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Spin-orbit driven Peierls transition and possible exotic superconductivity in CsW_2O_6

Sergey V. Streltsov,[1,2,*] Igor I. Mazin,[3] Rolf Heid,[4] and Klaus-Peter Bohnen[4]

[1]*M. N. Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620137 Ekaterinburg, Russia*

[2]*Ural Federal University, Mira Street 19, 620002 Ekaterinburg, Russia*

[3]*Code 6393, Naval Research Laboratory, Washington, DC 20375, USA*

[4]*Institute for Solid State Physics, Karlsruhe Institute of Technology (KIT), D-76021 Karlsruhe, Germany*

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We study *ab initio* a pyrochlore compound, CsW_2O_6, which exhibits a yet unexplained metal-insulator transition. We find that (1) the reported low-T structure is likely inaccurate and the correct structure has a twice larger cell; (2) the insulating phase is not of a Mott or dimer-singlet nature, but a rare example of a three-dimensional Peierls transition, with a simultaneous condensation of three density waves; (3) the spin-orbit interaction plays a crucial role, forming well-nested bands. The high-T (HT) phase, if stabilized, could harbor a unique $e_g + ie_g$ superconducting state that breaks time reversal symmetry, but is not chiral. This state was predicted in 1999, but not observed. We speculate about possible ways to stabilize the HT phase while keeping the conditions for superconductivity.

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Introduction. Insulating transition metal compounds with a partially filled d shell most often turns out to be locally magnetic (either forming a long-range magnetic order or remaining paramagnetic). There are some exceptions to this rule when, for instance, a transition metal ion is in a low-spin configuration due to strong crystal-field splitting [1]. Alternatively, a Haldane state may appear in low-dimensional materials with integer spins, as, e.g., in $Tl_2Ru_2O_7$ [2]. Yet another possibility is the formation of spin-singlet molecular clusters, such as dimers and trimers (as it happens in VO_2 [1], Li_2RuO_3 [3–6], or $Ba_4Ru_3O_{10}$ [7,8]) or even more complex objects (heptamers in AlV_2O_4 [9] or octamers in $CuIr_2S_4$ [10]). However, in order to get a singlet ($S = 0$) ground state one needs an even number of electrons (doubly) occupying the lowest energy levels in such clusters, as it occurs in Li_2RuO_3 or AlV_2O_4. In this sense, a recent discovery of zero magnetic susceptibility in the insulating β-pyrochlore CsW_2O_6, with an average occupancy of $\frac{1}{2}$ electron per site, looks very unusual [11].

This compound undergoes a metal-insulator transition at 210 K with a Pauli-like magnetic susceptibility for $T > 210$ K, while at lower temperatures, in an insulating phase, it is fully nonmagnetic [11]. The high-temperature (HT) phase is cubic (space group $Fd3m$) [12]. A complicated structure was proposed for the low-temperature (LT) phase, with a doubled unit cell (compared to the fcc Bravais lattice of two formula units), with a disproportionation into two types of W and three types of W-W bonds. The short bonds form one-dimensional (1D) zigzag chains [11]. At the same time, the average W-O distance (the valence bond sum) is nearly the same for both W, indicating an absence of charge order. Obviously, uniform 1D chains with a noninteger number of electrons per site cannot form a simple band insulator.

The insulating and nonmagnetic nature of the low-temperature phase of CsW_2O_6, given the absence of charge disproportionation, no di- or tetramer formation, and a $\frac{1}{2}$ electron per metal site, remains mysterious. Most usual suspects for explaining such transition patently fail in CsW_2O_6.

Indeed, (i) strong spin-orbit coupling (SOC), typical for 5d metals such as W, in principle may stabilize a nonmagnetic state with the orbital moment antiparallel to the spin and the total moment $J = 0$. However, while this may be the case for d^4 configurations [1,13], it is not possible for $d^{1/2}$ occupancy. Besides, this model cannot explain the insulating behavior.

(ii) Correlation effects such as a Mott-Hubbard transition with the possible formation of spin singlets below 210 K would result in the formation of local spin moments, manifestly absent at any temperature.

(iii) In principle, exotic electron-phonon coupling could stabilize bipolarons, whereupon every fourth W would have a nonmagnetic d^2 configuration, and all others a nonmagnetic d^0. However, that would generate a considerable O breathing distortion around the d^2 atom, which would be hardly possible to miss in the experiment. Besides, that would have to work against the Hubbard U, which, while small in W, would still amount to at least 1 eV.

We are left with the only possible scenario: The metal-insulator transition here is of Peierls type, and the low-T state is a band insulator. The reported low-T structure [11] does show symmetry lowering: Along the W-W nearest-neighbor directions the bonds alternate as short-short-long-long, reminiscent of the proposition of Mizokawa and Khomskii [14], who suggested that, in analogy with $MgTi_2O_4$, in $CuIr_2S_4$, $\frac{1}{2}$ hole per metal can form a quasi-1D band along the Ir-Ir bonds, resulting in a Peierls transition with tetramerization, e.g., $Ir^{3+}/Ir^{3+}/Ir^{4+}/Ir^{4+}/\cdots$. However, the experimentally suggested structure exhibits a different pattern, $W^{5.5+x}/W^{5.5-x}/W^{5.5+x}/W^{5.5-x}/\cdots$, and experiment does not show any charge disproportionation. That is to say, the structure proposed in Ref. [11] still leaves uniform quasi-1D zigzag chains running along the crystallographic b direction, which generate very metallic bands that cannot open a gap even if the density functional theory (DFT) bands are slightly off [see the discussion below and the corresponding band structure in the Supplemental Material (SM) [15]]. This suggests that the real crystal structure for the low-T phase may have a

*streltsov@imp.uran.ru

lower symmetry than that proposed in Ref. [11]. We will argue below that the transition in question is actually a three-dimensional (3D) Peierls transition, and that the true LT structure encompasses four, not two, cubic cells. The 3D Peierls transitions are extremely rare, but not impossible (for instance, the nearest-neighbor $sp\sigma$ tight-binding model on the perovskite lattice at some filling exhibits a perfect 3D nesting at $\mathbf{k} = [\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}]$ [16]).

We will present below accurate DFT calculations of the electronic structure of CsW_2O_6, and will show that upon including the spin-orbit interaction (which appears essential for explaining the phase transition), it exhibits a surprisingly simple Fermi surface (FS) with strong nesting for the three equivalent wave vectors $\mathbf{Q}_1 = [\frac{2\pi}{a},0,0]$, $\mathbf{Q}_2 = [0, \frac{2\pi}{a},0]$, $\mathbf{Q}_3 = [0,0, \frac{2\pi}{a}]$. This is conducive to the simultaneous condensation of the three corresponding charge density waves (CDWs). Importantly, such condensation corresponds to a fourfold, not eightfold, supercell, as one may think. The phonon spectra indicate instability exactly at these $\mathbf{Q}_1$, $\mathbf{Q}_2$, and $\mathbf{Q}_3$ points, and optimizing the crystal lattice starting from a structure inspired by these phonon modes, we obtained a lower-symmetry structure that opens a band gap. This structure is much lower in energy than the published structure and yields a nonmagnetic ground state, which agrees completely with experiment.

Finally, we will discuss an intriguing implication of stabilizing the HT structure at low temperature. We will argue that such a system could harbor a highly unusual, and so far yet to be observed, albeit theoretically predicted, superconducting state.

Computational results. The DFT calculations were performed using the full potential linearized augmented plane wave (LAPW) method (as implemented in the WIEN2K package [17]) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential [18]. The noninteracting susceptibility was computed on a fine mesh of 36 000 $\mathbf{k}$ points in the Brillouin zone. The optimization (atomic positions and cell shape were allowed to change) of the low-T crystal structure was performed in the pseudopotential VASP code [19] with the same type of exchange-correlation potential and taking into account SOC. Cs-s and W-p were treated as valence states. We used a cutoff of 700 eV and the $\mathbf{k}$ mesh $6 \times 6 \times 6$ for optimization. The maximal force in the converged structure was less than 1 meV/Å.

In agreement with Ref. [11], we find that the generalized gradient approximation (GGA)+SOC in the proposed LT structure gives a strongly metallic ground state, in drastic contrast to experiment. Moreover, this state turns out to be magnetic, with small, but solid, spin moments $m_s^{W1} \sim 0.19\mu_B$ and $m_s^{W2} \sim 0.13\mu_B$. While these moments are further partially reduced by orbital contributions $m_o^{W1} \approx m_o^{W2} \sim -0.05\mu_B$, they are still non-negligible, which again stresses a discrepancy with the experimental data. Moreover, there are enormous atomic forces up to 0.8 eV/Å, which make this structure unstable in the GGA+SOC. As expected, including Hubbard correlations within the GGA+U+SOC (we used $U = 2$ eV and $J_H = 0.5$ eV) only worsens the situation, as moments begin to grow, while the system remains metallic.

In order to gain more insight into the physics of the LT phase, we start by analyzing the band structure of the HT cubic phase. Without SOC there are five bands (Fig. 1) crossing the Fermi energy (E_F). Two bands with small dispersion cross

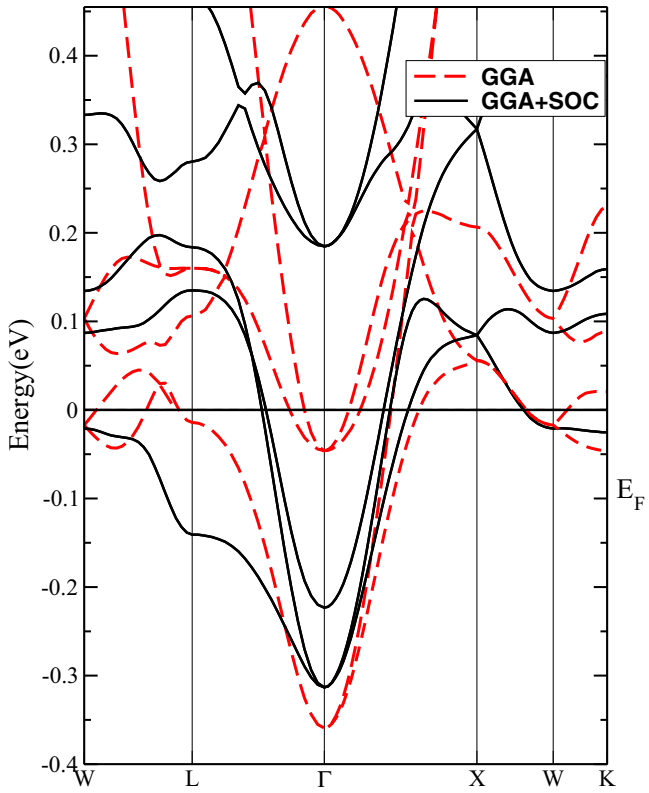

FIG. 1. The band structure obtained for the HT phase in the GGA and GGA+SOC calculations. Positions of the high-symmetry points in the Brillouin zone are shown in Fig. 2.

E_F in the W-L, W-X, and W-K directions, which results in a large density of states (DOS) at E_F and electronic instability. There are also two bands crossing E_F in the vicinity of the Γ point. All these bands are mostly of the tungsten t_{2g} character.

The SOC dramatically modifies the band structure. The Fermi surface is considerably simplified, and becomes canonically semimetallic. The unphysically large DOS is suppressed from ∼15 states/(eV f.u.) in nonmagnetic GGA to ∼6 states/(eV f.u.) in GGA+SOC. Two bands are crossing the Fermi level near Γ, and one near X, forming, respectively, two nearly degenerate electron pockets and three hole pockets per reciprocal cell. The former are nearly spherical, and the latter are more as rounded parallelepipeds.

This topology is prone to various instabilities. The energy mismatch when the Fermi surfaces are shifted by the corresponding wave vector varies between 0 and ∼50 meV. Thus, energy can be gained by generating three simultaneous CDWs that fold all three hole pockets right upon the electron pockets. As long as the potential generated by the CDW is larger than $V \gtrsim 50$ meV, a gap of the order of V will open, with a metal-insulator transition into a band insulator phase.[1] Finally,

[1]Note that this Fermi surface is topologically consistent with an excitonic insulator instability [26]. Since both the CDW and $\mathbf{q} \neq \mathbf{0}$ excitonic insulator break the same symmetries and both can be diagrammatically described as instabilities in the particle-hole channel [27], we do not distinguish these in the forthcoming discussion.

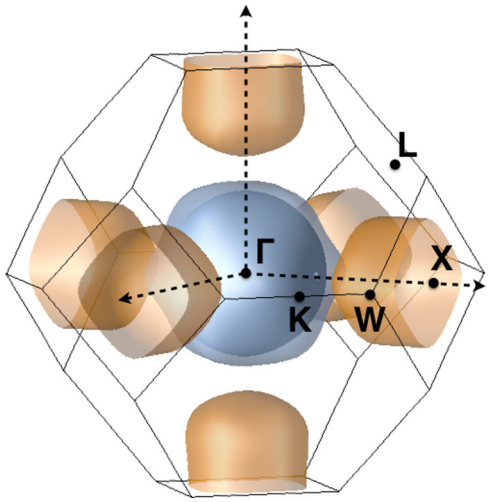

FIG. 2. The Fermi surface as obtained in the GGA+SOC calculation for the high-temperature phase.

as discussed below, arguably the most interesting instability this Fermi surface is conducive to is an unconventional superconductivity.

Experimentally, it is clear that the second option is realized in the actual material. Note that simultaneous condensation of the three CDWs in question quadruples, but not octuples, the unit cell. From the fact that the coordinates of the X point of the Brillouin zone are $(2\pi/a,0,0)$ it is obvious that going from an fcc Bravais lattice with the wave vectors $[a/2,a/2,0]$, $[a/2,0,a/2]$, and $[0,a/2,a/2]$ to a conventional cell with $[a,0,0]$, $[0,a,0]$, and $[0,0,a]$ corresponds to three CDWs with X, Y, and Z wave vectors.

Another way to look at this issue is to calculate, as it is often done [20], the noninteracting susceptibility, neglecting the $\mathbf{k}$ dependence of the matrix elements, defined as

$$\chi_0(\mathbf{q}) = \sum_{\mathbf{k},n,m} \frac{f_{\mathbf{k},n} - f_{(\mathbf{k}+\mathbf{q}),m}}{\varepsilon_{\mathbf{k},n} - \varepsilon_{(\mathbf{k}+\mathbf{q}),m}}, \tag{1}$$

where f and $\varepsilon_{\mathbf{k},n}$ are the occupation numbers and energies of the corresponding electronic states in the nonmagnetic GGA+SOC calculation, and n and m enumerate bands. The results are presented in Fig. 3 and clearly show peaks of $\chi_0(\mathbf{q})$ at the X, Y, and Z points, suggesting that the HT structure is unstable. While an account of the interaction and momentum

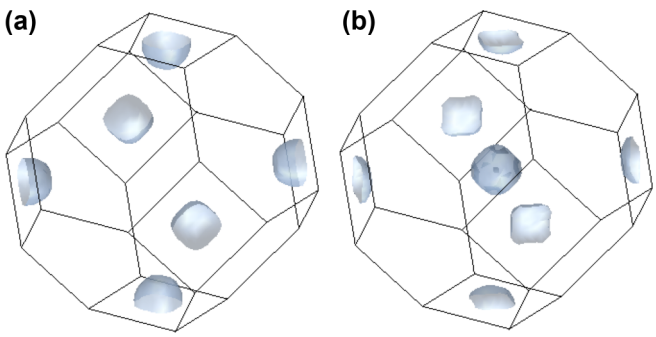

FIG. 3. (a) Real and (b) imaginary parts of the noninteracting susceptibility $\chi_0(\mathbf{q})$ calculated from the high-T band structure. Isosurfaces with $\chi_0(\mathbf{q}) = 92\%\chi_0^{\max}$ are shown.

matrix elements may change the shape of the full susceptibility $\chi(\mathbf{q})$, it is unlikely to change the enhancement at the X,Y,Z wave vectors, since it is driven by the phase space factor that is properly included already on the $\chi_0(\mathbf{q})$ level.

Keeping in mind these findings, we performed calculations of the phonon spectra using a relativistic linear response DFT technique [21] and found pronounced instabilities with the largest negative frequencies exactly at the X point (see SM for details of the calculations and the resulting phonon spectrum). Condensing these two phonon modes yields structures with the symmetry groups $R32$ and $R\bar{3}m$, respectively. An arbitrary linear combination of these phonons gives the $P4_132$ group. Optimizing the lattice in GGA+SOC within any of these groups leads to lower (compared to the reported structure) energies, but not insulating gaps. However, after checking the possible subgroups of the $P4_132$ group, we found that further lowering the symmetry to $P2_12_12_1$ opens a gap, decreases the energy even further (by ∼135 meV/f.u. as compared to that proposed in Ref. [11]), and make the system nonmagnetic, which agrees with the experimental data.

There are 16 W atoms in the unit cell in the optimized structure. Half of these W form short W-W bonds (3.47 Å), which result in an insulating ground state with four W bands below E_F, occupied by all eight available $5d$ electrons of 16 $W^{5.5+}$ ions (details of the crystal structure together with the corresponding band structure are given in SM). In no case should these short W-W bonds be considered dimers (typical distances in W dimers are ∼2.7 Å [22]), but rather they are a result of CDW formation. This is a consequence of the pyrochlore lattice, where oxygen is in between any two tungsten ions and prevents the formation of real dimers. While the average W-O bond distances for four inequivalent W in an optimized structure are nearly the same (∼1.95 Å), which agrees with results of Ref. [11], there is a certain charge modulation on the W sites (see SM), consistent with the formation of a CDW.

Superconductivity. Materials close to a CDW instability often harbor interesting superconductivity, which can either coexist with the CDW, or emerge upon suppression of the latter. As discussed below, doped CsW_2O_6 is a candidate for a highly unconventional superconducting state, as predicted by Agterberg *et al.* in 1999 [23], but has yet to be observed. Nor have any realistic candidates been identified so far.

Let us briefly remind the reader of the essence of this work. Imagine the same Fermi surface as depicted in Fig. 2, but without the electron pockets. Let us further suppose that there is a pairing interaction that is stronger at small momenta. When a sufficiently strong Coulomb interaction is present in the system (which is quite likely, given the small Fermi energy and thus small logarithmic renormalization), the superconductivity is optimized if the phase shift between the three inequivalent X pockets is maximized, that is, equals $2\pi i/3$. Although not pointed out in the original paper [23], this state can be classified as "$d + id$," which is a combination of the two states with the e_g symmetry, $Y_{x^2-y^2} \pm iY_{3z^2-1}$, or $(Y_{2,2} + Y_{2,-2})/\sqrt{2} \pm iY_{2,0}$ (the same combination was discussed by van den Brink and Khomskii in the context of the Jahn-Teller effect [24]).

One may argue that if an electron pocket is present, it has to have gap nodes. This is true, but these nodes are only point nodes at the eight directions $[\pm1,\pm1,\pm1]$, and thus the mean

square gap ($\sqrt{155/512} \approx 0.55$) is only 15% smaller than the maximal gap at ($\pm 1,0,0$), namely, $\sqrt{5/4\pi}$. Thus, this highly unconventional state is quite viable and may very well be realized in this material, if the high-temperature phase could be stabilized. Given that, as shown above, the metal-insulator transition in the real material is driven by a (spin-orbit-induced) Peierls instability, the most natural way to stabilize the HT phase is to dope it in order to destroy nesting. Indeed, a sister material, $CsTaWO_6$, occurs at all temperatures in a cubic phase isostructural to the HT phase of CsW_2O_6 [25]. This material is doped with $\frac{1}{2}$ hole per $5d$ metal ion, that is to say, W and Ta occur in the d^0 configuration, so it is useless from the point of view of superconductivity. Synthesizing intermediate materials of the composition $CsW_{1+x}Ta_{1-x}O_6$, $0 < x < 1$, is more promising and must be feasible. One caveat is in place: As any other d-wave superconductivity, this $e_g + ie_g$ state would be sensitive to impurity scattering, so the unavoidable W-Ta disorder may suppress or entirely destroy this superconducting state. Other possibilities include (i) introducing Cs vacancies, (ii) partially replacing O with N, or (iii) applying pressure (in the latter case the nesting would likely be unchanged, but the elastic energy penalty for the Peierls transition would increase).

Conclusions. CsW_2O_6 appears to be a highly interesting material, harboring quite unusual and even intriguing physics. So far it has been barely studied experimentally and had not to been investigated theoretically at all. We hope that our work will stimulate further research.

Our main results are as follows: A close inspection of the experimentally reported low-T structure reveals that it cannot possibly open an insulating gap, and at least a twice larger cell is needed, and that this structure generates large forces in DFT, signaling that it is far from the lowest-energy structure. Examining the high-T structure, which had been unambiguously established, we find that its fully relativistic (spin-orbit coupling is absolutely essential) Fermi surface exhibits an amazingly simple semimetal topology, with good electron-hole nesting that is quite visible in the calculated susceptibility. This nesting makes the high-T structure unstable against the simultaneous formation of three charge density waves, running in the three orthogonal crystallographic directions, i.e., susceptible to such a rare phenomenon as the 3D Peierls transition. A subsequent calculation of the phonon spectrum demonstrates that the largest negative phonon frequencies are exactly at those points of the Brillouin zone where the susceptibility diverges. The crystal structure obtained by the lattice optimization using eigenvectors of the phonon branches that are lowest in energy shows the formation of short W-W bonds for half of the W atoms in the unit cell. In this structure, CsW_2O_6 was found to be insulating and nonmagnetic, fully consistent with the available experimental data. Having demonstrated that the observed transition is nesting driven and thus must be very sensitive to band filling, we speculate that alloying with Ta should suppress the CDW state rather rapidly.

Finally, we note that the calculated topology of the Fermi surfaces (in the HT phase) is exactly the one required to realize an intriguing proposal of Gor'kov and his collaborators concerning a 3D d-wave state that breaks the time reversal symmetry without being chiral, and which can be characterized as a 3D version of the famous "$d + id$" state (which in this case becomes $e_g + ie_g$).

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Supplemental materials for Spin-orbit driven Peierls transition and possible exotic superconductivity in CsW_2O_6

Sergey V. Streltsov,[1,2,*] Igor I. Mazin,[3] Rolf Heid,[4] and Klaus-Peter Bohnen[4]

[1] *M.N. Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620137, Ekaterinburg, Russia*
[2] *Ural Federal University, Mira St. 19, 620002 Ekaterinburg, Russia*
[3] *Code 6393, Naval Research Laboratory, Washington, DC 20375, USA*
[4] *Institue for Solid State Physics, Karlsruhe Institute of Technology (KIT), D-76021 Karlsruhe, Germany*

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I. EXPERIMENTAL LT STRUCTURE

The crystal structure proposed by Hirai et al[1] for low-T phase consists of zigzag chains with shortened W-W bonds (3.598 Å), see Fig. 1 (left), propagating along the cubic $[1,1,0]$ direction (orthorhombic b). This structure can be also visualized as a network of tetramerized linear W chains running along the cubic $[1,0,1]$ and $[0,1,1]$ directions, as shown in Fig. 1 (right). This tetramerization, however, does not open the band gap as seen in Fig. 2 even if the spin-orbit coupling (SOC) or Hubbard correlations are taken into account. Indeed, given 4 electrons per unit cell, and accounting for the Kramer degeneracy, we observe that the gap can be opened only between the second (cyan in Fig. 2) and the third (black) bands. That would require lifting the bottom of the third band at Γ above the top of the second band (at R) by at least 0.3 eV. No meaningful manipulation with this electronic structure or atomic positions can possibly open the gap, unless the unit cell size is increased.

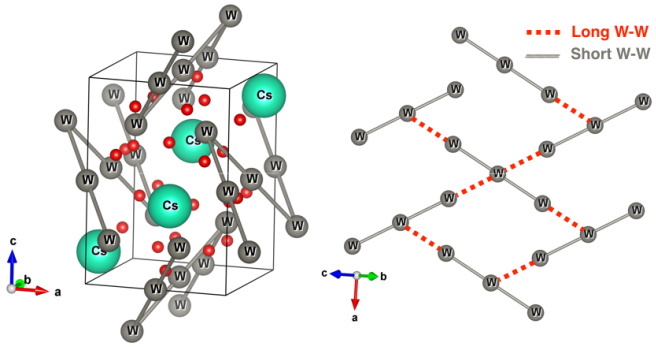

Figure 1: Crystal structure obtained in Ref. [1] for T=110 K (low-T phase). In right panel the W-W network is shown.

*Electronic address: streltsov@imp.uran.ru

II. PHONON CALCULATIONS

Phonon calculations for the fcc structure of CsW_2O_6 were performed within a mixed-basis pseudopotential framework [2, 3] using density-functional perturbation theory (DFPT) [4, 5]. Norm-conserving pseudopotentials including non-linear core corrections were constructed from all-electron relativistic atom calculations according to the scheme of Vanderbilt [6]. The spin-orbit coupling is incorporated within the pseudopotential approach [7, 8] and is treated fully self-consistently.[9]) Calculations were performed within the generalized-gradient approximation.[10] Plane waves up to a kinetic energy of 24 Ry were augmented with local functions of p and d type at the Cs sites, and s, p, and d types at W, and s and p at the O sites. This choice of the basis set guaranteed sufficient convergence of electronic and phononic properties. Brillouin zone summations were performed on a fcc 8×8×8 k-point mesh in combination with the standard

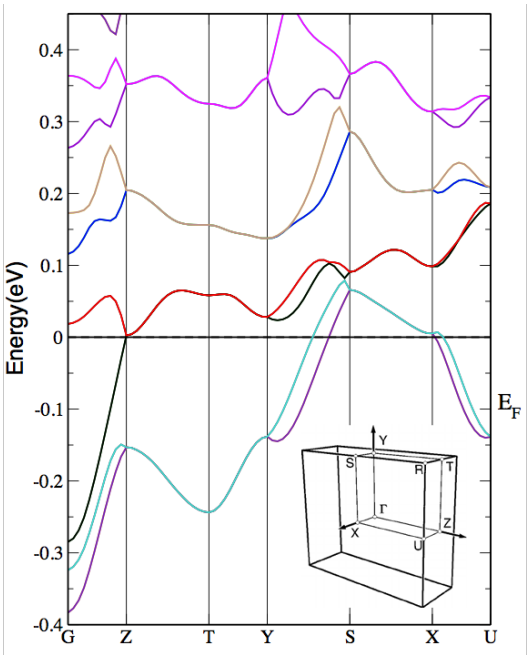

Figure 2: The band structure obtained for the LT structure of Ref. [1] in the GGA+SOC calculations (Wien2k).

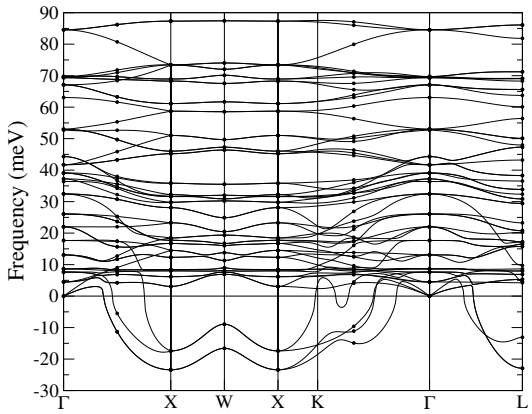

Figure 3: Phonon spectrum as obtained in the GGA+SOC calculations for the optimized high temperature structure.

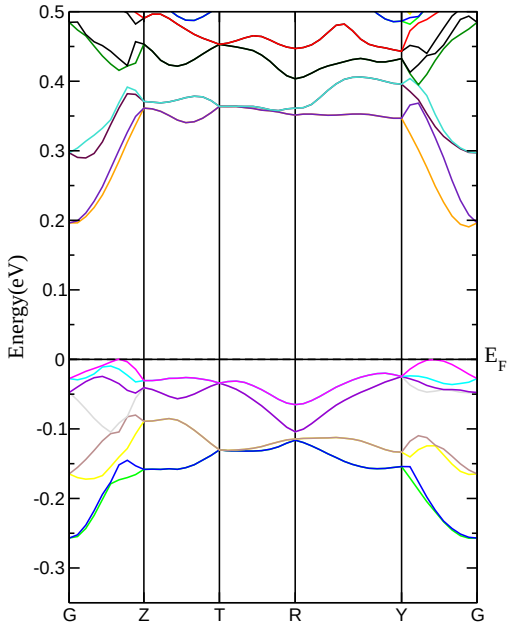

Figure 4: The band structure obtained for optimized low-T structure in the GGA+SOC calculations (Wien2k).

smearing technique [11] employing a Gaussian broadening of 0.1 eV. Dynamical matrices were determined via DFPT on a simple cubic 2×2×2 q-point mesh (32 points in the full Brillouin zone), and were then interpolated for arbitrary q points using a standard Fourier technique. Resulting phonon spectrum is shown in Fig. 3.

III. GGA+SOC OPTIMIZED STRUCTURE

As it is explained in the main part of the paper we optimized (in VASP) the crystal structure of CsW_2O_6 using combination of eigenvectors of two unstable phonon modes as an input. Resulting crystal structure of the $P4_132$ symmetry still gives metallic ground state, while further decrease of the symmetry down to $P2_12_12_1$ opens a gap. Corresponding band structure is shown in Fig. 4. CsW_2O_6 is a band insulator with both valence and conduction bands formed mostly by W 5d states. There are 16 W ions in the unit cell (4 classes with 4 equivalent W in each class) in the optimized $P2_12_12_1$ structure and eight d (each W is nominally 5.5+, i.e. $d^{0.5}$) electrons occupy all the valence bands.

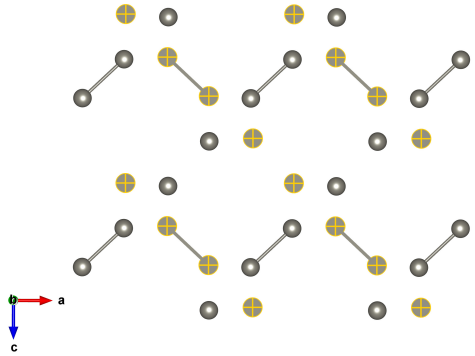

Figure 5: The W lattice in the GGA+SOC optimized $P2_12_12_1$ structure. W ions, which belong to two different ac planes are shown by different colours. No tetramerization is found in the b direction.

The crystal structure is characterized by tetramerized W-W chains running in two orthogonal directions in two different ac plane, see Fig. 5. The cif-file of optimized crystal structure is enclosed to this SM.

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