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Letter

$Pb_9Cu(PO_4)_6O$ is a charge-transfer semiconductor

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By means of density functional theory and constrained random phase approximation we analyze the band structure of $Pb_9Cu(PO_4)_6O$ (named LK-99). Our data show that the lead-phosphate apatite LK-99 in the proposed Cu-doped structure is a semiconductor with a predominant charge-transfer nature, a result incompatible with a superconducting behavior. In order to understand the interesting electronic and magnetic properties of this compound, it will be necessary to study the actual response to doping, the possibility of alternative structural and stoichiometric (dis)order, and to clarify the magnetic interactions as well as their impact on the electronic structure.

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Introduction. The announcement of the surprising discovery of superconductivity at room temperature and ambient pressure in $Pb_{10-x}Cu_x(PO_4)_6O$ (named LK-99) in the doping regime $0.9 < x < 1.1$ [1] ignited an intense debate in the condensed matter community to verify the alleged superconducting nature of LK-99 and to characterize its fundamental electronic properties [2–17]. The data and analyses currently available appear to refute the interpretations initially proposed, particularly with regard to the apparent vanishing of resistivity and to the actual presence of the Meissner effect, and indicate that LK-99 is not a superconductor, either at room temperature or otherwise [9,10,17–19]. Furthermore, although the synthesis procedure appears to be easily reproducible [3,20], doubts remain as to the precise composition, the possibility of coexistence of different phases or superstructures, and the presence of a certain degree of disorder [15,21].

Numerous computational simulations conducted on nearly regular crystal structures with the aim of defining and elucidating the band structure have yielded only partially consistent results, in particular on the metal or semiconductor character of the $x = 1$ phase $Pb_9Cu(PO_4)_6O$. The first density functional theory (DFT) results found a metallic band structure, apparently robust against the application of sizable on-site Hubbard U within the DFT+U approach [5–8,22]. Alternative DFT+U calculations have instead reported the opening of gap for a sound U of 4 eV [11], in agreement with DFT+dynamical mean-field theory (DMFT) data [12,14], suggesting that fractional deviation from the $x = 1$ doping limit would be necessary to establish a metallic state [12,23]. Further studies have linked the opening of the gap at $x = 1$ with the inclusion of spin-orbit coupling (SOC) [13] or with a specific choice of the substitutional doping site [16].

The aim of this Letter is to clarify the nature of the electronic ground state of $Pb_9Cu(PO_4)_6O$ using real and complex DFT+U methods complemented with constrained DFT calculations to assess the impact of the on-site U and SOC on the band structure. Our data indicate that, using the structure described in the literature [6], LK-99 at $x = 1$ is a semiconductor for realistic values of the on-site (static) U, above a critical $U_c \approx 1.6$ eV (see Fig. 1). By enabling the relaxation of the internal atomic positions, we observed a systematic increase of the band gap [see Fig. 1 in the Supplemental Material (SM) [24]], and a small reduction of U_c (0.8 eV). SOC does not play a significant role in the gap opening and only marginally modifies the band topology. The few hundred meV large gap is predominantly charge transfer in nature for U values in the regime predicted by the constrained random phase approximation (cRPA) (≈3.5–5.5 eV, in agreement with previous reports [12]).

Computational details. We used the Vienna *ab initio* simulation package (VASP) [25,26] within DFT in the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. We have tested two different schemes for +U corrections, the Dudarev [27] and the Lichtenstein [28] approaches, which have been proved to deliver the same outcome. For both DFT+U schemes we applied two different implementations: the conventional real version (std, in VASP jargon) and the complex representation (ncl, in VASP jargon). All data reported in the main text are obtained with the ncl version. The effect of SOC has been inspected within complex DFT+U. We used an energy cutoff of 600 eV and a k-point grid of $6 \times 6 \times 8$. All calculations were performed on the crystal structure reported in the literature [5–7], assuming a ferromagnetic ordering (FM). cRPA calculations were performed using VASP optimized projected localized orbitals (PLOs) [29–31] for constructing the correlated subspace.

Results and discussions. The parent compound of LK-99, lead-phosphate apatite with the chemical formula $Pb_{10}(PO_4)_6O$ [21,32], is a nonmagnetic insulator with a DFT band gap of about 2.7 eV opening between the O-p and Pb-p states [6,7]. Replacing Pb with Cu causes the formation of low-dispersing correlated Cu-d bands in the Fermi region [5–7]. In PBE, i.e., neglecting corrections to improve the treatment of electronic correlation, LK-99 exhibits a metallic ground state, characterized by a pair of entangled Cu-d bands crossing the Fermi energy [see Figs. 2(a) and 2(b)]. Similarly, using real DFT+U we obtain a metallic solution regardless on

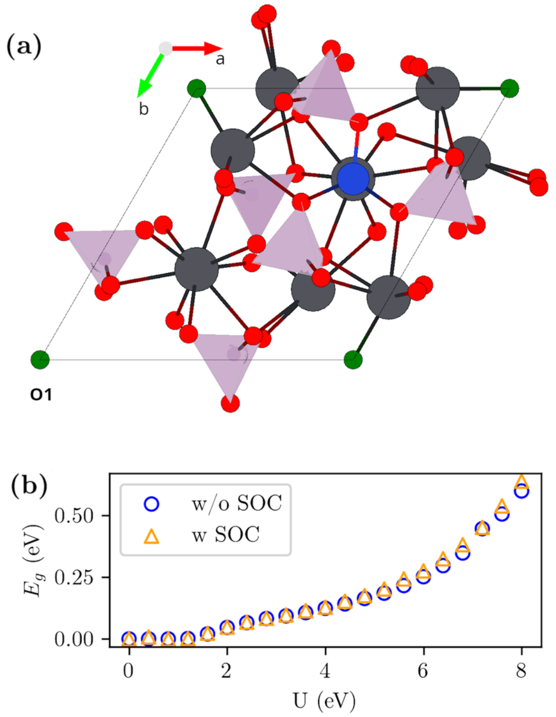

FIG. 1. (a) Graphical representation of the crystal structure of $Pb_9Cu(PO_4)_6O$ adapted from Refs. [6,7]. The shadowed tetrahedra represents the PO4 units. Large spheres indicate Pb atoms, with the blue one showing the substitutional Cu site. Small spheres are oxygen atoms. The extra oxygen, disconnected from the PO4 tetrahedra, is displayed in black and labeled O1. (b) Band gap E_g of $Pb_9Cu(PO_4)_6O$ as obtained from PBE+U as a function of the on-site U applied to the Cu-d states The PBE+U data are obtained within the complex DFT+U implementation with (w) and without (w/o) SOC.

the value of U, confirming previous reports [6,7]. However, within complex DFT+U the situation changes. In fact, the complex representation induces an orbital mixing within the d manifold in the imaginary part of the occupation matrix (see Figs. 3 and 4 in the SM [24]), which leads to the opening of the band gap [see Figs. 2(d) and 2(e)] and the breaking of k-point inversion symmetry (see Fig. 5 in the SM [24]). We note that this type of symmetry breaking has been reported to be connected with time-reversal symmetry breaking in collinear magnets [33]. An alternative mechanism for the band gap opening in LK-99 has been reported in Refs. [34,35], which invokes the breaking of the structural symmetry. Enabling SOC does not modify this result, although in the $U = 0$ (PBE) limit SOC splits the pair of correlated Cu-d bands near the Fermi region, establishing a weak metallic state [13]. The insulating phase obtained by complex DFT+U is energetically more favorable than the corresponding real DFT+U result and represents the ground state of $Pb_9Cu(PO_4)_6O$.

To quantify the degree of electronic correlation in $Pb_9Cu(PO_4)_6O$ we have extracted the effective on-site Coulomb (U) and exchange (J) interactions for the correlated Cu-d bands from cRPA adopting two different low-energy effective models depending on the number of states included in the correlated basis and on those included in the screening channel. In the first one ($d-d$), we used Cu-d_{xz} and d_{yz} projectors and excluded from the screening of the two topmost bands in Fig. 2(b), which have a mostly d character. In the second model ($p+d$), O1-p_x and p_y projectors are also considered in the construction of the correlated subspace and the four topmost bands are excluded from screening.

TABLE I. Interactions parameters U and J obtained by cRPA, compared with the values of Yue *et al.* [12].

		This work		Yue *et al.* [12]	
Model	No. of bands	U (eV)	J (eV)	U (eV)	J (eV)
$d-d$	2	3.53	0.77	2.94	0.61
$p+d$	4	5.51	0.78	5.67	0.65

The interaction parameters obtained, collected in Table I, indicate that U and J are to a good extent similar to those of cuprates [36] as noted in previous studies [12,23], and in good agreement with the cRPA data of Yue *et al.* [12]. We obtained U_{dd} between 3.5 eV ($d-d$ model) and 5.5 eV ($p+d$ model), while J is about 0.8 eV, essentially insensible to the model. The band structures obtained using the representative value $U - J = 3.7$ eV are displayed in Fig. 2. Based on the above data, we conclude that our results clearly indicate that LK-99 at $x = 1$ is a semiconductor in which the gap is opened due to correlation effects, not necessarily of a dynamic nature [11,12,14,23].

In a previous tight-binding study, Li *et al.* [23] have argued that LK-99 should exhibit either a Mott or a charge-transfer (CT)-like nature [37]. In a Mott insulator the gap is solely accounted by d bands and is opened between a lower Hubbard band and upper Hubbard band [38,39]. In a CT insulator, instead, the role of p states cannot be neglected and the gap is formed between an occupied (predominantly) p band and an empty d band [40]. By inspecting the change in the orbital character in the DFT+U electronic bands near E_F induced by U (see Fig. 2), it can be concluded that LK-99 belongs to the class of charge-transfer insulators. Without U the electronic structure includes two entangled Cu-d bands with $d_{yz}/d_{x^2-y^2}$ (upper) and d_{xz}/d_{xy} (lower) character (both around E_F), followed by lower-energy O-p states. The inclusion of U, rather than rigidly separating the two Cu bands near E_F, thus yielding a Mott solution, induces a substantial transfer of d electrons at lower energies leading to the formation of a $d-p$ gap that can be categorized as CT. The transition from the metallic $U = 0$ solution to the CT state can be appreciated in Fig. 3, where we show the evolution of the low-energy bands as a function of U. In the weakly correlated regime ($U < 1$ eV), the two d-band structure is roughly preserved, but for larger U there is a rapid shift from the Mott picture with the Cu-d electrons that are transferred to energies below -1 eV.

Conclusion and perspective. In summary, according to our simulations, the single-crystal LK-99 does not exhibit a metallic behavior. Enhancing the treatment of electronic correlation by utilizing realistic on-site U values and allowing for orbital symmetry breaking within the Cu-d states leads to the opening of an energy gap with a predominant CT character. This behavior is not consistent with the occurrence

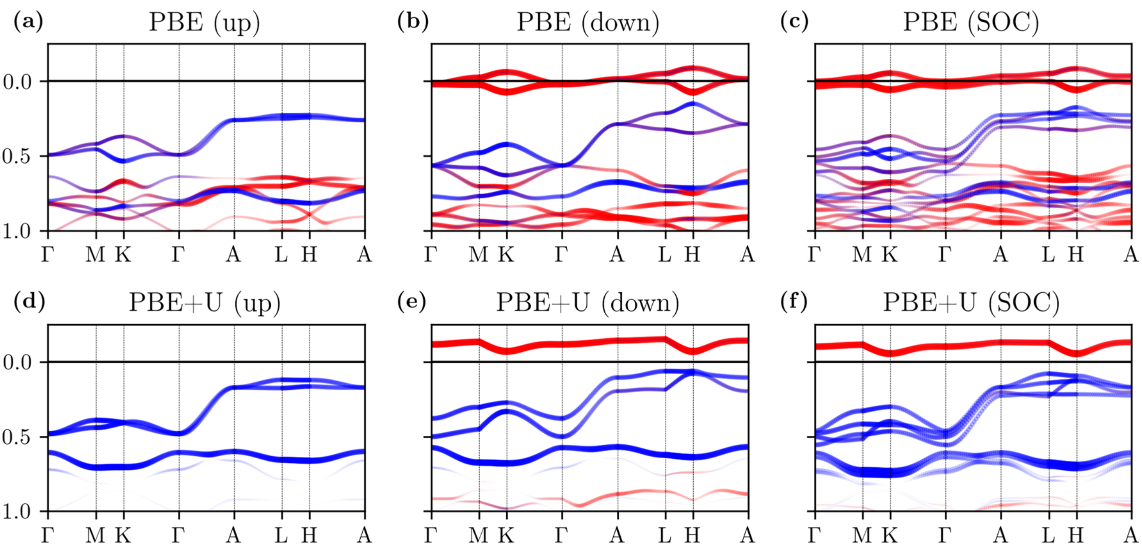

FIG. 2. Band structure of FM ordered Pb$_9$Cu(PO$_4$)$_6$O at (a)–(c) PBE level (without U) and (d)–(f) PBE+U with $U = 4.5$ eV and $J = 0.8$ eV. For calculations not including SOC, the bands are decomposed over both spins components (up and down). The color code identifies the orbital character of the bands: Cu-d orbitals are displayed in red whereas O1-p orbitals are given in blue. Band structures obtained with other (cRPA) values of U and J are displayed in the SM (Figs. 6 and 7) [24].

of superconductivity. There are some important aspects that will have to be studied in order to clarify the general validity of these conclusions in realistic conditions. First, recent experiments provide evidence that the LK-99 compound may have a different stoichiometry and structure than initially proposed [15,21,41,42], including uncertainties on the geometrical distribution of the extra oxygen. The second relevant issue is substitutional doping. Cu substitution is considered highly thermodynamically disfavored [15] and the incorporation of Cu at Pb sites proves to be extremely difficult [42]. Moreover, LK-99 synthesized with Cu$_2$S has a significant fraction of copper sulfide, which could be responsible for the sharp transitions in electrical resistivity and heat capacity [41]. This experimental evidence casts doubt on the possibility of achieving a realistic metallic state by doping the $x = 1$ insulating bands with holes or electrons [12,17]: It could be achieved in idealized computational simulations, but would be difficult to realize in real samples with this structure and stoichiometry. As a final point, it will be necessary to understand the magnetic nature of this material, which at the moment remains quite debated, in particular the diamagnetic or ferromagnetic character, the relationship with the levitation effect, and the possible interference between the magnetic and electronic degree of freedom [10,15,16].

To conclude, although there is now widespread awareness that LK-99 is not the room-temperature SC that

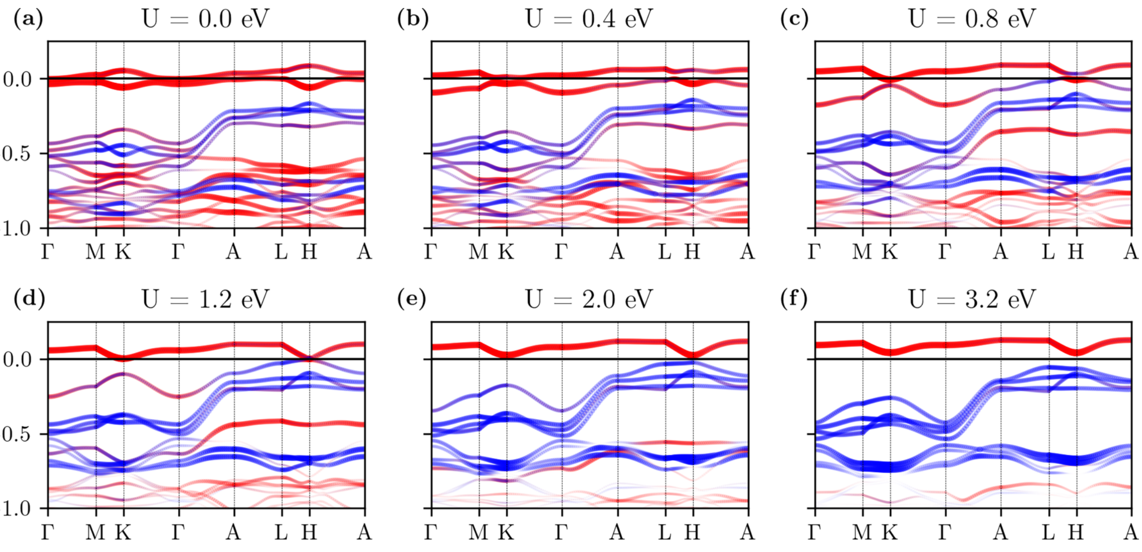

FIG. 3. Band structure of Pb$_9$Cu(PO$_4$)$_6$O at the PBE+U level including SOC for different values of U. The color code identify the orbital character of the bands: Cu-d orbitals are displayed in red whereas O1-p orbitals are given in blue. Through panels the transition from (a)–(d) metallic to (e), (f) CT insulator is observed.

was hoped for, it nevertheless appears to be a material with very interesting properties not yet understood, that could provide a basis for further studies and potential applications.

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