

# Breaking of Frustration by Coupled Rattler Ions in $\text{KOs}_2\text{O}_6$

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Using *ab initio* total energies and forces we derive effective Hamiltonian for potassium dynamics in  $\text{KOs}_2\text{O}_6$ , which takes place in an unusually low energy scale and is characterized by an on-site instability (rattler) and frustrated nearest-neighbor interaction. We investigate various limits for the potassium dynamics, and from classical simulations on up to  $6 \times 6 \times 6$  clusters we obtain inversion-symmetry breaking ordering involved selected commensurate wave vectors. We argue that the observed anomalies do not reflect intrinsic properties of the electron liquid but its coupling to an unconventional phononic bath, or the bath itself.

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The phenomenon of frustration, which gives rise many fascinating phenomena, is usually associated with the topology of non-bipartite lattices, where nearest-neighbor (nn) interactions and global connectivity compete in the lowering of energy. The issue of rattling atoms in spacious lattice sites [1, 2] is a separate occurrence that can also lead to a high degeneracy of low energy states. In this letter we address a situation where both of these phenomena arise: a four-fold single-site instability leads to rattling of cations on a diamond structure sublattice where nn interactions frustrate simple ordering of the displacements. The system deals with this coupling of rattling+frustration by commensurate ordering. Such a disorder-order transition may account for the second phase transition seen in  $\text{KOs}_2\text{O}_6$  ( $\text{KOsO}$ ) within the superconducting state, and the unusual low-energy dynamics and associated electron-phonon coupling can account for the qualitative differences in physical properties of  $\text{KOsO}$  compared to  $\text{RbOs}_2\text{O}_6$  ( $\text{ROsO}$ ) and  $\text{CsOs}_2\text{O}_6$  ( $\text{COsO}$ ), all of which have essentially identical average crystal structures and electronic structures. Furthermore, the ground state structure we obtain removes inversion symmetry, thereby adding a new aspect to the very active current interest in superconductivity of materials that lack a center of inversion. [3]

The pyrochlore-lattice-based structure with a potential to support magnetic frustration has attracted attention to  $\text{AOs}_2\text{O}_6$  (A=K, Rb,Cs) group. Recently superconductivity up to 10 K was discovered with a factor of three variation of  $T_c$  throughout the group (from 3.3 K in  $\text{COsO}$  to 9.7 K in  $\text{KOsO}$ ) [4–6]. Subsequent experiments revealed a broader picture of  $\text{RbOsO}$  and  $\text{COsO}$  being conventional metals with s-wave BCS superconductivity [7–9] while  $\text{KOsO}$  stands out with peculiar anomalies in superconducting as well as normal state, which include large upper critical field (about twice the Pauli limit) [4], anomalous nuclear spin relaxation rate [10] and indications of anisotropic order parameter from  $\mu\text{SR}$  experiments [11]. In the normal state the conductivity ex-

hibits a non-Fermi-liquid behavior [4], and the low temperature linear specific heat coefficient is estimated to be four times that of  $\text{ROsO}$  and  $\text{COsO}$  [12]. Recently an intriguing  $\lambda$ -shaped peak was observed in the specific heat of good quality  $\text{KOsO}$  crystals suggesting a phase transition at 7 K (i.e. within the superconducting state) [12]. Notably, the peak position and shape do not change even when the superconductivity is suppressed below 7 K by the external field. Insensitivity to such a profound change of the electronic state indicates that the peak is rooted in the lattice dynamics than the intrinsic electronic degrees of freedom. The striking contrast between the above observations and the almost identical crystallographic structures of the three compounds provides the main puzzle of this osmanate group.

Electronic structure investigations [13, 14] have revealed a considerable bandwidth of the Os  $5d t_{2g}$  12 band complex of about 3 eV which does not support the idea of local moment formation on the Os sites nor any emergence of frustration due to the pyrochlore topology of the Os sublattice. Instead we find that a significant frustration, not magnetic but structural, takes place on the diamond sublattice occupied by K ions. We have shown previously [13] that the symmetric ( $A_g$ ) potassium phonon mode is unstable and that energy can be lowered by several meV/atom(K) through a rather large displacement of the K ions. In this work, based on additional first principles calculations we construct an effective Hamiltonian describing fourfold symmetric displacements of K ions off the diamond lattice sites, with nn coupling leading to a highly frustrated system of displacements. Dynamic simulations for finite clusters reveal a broken symmetry (including removal of inversion) groundstate involving many primitive cells.

In Fig. 1 we show the  $\text{AOs}_2\text{O}_6$  lattice which consists of Os on a pyrochlore sublattice, having one O atom bridging each Os nn pair. The cavities in the Os-O network are filled with K ions, which themselves form a diamond lattice, composed of two *fcc* sublattices. Using a full-

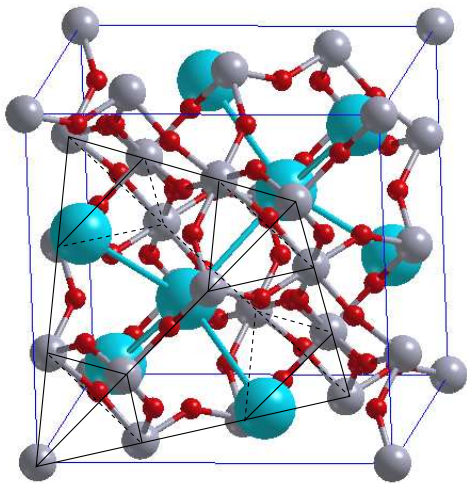


FIG. 1: The  $\text{AOs}_2\text{O}_6$  structure with Os (gray), O (red) and alkali metal (blue). The pyrochlore sublattice of Os atoms is highlighted. Notice the alkali sublattice with diamond structure.

potential linearized augmented-plane-waves code Wien2k [15] we have performed a series of calculations in which K ions move along the (111) direction: (i) the two *fcc* sublattices are displaced in opposite direction (symmetric  $A_g$  mode), (ii) same as (i) with the O positions allowed to relax, (iii) only one *fcc* sublattice is displaced. Comparing results (i) and (ii) we find a non-negligible O relaxation only for large K displacement (the energy vs displacement curve has slightly less steep walls when O ions are allowed to relax). Since the O relaxation effect is minor we consider the Os-O network to be rigid. Due to spacious channels in the Os-O network along the nn K-K joins, the nn Coulomb interaction is screened much less than the interactions between more distant neighbors. Therefore we neglect all interactions beyond the nearest neighbors.

The model Hamiltonian of the K sublattice has two potential energy terms, the site potential and the nn interaction. Parameters of both the site potential and the interaction can be obtained from the calculation of type (iii). In Fig. 2 we show the site potential along the (111) direction obtained from the total energy and the force calculations. To obtain a full three dimensional representation we first note that the tetrahedral site symmetry allows only spherical ( $l = 0$ ) and non-spherical terms with  $l = 3, 4, 6$  in the spherical harmonic expansion of the site potential up to  $l = 6$ . The odd part  $P_o(\xi)$  can be directly associated with  $\mathcal{Y}_{32}$  real spherical harmonic, while the even part  $P_e(\xi)$  is approximately spherical. The K-K interaction can be obtained from the force acting on a fixed ion as a function of the displacement of its neighbors. The simplest form of the pair force which can describe the calculated data is  $F(r) = A + Br$ , where  $r$  is

pair distance. In Fig. 3 we show the first principles force together with the above pair-force expression applied to the four nearest neighbors. Construction of the effective Hamiltonian is finalized by rewriting the interaction potential  $V(\mathbf{r}_1, \mathbf{r}_2) = A|\mathbf{r}_{12}| + \frac{B}{2}|\mathbf{r}_{12}|^2$  in terms of the local displacements. To avoid double counting, part of the interaction already included in the site potential must be subtracted. The interaction then is given by

$$W_{ij}(\xi_i, \xi_j) = V(\mathbf{R}_i + \xi_i, \mathbf{R}_j + \xi_j) - V(\mathbf{R}_i, \mathbf{R}_j + \xi_j) - V(\mathbf{R}_i + \xi_i, \mathbf{R}_j) + V(\mathbf{R}_i, \mathbf{R}_j), \quad (1)$$

where  $\xi_i, \xi_j$  stand for the displacements of ions at sites  $\mathbf{R}_i, \mathbf{R}_j$ . Such interaction is strongly directional (not central), which becomes obvious for small displacements when the interaction takes the dipole-dipole-like form

$$W_{ij}(\xi_i, \xi_j) \approx A \frac{(\mathbf{R}_{ij} \cdot \xi_i)(\mathbf{R}_{ij} \cdot \xi_j)}{R_{ij}^3} - \left(\frac{A}{R_{ij}} + B\right) \xi_i \cdot \xi_j. \quad (2)$$

Thus we have an effective Hamiltonian for the dynamics of potassium ions

$$\hat{H} = \sum_i \left( \frac{p_i^2}{2M} + P_e(\xi_i) + P_o(\xi_i) \mathcal{Y}_{32}(\hat{\xi}_i) \right) + \sum_{ij} W_{ij}(\xi_i, \xi_j), \quad (3)$$

where  $M$  is potassium atomic mass ( $M=71794m_e$ ). Note that even though the interaction part has a harmonic form for small displacements the site potential is strongly anharmonic due to its four symmetry related off-center minima.

We start by solving a single site problem on a real space  $101^3$  grid within cube of side 4 a.u. Such a spectrum up to 80 K is depicted with the horizontal lines in Fig. 2. The characterizing feature is a quasi-degenerate ground state consisting of a singlet and triplet split by 8 K. Alternatively the low energy Hilbert space can be spanned by four symmetry related “ $\text{sp}^3$ hybrid” orbitals associated with the four local minima of the site potential. The spectrum with singlet-triplet split groundstate separated by a considerably larger gap from higher excited states results in a Schottky anomaly in the specific heat. However, the position and sharpness of the peak in the experimental specific heat rules out the Schottky anomaly scenario, pointing instead to some sort of collective transition. Another unusual feature of the site Hamiltonian is that the groundstate is less localized than the excitations, measured by  $\langle r^2 \rangle$ .

To understand the interaction part of the Hamiltonian, here are two limiting cases: strong interaction and strong site potential. In the limit of strong interaction one can use the harmonic approximation (2) and treat the site potential as a perturbation of the standard phonon picture. However,  $\text{KO}_2$  does not belong to this limit. In the limit of strong site potential the low energy lattice

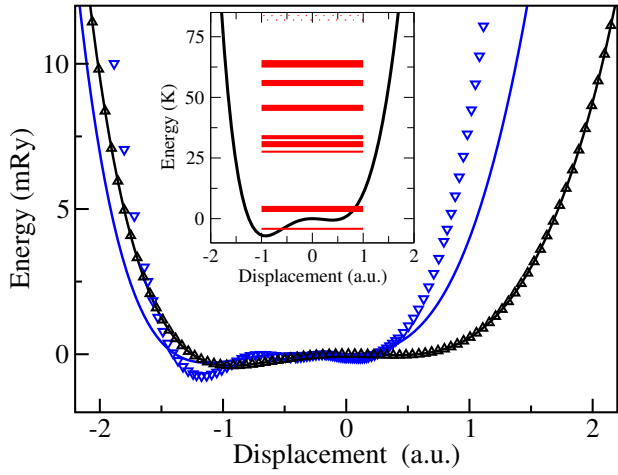


FIG. 2: The site part of the Hamiltonian obtained by measuring the total energy and force as one of the fcc sublattices of diamond lattice of K ions is displaced along (111) direction marked with black triangles and the polynomial fit (black line). The blue triangles are obtained by displacing the both sublattices symmetrically, while the solid line is the corresponding potential energy in the effective Hamiltonian (note that it was not obtained by fitting this data). In the inset we show the detail of the site potential together with low energy spectrum of the single site problem (marked with horizontal lines). The line thickness corresponds to the degeneracy (thinnest - singlet, thickest - triplet).

Hamiltonian can be built on products of a small number of the on-site states (e.g. the “sp<sup>3</sup>” quadruplet), provided the coupling to the product wave functions containing high energy on-site states is weak. Evaluating the diagonal  $\langle i, j | W | i, j \rangle$  and the leading off-diagonal  $\langle i, j | W | i, k \rangle$  matrix elements of the interaction for a two-site problem, we conclude that a simple “sp<sup>3</sup>” model is not accurate enough due to coupling to a large number of higher energy states.

We have shown previously that the site potential well in ROsO and COsO is much narrower than in KOsO. This has two consequences: the separation of the single site energy levels is larger, and importantly the alkali ions spend more time close to the well center resulting in smaller interaction matrix elements. Therefore the strong site potential limit is fulfilled and single site description becomes rather accurate. Indeed, the low temperature lattice contribution to the specific heat of ROsO and COsO is better described by Einstein modes than acoustic phonons [16].

To gain further insight we pursue the large  $M$  (classical) limit, focusing on possible ordering patterns by minimizing the potential energy for finite clusters. This is a formidable computational task due to a large number of local minima, as found by steepest descent minimization. To reach the most likely global minimum we have used a damped molecular dynamics combined with sim-

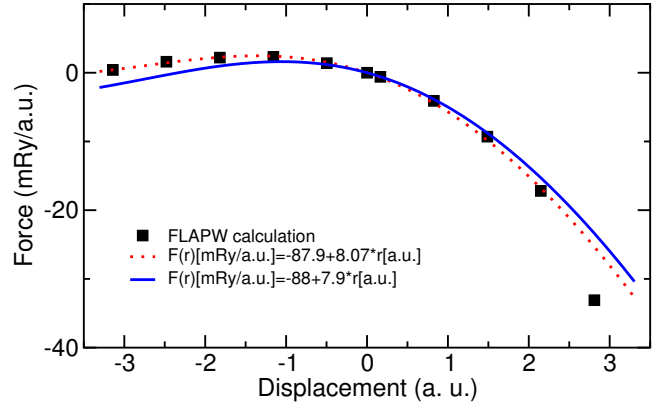


FIG. 3: The force acting on an ion in a central position when its neighbors are uniformly displaced along (111) direction. The symbols are obtained from the electronic structure calculation. The dotted line represents the fitted pair force with linear dependence of the separation of ions. The solid line is a modified fit actually used in the calculation. The modification was performed so that the proper minimum for the symmetric mode is obtained from the potential energy.

ulated annealing. Specifically we integrated the classical equation of motion

$$M \frac{d^2 \boldsymbol{\xi}}{dt^2} = \mathcal{F}(\boldsymbol{\xi}) - \beta(T) \frac{d\boldsymbol{\xi}}{dt} + \mathcal{G}(T) \quad (4)$$

where  $\boldsymbol{\xi}$  is the displacement vector,  $\mathcal{F}$  is the actual force, the  $\beta(T) \propto \sqrt{T}$  is a friction parameter and  $\mathcal{G}(T)$  is a random vector with a Gaussian distribution (centered at zero) and width at half maximum proportional to  $T$ . The parameter  $T$  is an artificial temperature parameter which was successively reduced according to  $T_i = \alpha T_{i-1}$  with  $\alpha$  in the range 0.98 to 0.995. The calculations were performed for up to 432 site clusters with periodic boundary conditions. To ensure high probability of finding the global minimum we have repeated the calculation several times starting from random initial conditions. For the  $1 \times 1 \times 1$  (single primitive cell) cluster, which allows only uniform displacement of the two *fcc* sublattices, a minimum of -2.0 mRy was found, corresponding to shifting all ions in the same direction along a cubic body diagonal by  $1.54a_0$  ( $1.24a_0$ ) for ions moving toward (away from) its nn site. The  $2 \times 2 \times 2$  cluster has significantly lower minimum of -17.1 mRy. As in the previous case the ions on one sublattice move toward one of their neighbor (by  $2.23a_0$ ) and on the other sublattice away from the neighbor (by  $1.94a_0$ ). The displacements are not uniform any more. Instead for each ion its four neighbors shift along all four possible nn bonds.

The ground state structures for 333 and larger clusters are difficult to visualize, but have several common features. The net displacement per sublattice is small (less than 0.1) compared to the large average displacement of  $2.0a_0$  ( $1.05 \text{ \AA}$ ) per site. Relaxing the periodic boundary

constraints by increasing the cluster size beyond  $3 \times 3 \times 3$  does not lead to a significant decrease of the energy below -18 mRy (see Table I). To analyze patterns we have Fourier-transformed the displacement fields.

$$S_\alpha(\mathbf{q}) = \frac{1}{N} \sum_i \exp(i\mathbf{q} \cdot \mathbf{R}_i) \xi_\alpha(\mathbf{R}_i), \quad (5)$$

where  $N$  is the number of atoms in the cluster and possible  $q$ 's are restricted by the periodic boundary conditions. For clusters  $3 \times 3$ ,  $4 \times 4 \times 4$ , and  $6 \times 6 \times 6$  very distinct ordering was found with most of the Fourier components vanishing (below  $10^{-8}$ ). The major features of the displacement patterns (dominant Fourier components) were the same, even for  $5 \times 5 \times 5$  where we were not able to find an unambiguous global minimum. In Table I we show the reciprocal lattice vectors corresponding to the largest amplitude  $|S(\mathbf{q})|$  (the amplitudes for different components of the displacement vector are of comparable size on both sublattices). Comparing the results for different clusters we observe that the Fourier transforms are characterized by 2 or 3 dominant  $q$ -components. Ordering with  $q=(2/3, 2/3, 0)$  or/and  $q=(1/2, 1/2, 1/2)$  appears whenever allowed by the cluster size. Their integer linear combinations have also non-vanishing but smaller (less than 30%) amplitude.

Now we consider the relation of our results to experimental data. The effective low-energy Hamiltonian is characterized by an unusually soft and broad local potential, which allows for large excursions (as large as 1 Å) of K ions away from high symmetry positions. As a consequence of these large excursions and close spacing of the local energy levels, the nn interaction between K ions provides significant but frustrating coupling. Our calculations provide a natural explanation for the second peak observed in the specific heat of  $\text{KOs}_2\text{O}_6$  [12] as a phase transition of the potassium sublattice to supercell order. Classical calculations for finite clusters provide a complicated but distinct pattern with multiple  $q$  ordering and large displacements. The quantum corrections to our classical simulations, which can be viewed as replacing point objects by density distributions, will force the ions away from the steep wall of the local potential wells thus reducing the displacements and reduce some-

TABLE I: Minimum potential energy and the dominant Fourier components (only one member of  $\pm\mathbf{q}$  pair is shown) for the ground states of clusters of different size (in brackets). The vectors are in the units of  $\frac{2\pi}{a}$  where  $a=10.101$  Å.

cluster size	E (mRy)	largest $ S(q) $ for
$1 \times 1 \times 1$ (2)	-1.99	
$2 \times 2 \times 2$ (16)	-17.11	$(1,0,0), (0,1,0), (0,0,1)$
$3 \times 3 \times 3$ (54)	-18.01	$(-\frac{2}{3}, 0, \frac{2}{3}), (\frac{2}{3}, 0, \frac{2}{3})$
$4 \times 4 \times 4$ (128)	-18.11	$(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}), (-\frac{1}{4}, \frac{1}{4}, \frac{3}{4}), (\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$
$5 \times 5 \times 5$ (250)	-18.11	$(\frac{3}{5}, \frac{3}{5}, -\frac{1}{5}), (\frac{3}{5}, -\frac{1}{5}, \frac{3}{5}), (\frac{1}{5}, -\frac{3}{5}, -\frac{3}{5})$
$6 \times 6 \times 6$ (432)	-18.20	$(0, -\frac{2}{3}, \frac{2}{3}), (-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, \frac{1}{6}, \frac{5}{6})$

what the effect of the interaction, which has a varying sign, relative to the site potential.

Due to large ionic radii the Rb and Cs ions experience much narrower potential wells and thus significantly weaker effective interaction (3) and consequent weaker and less anomalous electron-phonon coupling. Consequently their dynamics can be described by a set of independent harmonic oscillators which fits well the observed specific heat [16]. As a result of rattling (quasi degenerate groundstate of a single site problem) combined with the frustrated interaction in the K subsystem, the conduction electrons interact with a phononic bath with high density of low energy states. The anomalies of low temperature electronic properties such as non-Fermi-liquid conductivity [4] and large mass enhancement observed in specific heat [12] are not surprising in this context. Although we neglect (justifiably) the effect of oxygen relaxation on the low-energy K dynamics, our preliminary studies indicate this relaxation will be important for the coupling of the electronic system to the K dynamics. Finally we point out that for large excursions of potassium ion away from the central position interaction between the nuclear quadrupole moment and the electric field gradient arises, and should be observable in nuclear spin relaxation rates [10].

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