituted one of the lead ions in Pb10(PO4)6O with copper. Subsequently, we fixed the atomic positions of Pb, Cu, and extra-O ions and performed relaxation for all other structural parameters, including the crystal shape, volume, and positions of all the remaining atoms. The resulting lattice parameters $a = 9.748$ Å, $c = 7.218$ Å, and $V = 594$ Å$^3$ agree with the already published data [1,2,4].

The calculated DFT band structure and partial densities of states for the optimized cell of Pb9Cu(PO4)6O are depicted in Fig. 3. The copper ion states also form impuritylike energy bands near the Fermi level, in the energy region slightly higher than the extra-O bands. Two bands crossing the Fermi level are narrower than in previously presented works [2,4] precisely because we did not allow undesirable extra hybridization of Cu and extra-O ions with the nearest-neighbor ion states.

The crystal field of the trigonally distorted oxygen octahedra splits the Cu $d$ shell into a doubly degenerate subshell corresponding to the irreducible representation $e_g^*$ ($d_{xz}$ and $d_{yz}$ orbitals), doubly degenerate $e_g^*$ subshell ($d_{xy}$ orbitals), and $d_{3z^2−r^2}$ orbital that corresponds to the representation $a_{1g}$. This splitting is clearly seen in partial densities of states in the right panel of Fig. 3.

Two exceptionally narrow energy bands intersecting the Fermi level correspond primarily to electronic states with Cu $d_{xy}$ and $d_{xz}$ orbital symmetries. These partially filled bands...
have a width of only about 120 meV, suggesting that strong electronic correlations undoubtedly play a crucial role in their behavior. This fact was already accentuated before [2,4]. These energy bands are almost flat along the \( \Gamma-M-K-\Gamma \) path in the Brillouin zone. The \( \Gamma, K \), and \( M \) \( k \) points are located in the \( k_x-k_y \) plane. The copper energy bands are nondispersive, since the overlap between the orbitals in the \( ab \) plane of the cell is small.

The two bands within the energy range of \([-0.15, -0.01]\) eV below the Fermi level are attributed to the \( p_x \) and \( p_y \) orbitals of the extra-O ion. Due to the considerable distance between the Cu and extra-O ions (approximately 5.7 Å), there is minimal overlap between the copper ion orbitals and the extra-O \( p \) orbitals, resulting in negligible hybridization between them. Below, there are also Cu \( d_{x^2-y^2} \) and extra-O \( p_z \) orbitals. The width of the entire band set is about 350 meV.

The eight states mentioned above (five Cu \( d \) and three extra-O \( p \)) are the minimal basis for the model that could describe the spectral function in Pb\(_9\)Cu(PO\(_4\))\(_6\)O. Using the projection procedure (see Methods), we constructed eight Wannier functions with the symmetry of the corresponding atomic orbitals. Then the Hamiltonian of the Hubbard model Hamiltonian was constructed in the basis of these Wannier functions. The five Wannier functions with \( d \) symmetry were correlated and the three \( p \)-like Wannier functions were treated as noncorrelated states.

Next, this small Hamiltonian was solved within the DFT+DMFT method and the obtained spectral functions are shown in Fig. 4. The following experimental data [22] show that under normal conditions, LK-99 demonstrates insulating properties, thereby confirming the predictive outcome obtained in the present Letter. One can see that even such a small \( U = 1.8 \) eV opens the gap about 0.4 eV and leads to an insulator. The smaller values of \( U \) seem physically unjustified, while the larger values, e.g., typical for HTSC cuprates \( \approx 3 \) eV [23], will not change the picture of the Mott insulator regime.

Recently, several works [24–26] emerged that computed \( U \) and \( J \) values using the constrained random phase approximation (cRPA) approach. The values obtained for the Coulomb and Hund exchange parameters are consistent with those utilized in our study. Electronic states with \( e_g^\sigma \) and \( a_{1g} \) symmetry are completely filled. The spectral function of the \( e_g^\sigma \) states demonstrates the appearance of the lower and upper Hubbard bands at \(-1.1 \) and \( 0.6 \) eV, respectively. The obtained averaged squared magnetic moment is \( 0.99 \mu_B^2 \), which corresponds to a hole in doubly degenerate \( e_g^\sigma \) orbitals. The DFT+DMFT results show that taking into account the Coulomb correlation is important since it significantly changes the band structure in the vicinity of the Fermi level obtained in DFT and hence the Fermi-surface topology. Figure 4 shows that the top of the valence band is formed by extra-O \( p_x + p_y \) states which are reminiscent of the Pb\(_{10}\)(PO\(_4\))\(_6\)O since in the case of the absence of Cu the top of the valence band is also formed by extra-O \( p \) states. The spectral functions look similar to charge-transfer insulators, i.e., NiO or LiNiO\(_2\) [27], but the situation is different in Pb\(_9\)Cu(PO\(_4\))\(_6\)O. In charge-transfer insulators, the energy gap is formed by metal \( d \) states and the nearest ligand \( p \) states. In LK-99 the states that cross the Fermi level are \( p \) states of the extra-O ion which is at least 5.7 Å away from the copper ion. However, if we consider only the composition of the top of the valence band which consists of \( p \), and the bottom of the conducting band, formed by \( Cu \) \( d \) states, Pb\(_9\)Cu(PO\(_4\))\(_6\)O can be identified as a specific example of charge-transfer insulators.

Although our findings reveal the presence of a local magnetic moment on each copper ion, this analysis did not account for long-range magnetic order. Based on these results, two possible scenarios could be proposed: The compound may either behave as a paramagnet due to the thermal disordering of local magnetic moments or it can exhibit ferromagnetic properties. Also, note that a substantial distance between neighboring copper ions makes the possibility of antiferromagnetic ordering low, in contrast to HTSC cuprates. Increasing the Cu-Cu distance weakens the superexchange mechanism responsible for antiferromagnetic (AFM) ordering.

Additionally, if the copper ions form clusters due to their uneven distribution, as proposed in Ref. [22], AFM ordering within these clusters becomes feasible. However, this hypothesis requires further exploration, which is contingent upon the availability of new high-quality structural data.

We assume that in this case of narrow and well-separated bands in the vicinity of the Fermi level, moderate doping with either electrons or holes will not change the electronic spectrum significantly but primarily result in a shift of the Fermi level. For instance, additional electrons will lead to partial occupancy of the upper Hubbard band formed by \( e_g^\sigma \) states, similar to HTSC cuprates, and a transition from the Mott insulator state of stoichiometric Pb\(_9\)Cu(PO\(_4\))\(_6\)O into a regime of strongly correlated metal [28] will occur, accompanied by a substantial electronic mass enhancement.

On the other hand, the result of hole doping cannot be reliably deduced from these calculations since both the lower Hubbard band formed by \( Cu \) \( e_g^\sigma \) states and the \( p \) states of the extra O lie below the Fermi level. Additional meticulous examinations of the charge redistribution between these states, which also take into account the response of the crystal lat-
tice, are necessary for determining which of these states will accommodate the holes. This analysis will call the challenge for further investigations.

Conclusion. We investigated the electronic structure and the role of correlation effects in \( \text{Pb}_9\text{Cu}(\text{PO}_4)_6\text{O} \) within the frame of the DFT+DMFT approach. It was shown that proper accounting for the disorder in the occupation of extra-O and Cu/Pb sites in the parent lead apatite structure is especially important and can result in the appearance of narrow energy bands in the vicinity of the Fermi level in the case of the \( \text{LK}-99 \) compound. These energy bands originate from the overlap of two band groups, namely Cu \( d \) and extra-O \( p \) states.

Then, using the DFT+DMFT approach, we showed that accounting for Coulomb correlations leads to the band gap opening, which drastically changes the band structure obtained in DFT. However, the physical picture in this compound is much more complicated and cannot be reduced to a Mott insulator on a triangular lattice formed by the Cu \( d_{yz} \) and \( d_{zx} \) orbitals but could be considered as a specific example of a charge-transfer insulator with a remarkably complicated structure of the valence band of \( \text{Pb}_9\text{Cu}(\text{PO}_4)_6\text{O} \) formed not by the ligands closest to the Cu ion but by distant extra-O \( p \) states.

Acknowledgments. The DFT parts of the study were supported by the Ministry of Science and Higher Education of the Russian Federation (No. 122021000039-4, theme “Electron”). The DMFT results were obtained within the state assignment of the Russian Science Foundation (Project No. 19-72-30043).

[20] S. V. Krivovichev and P. C. Burns, Crystal chemistry of lead oxide phosphates: Crystal structures of \( \text{Pb}_2\text{O}(\text{PO}_4)_2 \), \( \text{Pb}_3\text{O}_2(\text{PO}_4)_2 \) and \( \text{Pb}_6\text{O}_5(\text{PO}_4)_3\text{O} \), Z. Kristallogr. 218, 357 (2003).


