

KOs₂O₆: Superconducting rattler

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Abstract

Electronic structure calculations and experimental data point to soft local vibrations of alkali ions in AOs₂O₆ (A = K, Rb, Cs). Due to its size the potassium ion experiences an extremely anharmonic and broad potential well. We use ab initio energies and forces to derive the Hamiltonian for the dynamics of K ions and solve the single site problem.

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The recently discovered osmate superconductors AOs₂O₆ (AOsO) [1–3] provide an interesting puzzle. Depending on the alkali element (K, Rb or Cs) their transport and thermodynamic properties differ significantly, while their crystallographic and electronic structures are essentially the same [4,5]. The pyrochlore-lattice-based structure which can potentially support magnetic frustration has originally attracted attention to the AOsO group. Discovery of 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) attracted both experimental and theoretical interest. Specific heat measurements [6,7] found a large enhancement of the linear specific heat coefficient over the bandstructure values (about 4 in ROsO and COsO and as large as 12 in KOsO). Recent density functional calculations [5] showed that the alkali ions are only weakly bound inside truncated-tetrahedral cavities of the pyrochlore lattice and that the effective potential that they experience is sensitive to the ionic radii. In particular, the K radius allows for excursion as large as 1 Å.

Using ab initio energies and forces [8] we have constructed an effective Hamiltonian for K dynamics

consisting of the on-site term and nearest-neighbor interaction. Here, we focus on the single site problem and discuss the interaction elsewhere. The alkali ions form a diamond lattice, where each site has a tetrahedral symmetry which allows the potential to be expanded as a sum of selected s, f, g, i, \dots spherical harmonics. We consider only the lowest even (s) and odd (f) spherical harmonics and approximate the on-site Hamiltonian with

$$\hat{H} = \frac{p^2}{2M} + P_e(\xi) + P_o(\xi)\mathcal{Y}_{32}(\hat{\xi}), \quad (1)$$

where ξ is the displacement of K ion. P_e and P_o are polynomial radial functions obtained by fitting the ab initio total energies as a function of displacements of single K ion along (1 1 1) direction with a polynomial and taking its odd and even part.

To find the lowest eigenstates of Hamiltonian (1) we have performed a constrained minimization on a $101 \times 101 \times 101$ uniform grid inside a cube with a side of $4a_0$. The potential as well as the lowest 20 eigenvalues are shown in Fig. 1. Notably the potential well does not have a single minimum at its center, but four symmetry-related minima. This is reflected in the spectrum has a quasi-four-fold degenerate ground state, spanned by orbitals located at the four minima, separated by about 25 K from higher energy states. Hopping between the four potential minima lifts the degeneracy by singlet–triplet splitting of about 8 K. The orbitals corresponding to four lowest eigenvalues are shown in Fig. 2.

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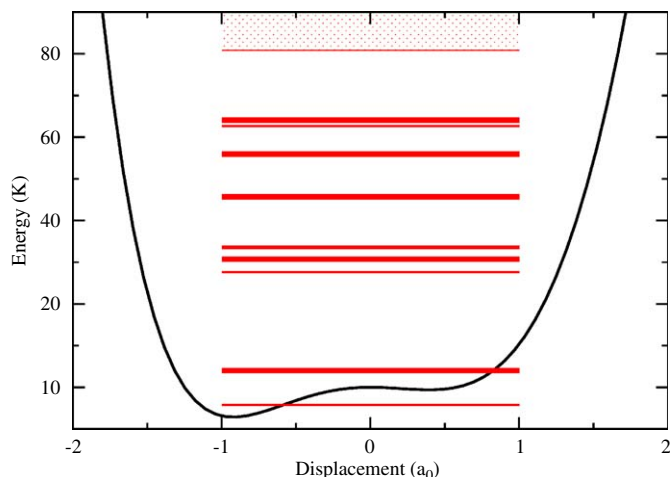


Fig. 1. Single site potential for K ion along (111) direction with the energy levels depicted by horizontal lines. Thickness reflects the degeneracy (from 1 to 3).

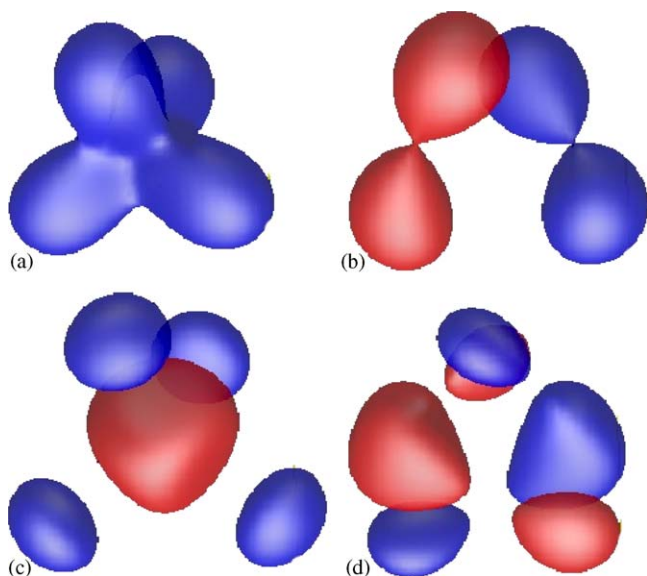


Fig. 2. The lowest energy orbitals: ground state singlet (a) and triplet (b) (only one orbital shown), and excited singlet (c) and triplet (d) (only one representative shown).

Significant deviation of the site potential from quadratic form brings several qualitative differences from a harmonic oscillator. The singlet–triplet split ground state separated by a large gap from the rest of the spectrum results in a Schottky anomaly in the specific heat (Fig. 3). The ground state built on off-center orbitals leads to increase of the mean square displacement $\langle \xi^2 \rangle$ (Debye–Waller factor) at low temperatures (Fig. 3).

Based on ab initio total energies we have found that the site potential for K ions allows for large excursion away from the central position. The single site low-energy dynamics is characterized by hopping between four

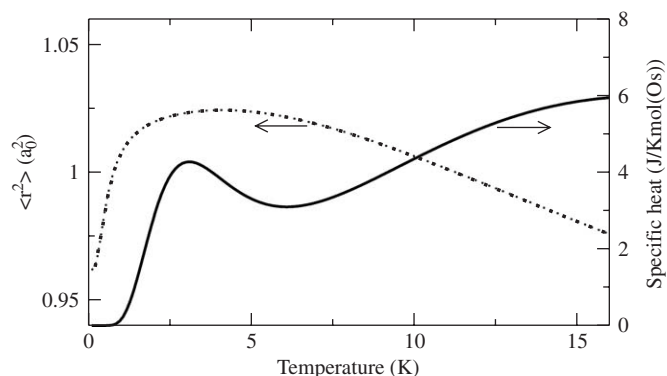


Fig. 3. The calculated specific heat and mean square displacement of K ion as a function of temperature.

off-center orbitals (rattling). However, the large excursions result in non-negligible dynamic coupling between nn K ions details of which will be published elsewhere. Narrower potential wells that restrict the displacements of larger alkali ions (Rb and Cs) reduce the dynamic coupling between sites and make the single site picture more appropriate. This is supported by lattice specific heat data [6] which can be fitted by Einstein oscillators. For the potassium system the single site limit provides an important starting point for investigation of the lattice dynamics. The energy scale of K dynamics (order of 1 K) suggests that the lattice does not freeze down to low temperatures and has to be taken into account in the interpretation of low temperature data.

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