A Possible Phase Transition in $\beta$-pyrochlore Compounds

Kazumasa HATTORI and Hirokazu TSUNETSUGU

Institute for Solid State Physics, University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa Chiba 277-8581, Japan

We investigate a lattice of interacting anharmonic oscillators by using a mean field theory and exact diagonalization. We construct an effective five-state hopping model with intersite repulsions as a model for $\beta$-pyrochlore AO$_2$O$_6$ (A=K, Rb or Cs). We obtain the first order phase transition line from large to small oscillation amplitudes as temperature decreases. We also discuss the possibility of a phase with amplitudes of order of 12 GHz. Key words: $\beta$-pyrochlore, anharmonic phonon

Recently, various unusual low-temperature properties of low-energy anharmonic phonons have attracted much attention. In $\beta$-pyrochlore compounds AO$_2$O$_6$ (A=K, Rb or Cs), low-energy anharmonic oscillations of A-ions are considered to play an important role for the realization of the unusual electrical resistivity and specific heat, strong coupling superconductivity and the nuclear magnetic relaxation time, especially in KO$_2$O$_6$. In these compounds, A-ions are located in large Os cages and form a diamond lattice structure. The cage opens in the four [111] directions, which are the bond directions of the diamond lattice, and it is expected that A-ion oscillations are anharmonic and have large amplitudes along these four directions. Since the atomic radius of K is the smallest among A-ions, the effects of anharmonicity are most prominent in KO$_2$O$_6$.

One of the most interesting phenomena in KO$_2$O$_6$ is the first order transition below the superconducting transition temperature $T_s$ = 9.6 K. The transition temperature $T_p$ = 7.5 K is robust upon applying magnetic fields up to 14 T. This suggests that the transition is driven by lattice degrees of freedom. Interestingly, it is found that, in the non-superconducting state under magnetic fields, the temperature ($T$) dependence of resistivity changes from an unusual $\sqrt{T}$ behavior to a $T^2$ dependence expected in the fermi liquid theory. Corresponding to this, the life time of quasiparticles becomes longer below $T_p$. The energy gap of the superconductivity observed in the photoemission spectroscopy also shows an anomaly at $T_p$. These experimental results suggest that quasiparticles are coupled to the lattice degrees of freedom leading to the first order transition.

As for the theories, it is proposed from the band structure calculation, that the effective potential of A-ion is shallow and even has a minimum at off-center positions, especially in KO$_2$O$_6$. Duhm and Ueda investigated the origin of the unusual temperature dependence of the resistivity and the saturation behavior of the NMR relaxation rate at high temperatures. As for the first order transition, Kuneš et al., proposed that it is multiple-q ordering of the potassium displacements. This scenario, however, contradicts the observations that symmetry is not broken below $T_p$ as various experiments show.

In this Letter, we extend the model used in Ref. 15 to include quantum hoppings by introducing five localized states of the ionic configurations. One of the five states is an on-center state and others are off-center ones. We analyze this model by using a mean field theory and exact diagonalization (ED) calculations. In our theory, the first order transition is characterized by the A-ion density at the on-center position, which is an order parameter in a sense of a liquid-gas transition. We will discuss implications of the present results for KO$_2$O$_6$ and physical consequences of this phase transition.

Before going into detailed calculations, we discuss the first order transition without symmetry breaking in KO$_2$O$_6$ from a phenomenological point of view. The local symmetry around A-ion is point group $T_d$ and local potential $V(r)$ of A-ion is approximated as $V(r) = a|\mathbf{r}|^2 + b\mathbf{r}\cdot\mathbf{z} + c|\mathbf{r}|^4 + c'(x^4 + y^4 + z^4) + O(|\mathbf{r}|^5)$, where $\mathbf{r} = (x, y, z)$ is the coordinates of A-ion from the on-center position of the diamond lattice. It is noted that the third order term $b\mathbf{r}\cdot\mathbf{z}$ can exist. Due to this term, $V(r)$ becomes shallow in the four [111] directions of the bonds in the diamond lattice. This makes s-wave ($\varphi_6$) and f-wave ($\varphi_{xyz}$) functions of oscillation states hybridized. Both of them belong to $A_1$ representation in $T_d$ point group. The one-body ground state $\Psi$ for the potential $V(r)$ is a linear combination of $\varphi_6$, $\varphi_{xyz}$ and other $A_1$ components: $\Psi = c_6\varphi_6 + c_{xyz}\varphi_{xyz} + \cdots$. The point is that $\Psi$ has inner degrees of freedom characterized by the coefficients $c_6$ and $c_{xyz}$, etc. These coefficients can vary without breaking any symmetry. In this Letter, we propose a minimal model to exhibit such variation as functions of $T$ and flatness of $V(r)$. When this variation becomes a sudden jump, the first order transition occurs. In this scenario, the $b$-term plays a more important role for anharmonicity and anisotropy than the fourth order terms. It is noted that this kind of transition is completely different in nature from classical structural transitions, which are described by the instability of some phonon modes.

Now, we introduce a minimal model to describe the phase transition at $T_p$ in KO$_2$O$_6$. We investigate a Hamiltonian of five localized states with inter-site repulsive interactions which are originated from Coulomb interactions between A- ions. The five localized states are one on-center ($\xi = 0$) and four off-center ($\xi = 1, 2, 3, 4$). We obtain the first order transition at $T_p = 7.5 K$. The transition temperature $T_p$ is robust upon applying magnetic fields up to 14 T. It is noted that this kind of transition is completely different in nature from classical structural transitions, which are described by the instability of some phonon modes.
and 4) states as shown in Fig. 1. These five states can describe two kinds of $A_1$ components: $\varphi_x$ and $\varphi_{xy}$, and also $p$-wave like components $\varphi_y$, ($i = x, y$ and z) which have the same symmetry $T_d$ as one-phonon states. The on-center state is located exactly at the diamond lattice site $\mathbf{x}_i = (x_i, y_i, z_i)$ where $i$ belonging to sublattice $\alpha(= A$ or $A \equiv B)$. Others are located at positions $\mathbf{x}_i + d_{\alpha \xi}$ shifted along the bond directions of the diamond lattice. We can regard that the parameter $|d_{\alpha \xi}|$ is implicitly included in parameters in our model Hamiltonian shown below. We note that $b$-term in $V(\mathbf{r})$ prefers wavefunctions having large weight in the bond directions, and thus Coulomb interactions for these wavefunctions become effectively large. These bases rather than phonon ones are expected to be a good starting point to discuss AOs$^2$O$_6$, since the local oscillations of A-ion is strongly anharmonic and large in the directions of the bonds especially for A=K. This choice of the bases corresponds to write $\Psi$ in the form of $c_\alpha \varphi_x + c_\alpha' \varphi_{xy}$. Here, $\varphi_x$ and $\varphi_{xy}$ correspond to the on-center state and a symmetric linear combination of off-center ones, respectively.

The Hamiltonian in this Letter is written as

$$H = \sum_{\alpha \xi \eta} \epsilon_\alpha \phi_{\alpha \xi \eta}^+ \phi_{\alpha \xi \eta} + \sum_{i j \alpha \beta \eta} U_{\alpha \beta} \phi_{i \alpha \eta} \phi_{j \beta \eta}, \quad (1)$$

where $\phi_{\alpha \xi \eta}^+$ represents a creation operator of the ionic state $|I\xi\eta\rangle$ localized at position $\xi$ on a site $i$ of sublattice $\alpha$ and $\eta_{\alpha \xi \eta} = \phi_{\alpha \xi \eta} \phi_{\beta \xi \eta}$. The five states labeled by $\xi$ and $\eta$ have hopping matrix elements $\epsilon_{\alpha \xi \eta}^\alpha$ with $\xi \neq \eta$ which represent the local quantum kinetic energy. We set $\epsilon_{\alpha \xi \eta}^\alpha = -t$ for $\xi \geq 1$ and $\epsilon_{\alpha \xi \eta}^\alpha = -t'$ for $\xi, \eta \geq 1$. For the low energy levels, we set $\epsilon_0^0 = 0$ and $\epsilon_{\alpha \xi \eta}^\alpha$ for $\xi \geq 1$. For the interaction terms, we use only the nearest neighbor Coulomb repulsion $U$ and the next nearest one $0 < U' < U$ as shown in Fig. 1 (b). This is because the screening by the electrons on the cage is not effective for these two terms because of the peculiar structure of the cage, but effective for others, and thus we neglect them.

First, we investigate this model by a mean field approximation (MFA) in the case that the translational symmetry is not broken. The mean field decoupling of the interactions leads the effective local energies $\epsilon_{\alpha \xi \eta}^\alpha = 4U'\langle n_\alpha \rangle$ and $\epsilon^\alpha = \epsilon + U(n_\alpha) + U'(n_{00})$, if the local symmetry $T_d$ is not broken. Here, $\langle \cdot \rangle$ denotes the thermal average and $\langle n_\alpha \rangle = \langle n_{00} \rangle$ with $\xi \geq 1$ and $\langle n_{00} \rangle = \langle n_{00} \rangle$. Now we can easily diagonalize the mean-field Hamiltonian, and show the eigenenergies and the eigenstates in Table I. There are two singlet $\langle A_1 \rangle$ and one triplet $\langle T_2 \rangle$ states.

The ground state $A_1^{(1)}$ is an in-phase combination of $\varphi_x$ and $\varphi_{xy}$, but the excited $A_1^{(2)}$ state is an out-of-phase one. Using these eigenstates, we calculate $\langle n_{00} \rangle = 1 - 4\langle n_\alpha \rangle$ such that the self-consistency is satisfied.

When we consider a symmetric phase with $\langle n_{00} \rangle = \langle n_{00} \rangle = n_0$ at $T = 0$, the self-consistency condition reads

$$2f(n_0) = \beta^{-1}(n_0) - \beta(n_0), \quad (2)$$

with $\beta(n_0) = (1 - n_0)/n_0$ and $f(n_0) = (\epsilon + U - U' - 3U + (2U' - U)/4)n_0)/4t$. A first order transition at $T = 0$ occurs if $U' - U/8 > 4t$ as $\epsilon$ is varied, since this condition is satisfied. Eq. (2) has three solutions. By using Eq. (2), the ground state energy per site $E_g$ is represented by the function of $n_0$ as $E_g = (U' - U/8)(1 - n_0)^2 - 2t\beta(n_0)$.

In Fig. 2, we show the mean field $\epsilon$-$T$ phase diagram for $U'/t = 0.6$, $U'/t = 0.5t$ and $t'/t = 0.4$ and 0.2. There are the first order transition line, and the second order transition to a symmetry broken phase (SBP). Between the two transitions, there is a region where $n_0$ remains $\sim 1/5$ down to $T = 0$ for $t'/t = 0.4$. In this region, the oscillation of A-ion becomes large and gains the kinetic energy rather than the potential energy. This intermediate region becomes smaller as $t'$ decreases and eventually the FE phase touches the first order transition line. When we increases $U$, the former is suppressed as understood from the $T = 0$ analysis above and becomes a crossover. On the other hand, the transition temperature to SBP is enhanced. This is because only $U$ enters in the self-consistent equation for SBP, and the other parameters are implicitly included in it through the energy levels.
First, we discuss the first order transition which is relevant to $\beta$-pyrochlore compounds, and then investigate the properties of SBP. Note that we consider the case of $\epsilon < 0$ is not realized in AOS$_2$O$_6$.

In Fig. 3 (a), the temperature dependence of $n_0$ is shown for various values of $\epsilon$. At high temperatures, the density $n_0$ is about 1/5. This means that the five positions are equally populated due to thermal fluctuations. As for the energy level, for $\epsilon = 0.8t$, $\epsilon_{T_2} - \epsilon_{A_4} \sim 3t$ and $\epsilon_{A_4} - \epsilon_{A_4} \sim 5t$ in the high temperature limit. In the case of large $\epsilon$, there is no discontinuous change but a smooth crossover to a large $n_0$ value with decreasing temperature. As $\epsilon$ decreases, the crossover becomes a jump, i.e., the first order transition. Just below the first order transition temperature $T_+^*$, $n_0$ suddenly increases in order to reduce the potential energy $\epsilon$ and the intersite repulsions. Consequently, $\epsilon_{T_2}$ increases below $T^*$. This means that the effective potential around the central position becomes steeper below $T^*$. This is understood by considering the $T = 0$ case. When $U - U/8 > 0$, which is automatically satisfied by that the first order transition at $T = 0$, $\epsilon_{T_2}$ increases as $n_0$ increases.

In Fig. 3 (b), we show the temperature dependence of the entropy. The entropy at high temperature approaches $\log 2$ per A-ion for $\epsilon/t \leq 1.4$, accompanying the first order transition. The released entropy becomes small as $\epsilon/t = 1.0$ and disappears at the critical end point $\epsilon \sim 1.4t$ and $T \sim 1.6t$ and also at $T^* \rightarrow 0$.

In the SBP, the average $\langle n_{A1} + n_{A2} - n_{A3} - n_{A4} \rangle = \langle n_{B3} + n_{B4} - n_{B1} - n_{B2} \rangle$ becomes finite uniformly. This means a finite polarization $P || [001]$, i.e., ferro-electric (FE) state. This phase is stabilized when $T_2$ states have a low excitation energy. This corresponds to small and/or negative $\epsilon$. The reentrant behavior as a function of temperature is due to the fact that the FE fluctuations arise from the excited $T_2$ states. It is noted that the FE state is six-fold degenerate ($P || \pm[100], \pm[010]$ and $\pm[001]$). For the three-dimensional six-state Potts model, it is known that the transition is the first order both from MFA and Monte Carlo simulations.$^{17}$ Our results of MFA is different from the result of MFA for the Potts model. This is because the symmetry $P \leftrightarrow -P$ is present in this model.

We have examined all the possible uniform symmetry broken patterns in our MFA. The phase with uniform polarizations is the most stable one. For example, a phase where the $B$-sublattice polarization is antiparallel to the $A$-sublattice one is not realized, because of repulsive interactions. The energy of another FE phase with $P || [111]$ is slightly higher than that of $P || [001]$. When we consider an order with the wavevector $Q_z = (2\pi,0,0)$, the order parameter is $(n_{A1} + n_{A2} - n_{A3} - n_{A4}) = \langle n_{B2} + n_{B3} - n_{B1} - n_{B4} \rangle \neq 0$. This corresponds to polarization $P_A || [001]$ and $P_B || [010]$ in the two sublattices. This state is one of the twelve-fold degenerate states: $P_\alpha \rightarrow -P_\alpha, A \leftrightarrow B$ and $Q_x \rightarrow Q_y$ or $Q_z$. The energy of these states becomes lower than that of the FE state when long-range repulsions are included.

Next, in order to investigate the effect of fluctuations beyond the MFA, we carry out ED calculations of this model. We use the cubic unit cell which includes eight A-ions and retains the $T_d$ symmetry with periodic boundary conditions. Since there is no conserving quantities such as spin or charge as in electron systems, the ED in larger system size is difficult at present. However, we can see the effects of the fluctuations in this size.

The expectation value $n_{A0} \equiv n_{0g}$ in the ground state is shown in Fig. 4 (a) as functions of $U$ and $\epsilon$. Here, $n_{0g}$ is independent on the site indices. We find a sharp change of $n_{0g}$ for relatively larger $U$ than in the case of mean field results. This may be due to the effects of the quantum fluctuations and finite size. In this calculation, the sharp change of $n_{0g}(\epsilon)$ is due to the anti-crossing of the ground and the first excited state as shown in Fig. 4 (b). Since the off-diagonal elements of the Hamiltonian (1) are all non-positive, we can apply the Perron-Frobenius theorem and prove that the ground state is always unique. This means there is no level crossing for the ground state. We expect this anti-crossing becomes narrower with increasing the system size, and evolves into a first order transition in the infinite size limit.

The presence of SBP is also reflected in the structure of excited states. When $\epsilon$ is smaller than $\sim t$, the first excited states are nine-fold degenerate as shown in Fig. 4 (b). As discussed before, six $Q = 0$ states and twelve $Q \neq 0$ states are degenerate in the MFA. In this finite size cluster, these eighteen states are coupled and split into a few multiplets and the lowest excited multiplet has nine states. This unusual large degeneracy is due to the special topology of eight-ion cluster. Each A-sublattice site is connected to all $B$-sublattice sites, and vice versa, and the total symmetry turns out to be $S_4 \otimes S_4 \otimes Z_2$, where $S_4^2$ and $Z_2$ represent $S_4$ group for sublattice $\alpha$ and the permutation $A \leftrightarrow B$, respectively. This special

![Fig. 3. Temperature dependence of (a) $n_0$ and (b) entropy. $U = 6t, U' = 5t$ and $t'/t = 0.4$.](image)

![Fig. 4. (a) Occupation number $n_{0g}$ as functions of $U$ and $\epsilon$. (b) Energy eigenvalues of four low-energy multiplets. Numbers represent the degeneracy. $U/U' = 1.2$ and $t'/t = 0.4$.](image)
symmetry is broken in larger system sizes and it remains as an interesting question how the degeneracy is lifted.

The tendency of the first order transition from small to large $n_{0\epsilon}$ as $\epsilon$ increases, is consistent with the results of MFA and due to the quantum fluctuations, the transition occurs at larger $U$ and $U'$ than in the MFA. In order to conclude whether the intermediate region obtained in the MFA, i.e., the region $\epsilon \approx 0$ for $t'/t = 0.4$ in Fig. 2 exists or not, it is needed to carry out detailed analysis of the finite size scaling for the energy of excited states.

As we discussed above, this model shows the first order transition at $T^*$ below which the on-center density suddenly increases. We believe that this corresponds to the first order transition at $T_p$ in KO$_2$O$_6$. Since anharmonicity for Rb and Cs compounds is weaker than that for K, we can regard that the cases for Rb and Cs correspond to the larger $\epsilon$ region in the phase diagram where there is no transition but a smooth crossover. The fact that this transition does not break any symmetries is consistent with experimental results. Recently, Yamaura et al. observed that the charge distributions of potassium shrinks below $T_p$ by the neutron experiments in KO$_2$O$_6$. This corresponds to the increase of $n_0$. In addition to this, the suppression of the quasiparticle $\epsilon$ in the case of shallow potentials. Since the potential in KO$_2$O$_6$ is expected to be the shallowest in three compounds of AO$_2$O$_6$ ($A=$K, Rb, and Cs), this explains why only KO$_2$O$_6$ shows the first order transition.

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