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Effective Hamiltonian for Potassium Dynamics in the β-pyrochlore Superconductor KOs_2O_6

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Based on *ab initio* energies and forces we construct an effective Hamiltonian for anharmonic dynamics of potassium cations in the β-pyrochlore compound KOs_2O_6. We solve numerically the single-site problem which is characterized by an extremely flat potential well allowing for large excursions of K ions, and illustrate graphically the K-ion wavefunctions in the four off-center (symmetry-breaking) sites. These large displacements from the ideal lattice site result in sizable K-K near-neighbor interactions through a screened Coulomb interaction. The matrix elements of the interaction in the basis of single-site eigenstates are calculated and discussed.

1 Introduction The recent discovery of osmanate superconductors AOs_2O_6 (AOsO) [1, 8, 3] motivated by interest in physics on the pyrochlore lattice has led to an interesting finding. Depending on the alkali element (K, Rb or Cs) the transport and thermodynamic properties of the compounds differ significantly, while their crystallographic and electronic structures are essentially the same [4, 5]. Superconductivity up to 10 K with a factor of three variation of T_c throughout the group (from 3.3 K in COsO to 9.7 K in KOsO) has attracted both experimental and theoretical interest. Specific heat measurements [6, 7] found a large enhancement of the linear specific heat coefficient over the band structure values (about 4 in ROsO and COsO and as large as 12 in KOsO).

The β-pyrochlore structure is a non-intuitive variant of the usual pyrochlore structure $A_2B_2O_7 \equiv A_2B_2O_6O'$ that has attracted attention largely due to the frustrated nature of magnetic order when there are antiferromagnetic interactions on the pyrochlore sublattice. In the β variant, the A sublattice is unoccupied, and the site O' that is normally occupied by an anion (oxygen or a halide) is occupied by a cation (alkali metal ion). The structure, illustrated in Fig. 1, is fcc $Fd\bar{3}m$, the same as the diamond structure, and it is a central feature in the discussion we present that the alkali ion lies on a diamond sublattice. The structure is discussed more fully in Ref. [4]. Initially the focus fell on the Os $5d$, O $2p$ complex of electronic states, and whether correlated behavior is present. However, the lattice constants and electronic structures are virtually identical, and we have looked elsewhere to address the unusual behavior of KOsO compared to that in ROsO[8] and COsO.

Recent density functional calculations [4] showed that the alkali ions are only weakly bound inside cavities in the pyrochlore lattice of Os atoms and that the effective potential they experience is sensitive to size of the ion. In particular the potassium ion is free to move over a linear distance as large as 1 Åin the $< 111 >$ directions. Moreover the coupling of the potassium ion to the Os-O sublattice is rather weak, reflected by the fact that non-negligible O relaxation takes place only for large potassium displacements. Different energy scales and weak coupling suggest the K and Os-O sublattices can be well approximated at low temperature as decoupled systems. Since the electronic states associated with the alkali cation (each alkali ion donates an electron to the Os $5d$ band) are nowhere close to the Fermi level the alkali ions act as

weak vibrational scatterers of the free electrons. Based on these observations we use *ab initio* energies and forces [9] to construct a Hamiltonian for the potassium dynamics within a background of the rigid Os-O substructure which provides effective potential wells at the alkali sites.

2   Effective Hamiltonian   In order to build the potential energy part of the Hamiltonian one needs to know the total energy as a function of displacements of the alkali ions away from their sites which form a diamond lattice. For practical reasons (computational cost) and well as simplicity of the model we make several simplifying but justified assumptions. First, we split potential energy into a single particle (single site) term and an inter-site interaction. Second, we assume that only interaction between the nearest neighbors (NN) needs to be considered. This assumption is justified by metallic screening of the Coulomb interaction between alkali ions and inspection of the crystal structure which reveals open channels in the Os-O cage along the NN directions ("bond" directions of the diamond sublattice). Third, we simplify the single site potential by keeping only the lowest order even ($l = 0$) and odd ($l = 3$) terms 1 in the spherical harmonics expansion (note that the single site potential has tetrahedral symmetry).

$$\hat{H}_{site} = \frac{\vec{p}^2}{2M} + P_e(\xi) + P_o(\xi)\mathcal{Y}_{32}(\hat{\xi})$$

$$\text{with} \quad \mathcal{Y}_{32} = \frac{3}{2\sqrt{3}}\cos\theta\sin^2\theta(\cos^2\phi - \sin^2\phi) \tag{1}$$

The displacement coordinate is $\vec{\xi} = \xi\hat{\xi}$, and θ, ϕ are the spherical coordinates; $\vec{p}$ is the conjugate momentum. The polynomials $P_e(\xi)$ and $P_o(\xi)$ were obtained as follows. The diamond lattice consists of two fcc sublattices A and B such that the nearest neighbors of a site on sublattice A belong to sublattice B and vice versa. Keeping sublattice A fixed and moving sublattice B along the $< 111 >$ direction we obtain the single site potential by calculating the total energy (and the force on ions on B sublattice) as a function of displacement. The $P_e(\xi)$ and $P_o(\xi)$ are the even and odd part of the polynomial fit (note that the linear term is zero by symmetry).

   The interaction term can be obtained by calculating the force acting on an ion on the sublattice A. The total force is the sum of pair interactions with its four neighbors. Taking the constant and linear term in the expansion of the pair force as a function of NN distance is enough to describe the *ab initio* results in
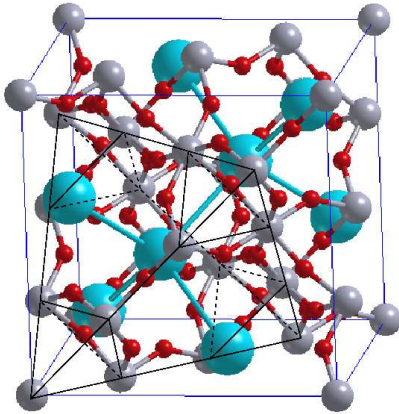

Fig. 1   The β-pyrochlore structure of KOs_2O_6. The largest atoms shown here are the K cations, which lie on a diamond sublattice. The midsize atoms are Os, coordinated octahedrally by oxygen (small dark spheres). Each O ions bridges two OsO_6 octahedra, as in the perovskite structure. However, the Os ions lie on a pyrochlore sublattice of interlinked Os_4 tetrahedra.

the full range of displacements. Part of the effect of the pair force is already included in the single site potential. To avoid double-counting, the effective interaction can be written as

$$
\begin{aligned}
W_{ij}(\boldsymbol{\xi_i}, \boldsymbol{\xi_j}) =& V(\mathbf{R_i} + \boldsymbol{\xi_i}, \mathbf{R_j} + \boldsymbol{\xi_j}) - V(\mathbf{R_i}, \mathbf{R_j} + \boldsymbol{\xi_j}) \\
& - V(\mathbf{R_i} + \boldsymbol{\xi_i}, \mathbf{R_j}) + V(\mathbf{R_i}, \mathbf{R_j}),
\end{aligned}
\tag{2}
$$

where $\boldsymbol{\xi_i}, \boldsymbol{\xi_j}$ stand for the displacements of ions at sites $\mathbf{R_i}, \mathbf{R_j}$ and $V(\mathbf{r_1}, \mathbf{r_2}) = a|\mathbf{r_{12}}| + \frac{b}{2}|\mathbf{r_{12}}|^2$ is the pair potential. The interaction $W_{ij}(\boldsymbol{\xi_i}, \boldsymbol{\xi_j})$ is strongly directional (not central), which becomes obvious for small displacements when it takes the dipole-dipole-like form

$$
W_{ij}(\boldsymbol{\xi_i}, \boldsymbol{\xi_j}) \approx a \frac{(\mathbf{R_{ij}} \cdot \boldsymbol{\xi_i})(\mathbf{R_{ij}} \cdot \boldsymbol{\xi_j})}{R_{ij}^3} - (\frac{a}{R_{ij}} + b)\boldsymbol{\xi_i} \cdot \boldsymbol{\xi_j}.
\tag{3}
$$

In Table 1 we summarize the parameters of the site potential and interaction. The construction of the model is concluded by specifying the Hilbert space in which it lives. Since the particles in our problem are massive and well confined by their respective site potentials we neglect tunneling and exchange processes. The Hilbert space for the lattice can be then built on the basis of products of single site functions without need for (anti)symmetrization.

Table 1 Coefficients of the polynomial fit and the pair interaction parameters

Power	2	3	4	5	6	a (K)	b (K)
a_n (K)	-88.2	101.8	103.2	-26.7	0.5	-13.9×10^3	615

2.1 Matrix representation We aim at building a matrix representation of the Hamiltonian on the basis of product of eigenfunctions of the single site problem [10]. Using numerical solution on a real space grid ($101 \times 101 \times 101$) we find the lowest twenty eigenstates up to 80 K (see Table 2). Note that the ground state is a singlet followed by a low-lying triplet. Alternatively this 4-dimensional subspace can be spanned by four orbitals localized in the off-center minima of the site potential shown in Fig. 2. For reasons discussed below it is more advantageous to work with these localized off-center orbitals that the 4 lowest eigenstates. A tractable lattice problem has to contain only a small number of states per site. In the following we investigate the possibility of building a lattice Hamiltonian on the basis of these four orbitals.

The interaction gives rise to several different types of matrix elements, which we denote as follows: $(AB|W|AB)$ is the direct interaction between the charge density corresponding to orbital A at one site and orbital B at its NN site; $(AB|W|AC)$ is the interaction-induced hopping which involves the charge density of orbital A and overlap density of orbitals B and C, and finally $(AD|W|BC)$ which is the 'pair hopping' involving overlap densities at both sites. Using a coarse grained ($22 \times 22 \times 22$) grid we have calculated the interaction matrix elements for all previously evaluated single site states. It was determined that the matrix elements of $(AD|W|BC)$ type are much smaller than these of $(AB|W|AC)$ and can be neglected. The $(AB|W|AB)$ matrix elements, while large compared to the single site energy scale, contribute only to the diagonal terms of the lattice Hamiltonian and therefore do not couple the 4-state subspace to the higher excited states.

In Table 3 we show the $(AB|W|AB)$ matrix elements in the 4-state subspace for one of the four possible NN bond directions (see the geometry in Fig. 3). Somewhat counterintuitively the situation when the distance between ions is largest is the least favorable. While the pair interaction between ions is always repulsive, the sign of the effective interaction, after subtracting the part already included in the site potential, varies through the space. Evaluating the diagonal matrix elements involving the higher excited states reveals that the two lowest configurations listed in Table 3 are also overall lowest states. The off-diagonal

Table 2 Eigenstates of the single site problem less than 80 K.

Index	Degeneracy	Eigenvalue (K)
1	1	0.
2-4	3	8.2
5	1	31.8
6-8	3	34.9
9-10	2	37.8
11-13	3	49.9
14-16	3	60.1
17	1	66.9
18-20	3	68.3

element between the low-energy configurations are $(11|W|13)$=15 K and $(13|W|23)$=19 K. Now the advantage of choosing the localized orbitals instead of the their singlet and triplet combinations is obvious. It introduces an off-diagonal matrix element of about 2 K due to the site potential, but at the same time it puts the much larger interaction part of the Hamiltonian close to diagonal form by strongly reducing the overlap charges.

To assess the feasibly of a 4-state model we have to calculate the coupling of the two configurations to the higher excited states. The off-diagonal elements and the corresponding differences of the diagonal elements, which consist of the $(AB|W|AB)$ term and the site energy of the excited state, involving $(11|$ and $(13|$ states are listed in Table 4.   Inspection of Table 4 suggests that the off-diagonal elements are approximately an order of magnitude smaller that the differences of corresponding diagonal elements of the Hamiltonian, with several cases where the coupling is 2-3 times stronger. This is certainly not a negligible coupling, the first order correction to $(11|H|11)$ and $(13|H|13)$ are 186 K and 171 K respectively. On the other hand while renormalizing strongly the 4-state Hamiltonian its basic structure with $(11|$, $(13|$ and the
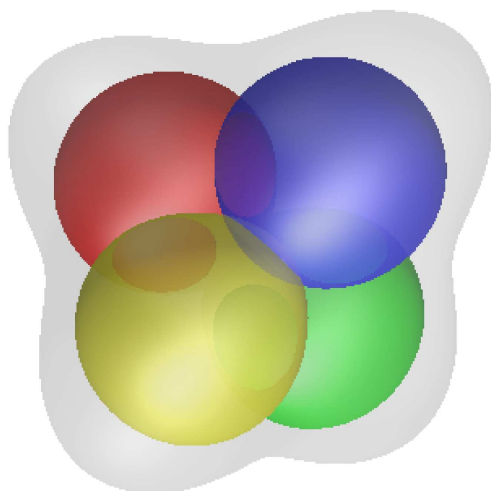

Fig. 2 The four localized orbitals that span the single site singlet-triplet split ground state (about 95% of the density is inside each contour).

Table 3 Diagonal $(AB|W|AB)$ matrix elements in Kelvins within the basis of the four localized orbitals along a particular bond. The corresponding geometry is shown in Fig. 3 (the matrix elements for the three remaining bond direction are obtained by permutation of the orbital indices).

$A\backslash B$	1	2	3	4
1	-177	147	-154	147
2	147	-177	-154	147
3	-154	-154	579	-154
4	147	147	-154	-177

symmetry related configurations as favorable and $(33|$ and $(12|$ unfavorable should be preserved (see Fig. 2 for the configurations. Systematic decoupling of the 4-state subspace, which introduces also more than two-particle interactions on the lattice, is beyond the scope of this paper.

3 Summary Based on *ab initio* electronic structure methods we have introduced an effective Hamiltonian for highly anharmonic dynamics of potassium ions in the β-pyrochlore compound KOs_2O_6. We have solved the single site problem and investigated the possibility of formulating a lattice Hamiltonian with 4-states per site. While we were not able to derive the 4-state Hamiltonian by systematic decoupling of the excited states, our results suggest this type of Hamiltonian to be a promising candidate for describing the low energy dynamical behavior of KOsO, and we expect to pursue its predictions.[10] The simplest form of such Hamiltonian, after keeping only the diagonal elements, is an anisotropic 4-state Potts model for which our calculations provide information about the bond energies of different configurations. Alternatively one can consider a dynamical mean field approach in which a single site problem is solved in a time dependent external field, which is determined selfconsistently.

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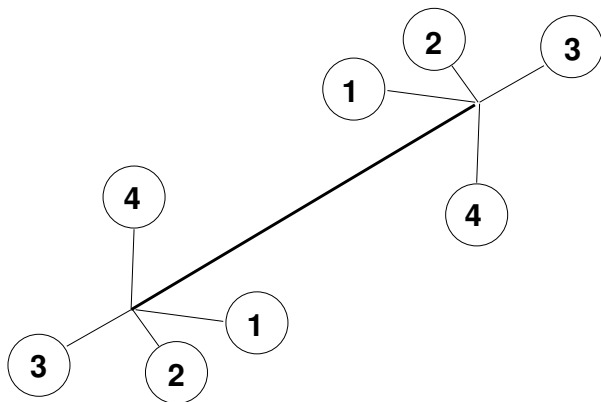[3] S. Yonezawa, Y. Muraoka, and Z. Hiroi, J. Phys. Soc. Japan **73**, 1655 (2004).

Fig. 3 The localized orbitals and their indexing. The bond shown in the figure is one of the four along the body diagonals of the cubic cell. Like-numbered orbitals are inversion symmetric with respect to the bond center.

Table 4 Off-diagonal $(AB|W|AC)$ matrix elements and the corresponding difference of the diagonal elements $\Delta = (AB|H|AB) - (AC|H|AC)$ in Kelvin.

A B C	$(AB\|W\|AC)$	Δ	A B C	$(AB\|W\|AC)$	Δ	A B C	$(AB\|W\|AC)$	Δ
1 1 5	63	200	1 3 5	53	177	3 1 5	51	214
1 1 6	39	207	1 3 6	38	184	3 1 6	45	217
1 1 7	10	201	1 3 7	47	178	3 1 7	45	217
1 1 8	10	201	1 3 8	47	178	3 1 8	45	217
1 1 9	20	200	1 3 9	17	177	3 1 9	60	222
1 1 10	49	211	1 3 10	46	188	3 1 10	37	220
1 1 11	31	219	1 3 11	33	195	3 1 11	3	335
1 1 12	49	212	1 3 12	18	189	3 1 12	16	147
1 1 13	42	215	1 3 13	24	192	3 1 13	3	246
1 1 14	31	184	1 3 14	51	160	3 1 14	12	371
1 1 15	26	269	1 3 15	24	247	3 1 15	24	181
1 1 16	32	225	1 3 16	21	202	3 1 16	41	186
1 1 17	28	235	1 3 17	27	212	3 1 17	24	248
1 1 18	20	263	1 3 18	17	240	3 1 18	28	157
1 1 19	26	197	1 3 19	27	174	3 1 19	22	310
1 1 20	25	230	1 3 20	26	223	3 1 20	8	297

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