Anomalous Isotope Effect in Rattling-Induced Superconductor

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In order to clarify that the Cooper pair in $\beta$-pyrochlore oxides is mediated by anharmonic oscillation of guest atom, i.e., rattling, we propose an experiment to detect anomalous isotope effect. In the formula of $T_c \propto M^{-\eta}$, where $T_c$ is superconducting transition temperature and $M$ denotes mass of the oscillator, it is found that the exponent $\eta$ is increased with the increase of anharmonicity of a potential for the guest atom. We predict that $\eta$ becomes larger than 1/2 in rattling-induced superconductor, in sharp contrast to $\eta = 1/2$ for weak-coupling superconductivity due to harmonic phonons and $\eta < 1/2$ for strong-coupling superconductivity with the inclusion of the effect of Coulomb interaction.

KEYWORDS: Isotope effect, rattling, superconductivity, $\beta$-pyrochlore

1. Introduction

Recently, exotic magnetism and novel superconductivity have attracted much attention in the research field of condensed matter physics. In particular, strongly correlated electron systems with cage structure have been focused both from experimental and theoretical viewpoints. In such cage-structure materials, a guest atom contained in the cage feels a highly anharmonic potential and it oscillates with relatively large amplitude in comparison with that of the lattice vibration in metals. Such oscillation of the atom in the cage is called rattling, which is considered to be an origin of interesting physical properties of cage-structure compounds.

Among several interesting phenomena in cage-structure materials, since the discovery of superconductivity with relatively high superconducting transition temperature $T_c$ in $\beta$-pyrochlore oxides AOS$_2$O$_6$ (A = K, Rb, and Cs), phonon-mediated superconductivity has attracted renewed attention from the viewpoint of anharmonicity. It has been observed that $T_c$ increases with the decrease of radius of A ion: $T_c$=9.6K for A=K, $T_c$=6.4K for A=Rb, and $T_c$=3.25K for A=Cs. The difference in $T_c$ has been considered to originate from the anharmonic oscillation of A ion. In fact, the anharmonicity of the potential for A ion has been found to be enhanced, when we change A ion in the order of Cs, Rb, and K due to the first-principles calculations.

As for the mechanism of superconductivity in $\beta$-pyrochlore oxides, theoretical investigations have been done. Hattori and Tsunetsugu have investigated a realistic model including three dimensional anharmonic phonons with tetrahedral symmetry and have confirmed that $T_c$ is strongly enhanced with increasing the third-order anharmonicity of the potential. Chang et al. have discussed the superconductivity by using the strong-coupling approach in the anharmonic phonon model including fourth-order terms. The present authors have revealed the anharmonicity-controlled strong-coupling tendency for superconductivity induced by rattling from the analysis of the anharmonic Holstein model in the strong-coupling theory.

From these experimental and theoretical efforts, it has been gradually recognized that the superconductivity in $\beta$-pyrochlore oxides is induced by anharmonic oscillation of alkali atom contained in a cage composed of oxygen and os-
effect is certainly the anharmonicity of potential, leading to the conclusion that $\eta > 1/2$ can be the evidence of superconductivity induced by anharmonic phonons. We propose an experiment on the isotope effect in order to clarify a key role of rattling in $\beta$-pyroclore oxides.

The organization of this paper is as follows. In Sec. 2, we show the anharmonic Holstein Hamiltonian and explain the model potential for anharmonic oscillation. We also provide the brief explanation of the formulation of the Migdal-Eliashberg theory to evaluate superconducting transition temperature $T_c$. In Sec. 3, we exhibit our calculated results on $T_c$ and the values of $\eta$. We also discuss $T_c$ and $\eta$ on the basis of the McMillan formula. It is emphasized that the anomalous value of $\eta$ larger than 1/2 certainly originates from the anharmonicity. Finally, in Sec. 4, we briefly discuss the effect of the Coulomb interaction on $\eta$ and summarize this paper. Throughout this paper, we use such units as $\hbar = k_B = 1$.

2. Model and Formulation

2.1 Anharmonic Holstein model

In this paper, we consider the Holstein model in which conduction electrons are coupled with anharmonic local oscillations. The model is given by

$$H = \sum_{k, \sigma} \varepsilon_k c_{k \sigma}^\dagger c_{k \sigma} + \sum_i [H_i^{(1)} + H_i^{(2)}],$$

(1)

where $k$ is momentum of electron, $\varepsilon_k$ denotes the energy of conduction electron, $\sigma$ is an electron spin, $c_{k \sigma}$ is an annihilation operator of electron with $k$ and $\sigma$, and $i$ denotes atomic site. Throughout this paper, we consider half-filling case and the electron bandwidth $W$ is set as unity for an energy unit.

In eq. (1), $H_i^{(1)}$ and $H_i^{(2)}$, respectively, denote electron-vibration coupling and vibration terms at site $i$, expressed by

$$H_i^{(1)} = gQ_i \rho_i,$$

(2)

and

$$H_i^{(2)} = P_i^2 / (2M) + V(Q_i),$$

(3)

where $g$ is electron-vibration coupling constant, $\rho_i$ denotes local charge density given by $\rho_i = \sum_{\sigma} c_{i \sigma}^\dagger c_{i \sigma}$, $c_{i \sigma}$ is an annihilation operator of electron at site $i$, $Q_i$ is normal coordinate of the oscillator, $P_i$ indicates the corresponding canonical momentum, $M$ is mass of the oscillator, and $V$ denotes an anharmonic potential for the oscillator, given by

$$V(Q_i) = k Q_i^2 / 2 + k_4 Q_i^4 + k_6 Q_i^6.$$  

(4)

Here $k$ denotes a spring constant, while $k_4$ and $k_6$ are the coefficients for fourth- and sixth-order anharmonic terms, respectively.

Let us provide a comment on the present potential $V(Q_i)$ composed of second-, fourth-, and sixth-order terms. It may be possible to prepare a simpler anharmonic potential with negative second-order coefficient and positive $k_4$, but we intend to use the potential with positive second-order coefficient, since it seems to be natural to consider that the spring constant is taken to be positive in the oscillation problem. Then, in order to prepare the symmetric potential which has a wide and flat region in the bottom, we set negative $k_4$ and positive $k_6$ in the model potential. For the case of $k_4 = k_6 = 0$, we immediately obtain the harmonic potential. We believe that the present model is useful for the purpose to grasp easily the effect of anharmonicity in comparison with the results of the harmonic potential. Note, however, that it is necessary to pay our attention to the artificial aspects of the present model potential.

Now we define the phonon annihilation operator $a_i$ at site $i$ through the relation of $Q_i = (a_i^\dagger + a_i)/\sqrt{2M\omega}$, where $\omega$ denotes the energy of oscillation, given by $\omega = \sqrt{k/M}$. Then, we rewrite eqs. (2) and (3), respectively, as

$$H_i^{(1)} = \sqrt{\alpha\omega}(a_i + a_i^\dagger)\rho_i,$$

(5)

and

$$H_i^{(2)} = \omega[a_i a_i^\dagger + 1/2 + \beta(a_i + a_i^\dagger)^4 + \gamma(a_i + a_i^\dagger)^6],$$

(6)

where $\alpha$ is non-dimensional electron-phonon coupling constant, defined by

$$\alpha = g^2 / (2M\omega^3),$$

(7)

and $\beta$ and $\gamma$ are non-dimensional fourth- and sixth-order anharmonic parameters, given by

$$\beta = k_4 / (4M^2\omega^3), \quad \gamma = k_6 / (8M^3\omega^4).$$

(8)

With the use of non-dimensional parameters $\alpha$, $\beta$, and $\gamma$, it is convenient to rewrite the potential $V$ as

$$V(q_i) = \omega_0 q_i^2 + 16\alpha \beta q_i^4 + 64\alpha^2 \gamma q_i^6,$$

(9)

where $q_i$ is non-dimensional displacement defined by $q_i = Q_i / \ell$ and the length scale $\ell$ is given by $\ell = \sqrt{2\epsilon/(M\omega)}$.

2.2 Dependence of parameters on oscillator mass

In order to discuss the isotope effect on $T_c$, let us define the $M$ dependence of parameters. It is well known that $\omega$ is in proportion to $M^{-1/2}$ from $\omega = \sqrt{k/M}$, when we assume that the spring constant $k$ does not depend on $M$. If we further assume that $g$ is independent of $M$, we obtain $\alpha \propto M^{1/2}$. Concerning anharmonicity parameters $\beta$ and $\gamma$, we obtain the relations of $\beta \propto M^{-1/2}$ and $\gamma \propto M^{-1}$ by further assuming that $k_4$ and $k_6$ are independent of $M$. We define $m$ as the mass ratio of the guest atom due to the replacement by the isotope. Then, we obtain $m$ dependence of parameters as

$$\omega = \omega_0 \sqrt{m}, \quad \alpha = \alpha_0 \sqrt{m}, \quad \beta = \beta_0 / \sqrt{m}, \quad \gamma = \gamma_0 / m,$$

(10)

where the subscript “0” denotes the quantity before we consider the change of the oscillator mass. Note that the length scale $\ell$ does not depend on $m$.

For the discussion of $T_c$, we define an electron-phonon coupling constant $\lambda$. In general, we cannot obtain $\lambda$ analytically for anharmonic phonons, but for the case of harmonic phonons ($\beta_0 = \gamma_0 = 0$), we simply obtain $\lambda \propto 2\alpha\omega / W$ with electron bandwidth $W$. As easily understood from the $m$ dependence of parameters, $\lambda$ for harmonic phonons does not depend on $M$. Thus, as a quantity to indicate the strength of electron-phonon coupling for superconductivity, it is useful to define $\lambda_0$ as

$$\lambda_0 = 2\alpha_0\omega_0 / W.$$  

(11)

Here we discuss the shape of the anharmonic potentials considered in this paper. As already mentioned in our previous papers, the potential shapes are classified into three
condition. As for electron-phonon coupling constant note that the potential shapes are independent of paper self-contained, in this subsection, we briefly explain the ory for superconductivity in the anharmonic Holstein model 2.3 Migdal-Eliashberg formalism this paper, we set

\[ T_n = \frac{1}{\beta} \left( \omega_n - \varepsilon_k - \Sigma(i\omega_n) \right) \]  

Here \( \Sigma(i\omega_n) \) is normal electron self-energy. In the second-order perturbation theory in terms of \( g, \Sigma \) is expressed as

\[ \Sigma(i\omega_n) = -\alpha g^2 T \sum_{n'k'} D_0(i\omega_n - i\omega_{n'}) G(K', i\omega_{n'}) \]  

Since we consider Einstein-type local phonon, the site dependence of \( D_0 \) does not appear and in the adiabatic approximation, electron self-energy does not depend on momentum.

Concerning the phonon Green’s function of the anharmonic phonon system, we use \( D_0 \) instead of dressed phonon Green’s function by ignoring the phonon self-energy effect. In the spectral representation, \( D_0 \) is given by

\[ D_0(i\nu_n) = \frac{\rho_{ph}(\Omega)}{i\nu_n - \Omega} d\Omega, \]

where \( \nu_n \) is the boson Matsubara frequency defined by \( \nu_n = 2n\pi T \), and \( \rho_{ph}(\Omega) \) is phonon spectral function, given by

\[ \rho_{ph}(\Omega) = \sum_{K,L} A_{K,L} \delta(\Omega + E_K - E_L). \]

Here \( E_K \) is the \( K \)-th eigenenergy of \( H_1^{(2)} \) and the spectral weight \( A_{K,L} \) is given by

\[ A_{K,L} = \frac{1}{Z} \left| e^{-E_K/T} - e^{-E_L/T} \right| [K]|q_i + q_i'|L|^2, \]

where \( |K\) is the \( K \)-th eigenstate of \( H_1^{(2)} \) and \( Z \) is the partition function, given by \( Z = \sum_K e^{-E_K/T} \).

In order to obtain \( T_c \), first we calculate the normal self-energy \( \Sigma \) by solving eqs. (15) and (16) in a self-consistent manner. Next we solve the gap equation eqs. (13) and (14) by using \( G \) in eq. (15). Then, we obtain \( T_c \) as a temperature at which the positive maximum eigenvalue of eq. (13) becomes unity. In actual calculations, we assume the electron density of states \( 1/W \) with rectangular shape of the electron bandwidth \( W \). Note here that \( W \) is taken as the energy unit \( W = 1 \) in this paper. For the sum on the imaginary axis, we use 32768 Matsubara frequencies. Note also that we safely calculate \( T_c \) larger than 0.001 for this number of Matsubara frequencies. In order to accelerate the sum of large amount of Matsubara frequencies in eqs. (13) and (16), we exploit the fast-Fourier-transformation algorithm. For the evaluation of the eigenvalue of the gap equation eq. (13), we use the power method. Note again that we set \( \omega_0 = 0.05 \) and \( \lambda_0 = 2\alpha_0 \omega_0 / W = 0.5 \) in the calculations.

3. Calculated Results

3.1 Superconducting transition temperature

Before proceeding to the discussion on the isotope effect, we exhibit the results on the superconducting transition temperature \( T_c \) for the case of \( m = 1 \). In Fig. 2(a), we depict \( T_c \) vs. \( \beta_0' \) by open symbols for \( \gamma_0 = 10^{-2}, 10^{-4}, \) and \( 10^{-3} \).

Note that sixth-order anharmonicity is the largest in the case of \( \gamma_0 = 10^{-3} \), since it increases with the increase of \( \gamma_0 \). Among the three curves for \( T_c \), for \( \gamma_0 = 10^{-4} \) and \( 10^{-3} \), it is found that \( T_c \) increases with the decrease of \( \beta_0' \) in the range of \( \beta_0' > -1 \) and it turns to be decreased at \( \beta_0' = -1 \). Namely, the curve for \( T_c \) forms a peak structure around at \( \beta_0' = -1 \).
by $\omega_{\text{log}} = \exp((\log \Omega))$, where $(\log \Omega)$ is given by

$$
(\log \Omega) = \frac{\lambda \omega}{\lambda_{\text{eff}}} \int_{\Omega}^{\infty} \rho_{\text{ph}}(\Omega) \frac{d\Omega}{\Omega}.
$$

Note that $\omega_{\text{log}}$ and $\lambda_{\text{eff}}$ depend on $T$, since $\rho_{\text{ph}}(\Omega)$ includes the Boltzmann factor. Namely, eq. (20) becomes the self-consistent equation for $T_c$. Thus, we define $T_{c}^{\text{Me}}$ as a temperature at which the left- and right-hand terms of eq. (20) are equal to each other.

In Fig. 2(a), we depict $T_{c}^{\text{Mc}}$ as functions of $\beta'_0$ for $\gamma_0 = 10^{-5}$, $10^{-4}$, and $10^{-3}$. For small $\gamma_0$ such as $\gamma_0 = 10^{-5}$, it is difficult to perform the self-consistent calculation of $T_{c}^{\text{Me}}$ in the vicinity of $\beta'_0 = -1.0$, when $T_{c}^{\text{Me}}$ becomes very low. However, for $\gamma_0 = 10^{-5}$ and $10^{-4}$, it is found that in the wide range of $\beta'_0$, $T_{c}^{\text{Me}}$ well reproduces $T_c$ obtained by the Eliashberg equation. For $\gamma_0 = 10^{-3}$, $T_{c}^{\text{Me}}$ is similar to the solution of the Eliashberg equation in the region of $\beta'_0 > -0.8$, while in $\beta'_0 < -0.8$, the magnitude of $T_{c}^{\text{Me}}$ is different from that of $T_c$, although $T_{c}^{\text{Me}}$ qualitatively exhibits the behavior with the peak formation in $T_c$.

In Figs. 2(b) and 2(c), we show $\omega_{\text{log}}$ and $\lambda_{\text{eff}}$ at $T = T_{c}^{\text{Me}}$. For harmonic phonons, we obtain $\omega_{\text{log}} = \omega$ and $\lambda_{\text{eff}} = \lambda_0$ from the spectral function of $\rho_{\text{ph}}(\Omega) = \pm \delta(\Omega \mp \omega)$. For $\gamma_0 = 10^{-5}$ and $10^{-4}$, $\omega_{\text{log}}$ is almost equal to $\omega(= 0.05)$ in the range of $\beta'_0 > -0.2$. We also observe $\lambda_{\text{eff}} \approx \lambda_0(= 0.5)$ in the same range of $\beta'_0$. It is considered that the guest ion exhibits the harmonic oscillation around at the origin of the potential. Since $\omega_{\text{log}}$ and $\lambda_{\text{eff}}$ moderately deviate from $\omega$ and $\lambda$, respectively, for $-1.0 < \beta'_0 < -0.2$, anharmonicity slightly affects them and $T_c$ slowly increases with the decrease of $\beta'_0$. For $\beta'_0 < -1.0$, since the decrease of $\omega_{\text{log}}$ and the increase of $\lambda_{\text{eff}}$ are very rapid, it is considered that $T_c$ rapidly decreases. Note that for $\gamma_0 = 10^{-5}$, it is difficult to obtain reliable solutions of eq. (20) with eqs. (21) and (22) at $\beta'_0 \approx -1.0$, since $\lambda_{\text{eff}}$ and $\omega_{\text{log}}$ depend so sensitively on $\beta'_0$ at the region.

For $\gamma_0 = 10^{-3}$, $\omega_{\text{log}}$ and $\lambda_{\text{eff}}$ are significantly different from harmonic results for the wide region of $\beta'_0$, since the dependence of eigenenergies on $\beta'_0$ is rather different from that of harmonic phonons for large $\gamma$. We observe that the value of $T_c$ changes in the wide region of $\beta'_0$ for $\gamma_0 = 10^{-3}$. With the decrease of $\beta'_0$, $\omega_{\text{log}}$ decreases and $\lambda_{\text{eff}}$ increases monotonically. It is understood that the peak of $T_c$ is formed due to the competition of decreasing $\omega_{\text{log}}$ and increasing $\lambda_{\text{eff}}$.

### 3.2 Exponent of the isotope effect

Now we consider the exponent $\eta$ of the isotope effect, which is evaluated by

$$
\eta = -\frac{d \log T_c}{d \log m}.
$$

Since we cannot analytically calculate $\eta$, the derivative in eq. (23) is approximated by the differentiation in terms of $m$. Namely, $d \log T_c / d \log m$ is numerically estimated as

$$
\frac{d \log T_c}{d \log m} = \frac{\log T_c(m = 1.01) - \log T_c(m = 1)}{\log 1.01}.
$$

where $T_c(m)$ denotes $T_c$ for the case of mass ratio $m$.

In Fig. 3, we depict $\eta$ vs. $\beta'_0$ by open symbols for $\gamma_0 = 10^{-5}$, $10^{-4}$, and $10^{-3}$. For $\gamma_0 = 10^{-5}$ and $10^{-4}$, at $\beta'_0 = 0$, $\eta$ is almost equal to $1/2$ which is the value for harmonic phonons. These results seem to be natural, when we recall that the effect

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**The maximum value of $T_c$ depends on $\gamma_0$. In our previous work, the highest $T_c$ has been found for $\gamma_0 = 10^{-3}$.** For the case of $\gamma_0 = 10^{-5}$, we also observe that $T_c$ increases with the decrease of $\beta'_0$ in the range of $\beta'_0 > -1$, but the rate of the increase is very slow.

Note that for small $\gamma_0$, it is found that $T_c$ suddenly decreases at $\beta'_0 = -1.0$, because $T_c$ is strongly influenced by the change of the anharmonic potential from rattling- to off-center type, as observed in Fig. 1. The calculation of $T_c$ in the present approximation is not considered to be valid for the off-center type potential, since double degeneracy in the phonon energy affects seriously on the low-energy electron states. This point will be discussed later again in Sec. 4, but in any case, the extension of the calculation to the off-center type potential is one of our future problems.

In order to understand the formation of the peak in $T_c$, we consider the McMillan formula. The McMillan formula of $T_c$ which we should analyze is given by

$$
T_{c}^{\text{Me}} = \frac{\omega_{\text{log}}}{1.20} \exp \left( -\frac{1 + \lambda_{\text{eff}}}{\lambda_{\text{eff}}} \right),
$$

where the effective Coulomb interaction is simply ignored in the present calculations, but this point will be also discussed later in Sec. 4. Note that we replace a numerical factor 1.04 in front of $1 + \lambda_{\text{eff}}$ in the original formula with the unity by following Allen and Dyne. Here $\lambda_{\text{eff}}$ indicates the effective electron-phonon coupling constant, given by

$$
\lambda_{\text{eff}} = \frac{\lambda \omega}{2} \int_{-\infty}^{\infty} \rho_{\text{ph}}(\Omega) \frac{d\Omega}{\Omega},
$$

and $\omega_{\text{log}}$ indicates the characteristic phonon energy defined

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**Fig. 2.** (Color online) (a) Superconducting transition temperature $T_c$ vs. $\beta'_0$ for $\gamma_0=10^{-5}$, $10^{-4}$, and $10^{-3}$. Curves indicate $T_c$ calculated by the McMillan formula. (b) Characteristic phonon energy $\omega_{\text{log}}$ vs. $\beta'_0$. (c) Effective electron-phonon coupling constant $\lambda_{\text{eff}}$ vs. $\beta'_0$.**
of anharmonicity is weak at $\beta_0' = 0$, as observed in Fig. 1 for the potential shape. When $\beta_0'$ is decreased, $\eta$ slowly increases in the range of $\beta_0' > -1$ and it rapidly increases in the region of the off-center type potential. For $\gamma_0 = 10^{-3}$, $\eta$ is less than 1/2 in the range of $0 > \beta_0' > -0.5$. However, $\eta$ is larger than 1/2 for $\beta_0' < -0.5$ and it also rapidly increases in region of the off-center type potential through the broad peak around at $\beta_0' \sim -0.8$.

In order to clarify the origin of $\eta$ larger than 1/2, we decompose $\eta$ into four parts as

$$\eta' = \eta_\alpha + \eta_\omega + \eta_\beta + \eta_\gamma,$$  

(25)

where $\eta_\alpha$, $\eta_\omega$, $\eta_\beta$, and $\eta_\gamma$ are given by

$$\eta_\alpha = -\frac{\partial \log \alpha}{\partial \log m} \frac{\partial \log T_c}{\partial \log \alpha} = -\frac{1}{2} \frac{\partial \log T_c}{\partial \log \alpha},$$

$$\eta_\omega = -\frac{\partial \log \omega}{\partial \log m} \frac{\partial \log T_c}{\partial \log \omega} = \frac{1}{2} \frac{\partial \log T_c}{\partial \log \omega},$$

$$\eta_\beta = -\frac{\partial \log \beta}{\partial \log m} \frac{\partial \log T_c}{\partial \log \beta} = \frac{1}{2} \frac{\partial \log T_c}{\partial \log \beta},$$

$$\eta_\gamma = -\frac{\partial \log \gamma}{\partial \log m} \frac{\partial \log T_c}{\partial \log \gamma} = \frac{1}{2} \frac{\partial \log T_c}{\partial \log \gamma},$$

(26)

respectively. Note that we consider $\alpha$, $\omega$, $\beta$, and $\gamma$ as variables of $T_c$ and $\eta$. In order to distinguish $\eta'$ of eq. (23) and eq. (25), we use the notation of $\eta'$ in eq. (25).

It is instructive to evaluate eq. (25) for the case of harmonic phonons. By calculating eqs. (26) with the use of eq. (20) for the harmonic case, we obtain

$$\eta_\alpha = 1/2 - \eta_\omega = -1/(2\lambda_0), \quad \eta_\beta = \eta_\gamma = 0.$$  

(27)

Thus, irrespective of the value of $\lambda_0$, we obtain $\eta_\alpha + \eta_\omega = 1/2$, which is just the exponent of the normal isotope effect.

As for the evaluation of eqs. (26) for anharmonic phonons, each derivative is also approximated by the differentiation. Then, we numerically estimate $\partial \log T_c/\partial \log x$ as

$$\frac{\partial \log T_c}{\partial \log x} = \frac{\log T_c(x + \Delta x) - \log T_c(x)}{\log(x + \Delta x) - \log x},$$

(28)

where $T_c(x)$ indicates $T_c$ as a function of $x$, $\Delta x$ indicates small deviation of $x$, and $x$ denotes the variable among $\alpha$, $\omega$, $\beta$, and $\gamma$. In order to obtain enough precision of the numerical differentiation, we choose $\Delta x/x = 0.1\% \sim 0.001\%$. At $\beta_0' \sim -1$, we set $\Delta x/x = 0.001\%$ for $\gamma_0 = 10^{-4}$, but it is difficult to obtain reliable values for $\beta_0' < -1$. For $\gamma_0 = 10^{-5}$, it is also difficult to evaluate $\eta$ with enough precision for $\beta_0' \leq -1$, even if we set $\Delta x/x = 0.001\%$. In Fig. 3, we depict $\eta'$ by curves on the open symbols of $\eta$ for $\gamma_0 = 10^{-5}$, $10^{-4}$, and $10^{-3}$. Note that for $\gamma_0 \leq 10^{-3}$, we do not show the curves in the region of $\beta_0' \leq -1.0$, since we could not evaluate each term of eqs. (26) with enough precision. At $\beta_0' \sim -1$, since $\eta_\beta$ and $\eta_\gamma$ are very sensitive for anharmonicity, evaluation is difficult. However, it is considered that $\eta'$ agrees well with $\eta$ within the numerical error-bands.

In Figs. 4(a)-4(d), we show $\eta_\alpha$, $\eta_\beta$, $\eta_\omega$, and $\eta_\gamma$, respectively, as functions of $\beta_0'$. In Figs. 4(e) and 4(f), we depict $\eta_\beta + \eta_\gamma$ vs. $\eta_\omega$ and $\eta_\beta + \eta_\gamma$, respectively. In addition, we also show the parts of $\eta'$ evaluated from the McMillan formula of $T_c$ by broken curves in Figs. 4(a)-4(f). We observe that each term of the exponent $\eta'$ evaluated from the McMillan formula reproduces well the corresponding result of the Eliashberg equation. Thus, it is possible to discuss the behavior of $\eta$ and $\eta'$ on the basis of the McMillan formula.

In Figs. 4(a) and 4(c), $\eta_\alpha$ and $\eta_\omega$ are shown. At $\beta_0' = 0$, we find $\eta_\alpha \approx -1$ and $\eta_\omega \approx 1.5$, which are the values for the harmonic phonons with $\lambda_0 = 0.5$. With the decrease of...
$\beta'_0$, $\eta_\alpha$ increases and $\eta_\omega$ decreases due to the effect of anharmonicity, but the sum of $\eta_\alpha + \eta_\omega$ is still almost 0.5 for the wide range of $\beta'_0$, as observed in Fig. 4(c). Namely, as long as the anharmonicity is not so strong, the exponent 1/2 of the normal isotope effect originates from $\eta_\alpha + \eta_\omega$ even for the anharmonic potentials.

In Figs. 4(b) and 4(d), we depict $\eta_\beta$ and $\eta_\gamma$. They are almost zero at $\beta'_0 = 0$, when anharmonicity is weak. With the decrease of $\beta'_0$, $\eta_\beta$ increases and $\eta_\gamma$ decreases. Note that $\beta$ plays a role to expand the width of anharmonic potential, as observed in Fig. 1. Thus, $\eta$ is enhanced with the increase of the amplitude of the guest ion for $\beta'_0 > -1.0$. For $\beta'_0 < -1.0$, since the potential shape is suddenly changed to the off-center type, $\eta_\gamma$ is also suddenly changed, but we are not interested in such behavior at the present stage. On the other hand, we note that $\gamma$ plays a role to reduce the width of anharmonic potential. The effect of $\gamma$ decreases the amplitude of the guest ion and it also decreases $\eta$ for $\beta'_0 > -1.0$.

In Fig. 4(f), we depict $\eta_\beta + \eta_\gamma$, which increases with the decrease of $\beta'_0$. At $\beta'_0 \sim 0$, since the fourth- and sixth-order anharmonicity are very small, $\eta_\beta + \eta_\gamma$ is almost zero. For $\gamma_0 = 10^{-3}$, the sixth-order anharmonicity is moderately strong and $\eta_\beta + \eta_\gamma$ slightly deviates from zero. The behavior of $\eta_\beta + \eta_\gamma$ is quite similar to that of $\eta - 1/2$. In short, it is found that $\eta_\alpha + \eta_\omega \approx 1/2$ and $\eta_\beta + \eta_\gamma$ determines the deviation of $\eta$ from 1/2. We consider that $\eta_\alpha + \eta_\omega$ represents the normal isotope effect of $\eta = 1/2$, while $\eta_\beta + \eta_\gamma$ indicates the effect of anharmonicity on the exponent of the isotope effect.

In Figs. 5(a)-5(d), we depict $\eta_\alpha + \eta_\omega$ and $\eta_\beta + \eta_\gamma$ for $\gamma_0 = 10^{-5}$ and $10^{-3}$. We again observe that $\eta_\alpha + \eta_\omega \approx 1/2$ and the behavior of $\eta_\beta + \eta_\gamma$ determines the deviation of $\eta$ from 1/2, except for the results in the vicinity of $\beta'_0 = -1.0$ for $\gamma_0 = 10^{-3}$. It is considered that $\eta > 1/2$ in the rattling-type potential is mainly caused by the anharmonicity.

Here we provide a comment on non-monotonic behavior of $\eta$ in Fig. 4 for $\gamma_0 = 10^{-3}$ and $-1.0 < \beta'_0 < -0.8$. Since $\eta_\alpha + \eta_\omega$ is almost equal to 1/2 even for the case of $\gamma_0 = 10^{-3}$, such non-monotonic behavior originates from the anharmonicity part $\eta_\beta + \eta_\gamma$, as observed in Fig. 5(d). Roughly speaking, we consider that the peak structure is formed by the competition of increasing $\eta_\beta$ and decreasing $\eta_\gamma$ when $\beta'_0$ is decreased. Note that we do not further pursue the origin of each behavior of $\eta_\beta$ and $\eta_\gamma$ at the present stage, since it will depend on the anharmonic potential. It is emphasized here that the behavior of $\eta_\beta + \eta_\gamma > 0$ characterizes the anomalous exponent $\eta > 1/2$ in the region of rattling-type potential.

4. Discussion and Summary

In this paper, we have evaluated the exponent $\eta$ of the isotope effect for rattling-induced superconductor in the strong-coupling analysis by solving the gap equation of the Migdal-Eliashberg theory. First, we have obtained that $\eta$ is larger than 1/2 due to the increase of anharmonicity in the region of the rattling-type potential. Next, we have investigated the origin of $\eta > 1/2$ by evaluating four parts of $\eta$ with the use of the chain rule of the derivative. It has been clearly shown that the deviation of $\eta$ from 1/2 is due to the anharmonicity. Then, we have considered that $\eta > 1/2$ can be the evidence of rattling-induced superconductor.

Here we discuss the reliability of the result in the off-center type potential with $\beta'_0 < -1.0$. For the purpose, we focus on the validity of the adiabatic approximation in such a region. We consider the adiabatic approximation as $\omega < W$, but in the present calculation, we have found that $\lambda_{\text{eff}}$ monotonically increases with the decrease of $\beta'_0$. The increase of $\lambda_{\text{eff}}$ indicates the strong-coupling tendency, leading to the reduction of the effective bandwidth $W^\star$. Namely, $W^\star$ decreases with the decrease of $\beta'_0$. Here we note that $\lambda_{\text{eff}}$ is rapidly enhanced in the off-center type potential region. Even if $W$ is much larger than the phonon energy $\omega$, $W^\star$ eventually becomes comparable with $\omega$, leading to the violation of the adiabatic condition in the off-center type potential region. Thus, it is necessary to recognize that the results in the region of the off-center type potential are not reliable even in the strong-coupling analysis.

It is one of our future problems to develop a theory to consider non-adiabatic effect through the electron-phonon vertex corrections in the region of the off-center type potential.

Let us briefly discuss the effect of the Coulomb interaction, which has been perfectly ignored in the present model. In the famous McMillan formula, $\eta$ is expressed by

$$\eta = \frac{1}{2} \left[ 1 - \frac{(1 + \lambda)(1 + 0.62\lambda)\mu^2}{\lambda + \mu^2(1 + 0.62\lambda)} \right],$$

where $\mu^* = (U/W)/[1 + (U/W) \log(W/\omega_0)]$ with the short-range Coulomb repulsion $U$. From this expression, we easily understand that $\eta$ becomes smaller than 1/2, as observed in actual materials, when we include the effect of the Coulomb interaction. In this sense, our result of $\eta > 1/2$ is peculiar and it can be the evidence for superconductivity induced by anharmonic phonons.

For $\beta$-pyrochlore oxides, electron-phonon coupling constant is larger than about 0.8 and $\mu^*$ is considered to be about 0.1. If we simply use eq. (29) for the evaluation of $\eta$, we obtain $\eta \approx 0.49$ and the reduction from 0.5 is very small. It is true that $\eta$ is reduced when we include the effect of the Coulomb interaction, but in $\beta$-pyrochlore oxides, we imag-
ine that the effect of the Coulomb interaction is not strong enough to reduce significantly the value of $\eta$. In fact, recent de Haas-van Alphen oscillation measurements of $\text{KOS}_2\text{O}_8$ have clearly suggest that the mass enhancement of quasi-particle originates from the electron-rattling interaction and the effect of the Coulomb interaction is considered to be small.\(^{37}\)

Finally, we provide a brief comment on the parameter region corresponding to actual $\beta$-pyrochlore oxides. We expect that the parameters of $\gamma_0 = 10^{-3}$ and $-1.0 < \beta_0^I < -0.6$ correspond to $\beta$-pyrochlore oxides, because the potential for those parameters exhibits the flat and wide region at the bottom, leading to rattling oscillation which will enhance $T_c$. However, there are insufficient evidences to prove such correspondence at the present stage. In order to discuss actual materials quantitatively on the basis of our scenario, it is necessary to develop further our studies in future.

In summary, we have found that the isotope effect with the exponent $\eta > 1/2$ occurs for superconductivity due to electron-rattling interaction. From the detailed analysis of $\eta$, we have confirmed that the deviation of $\eta$ from $1/2$ originates from the anharmonicity. It is highly expected that the detect of this anomalous isotope effect can be the evidence of superconductivity induced by rattling in $\beta$-pyrochlore oxides.

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1) *Kondo Effect - 40 Years after the Discovery*, J. Phys. Soc. Jpn. **74** (2005) 1-238.
2) *Frontiers of Novel Superconductivity in Heavy Fermion Compounds*, J. Phys. Soc. Jpn. **76** (2007) 051001-051013.
3) *Recent Developments in Superconductivity*, J. Phys. Soc. Jpn. **81** (2012) 011001-011013.
4) Y. Yanase, T. Jujo, T. Nomura, H. Ikeda, T. Hotta, and K. Yamada: Phys. Rep. **387** (2003) 1.
5) T. Hotta: Rep. Prog. Phys. **69** (2006) 2061.
6) Y. Kuramoto, H. Kusunose, and A. Kiss: J. Phys. Soc. Jpn. **78** (2009) 072001.
7) P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani, and G. H. Lander: Rev. Mod. Phys. **81** (2009) 807.
8) H. Sato, H. Sugawara, Y. Aoki, and H. Harima: *Handbook of Magnetic Materials* Volume 18, ed. K. H. J. Buschow, pp. 1-110, Elsevier, Amsterdam, 2009.
9) S. Yonezawa, Y. Muraoka, Y. Matsushima, and Z. Hiroi: J. Phys.: Condens. Matter **16** (2004) L9.
10) S. Yonezawa, Y. Muraoka, Y. Matsushima, and Z. Hiroi: J. Phys. Soc. Jpn. **73** (2004) 819.
11) S. Yonezawa, Y. Muraoka, and Z. Hiroi: J. Phys. Soc. Jpn. **73** (2004) 1655.
12) Z. Hiroi, S. Yonezawa, Y. Nagaio, and J. Yamaura: Phys. Rev. B. **76** (2007) 014523.
13) S. M. Kazakov, N. D. Zhigadlo, M. Brühwiler, B. Batlogg, and J. Karpinski: Supercond. Sci. Technol. **17** (2004) 1169.
14) M. Brühwiler, S. M. Kazakov, N. D. Zhigadlo, J. Karpinski, and B. Batlogg: Phys. Rev. B **70** (2004) 020503(R).
15) M. Brühwiler, S. M. Kazakov, J. Karpinski, and B. Batlogg: Phys. Rev. B **73** (2006) 094518.
16) Y. Nagaio, J. Yamaura, H. Ogusu, Y. Okamoto, and Z. Hiroi: J. Phys. Soc. Jpn. **78** (2009) 064702.
17) J. Kuneš, T. Jeong, and W. E. Pickett: Phys. Rev. B **70** (2004) 174510.
18) K. Hattori and H. Tsunetsugu: Phys. Rev. B **81** (2010) 134503.
19) K. Hattori and H. Tsunetsugu: J. Phys. Soc. Jpn. **80** (2011) 023714.
20) J. Chang, I. Eremin, and P. Thalmeier: New J. Phys. **11** (2009) 055068.
21) K. Oshiba and T. Hotta: Proc. of the International Conference on Heavy Electrons 2010 (ICHE2010), J. Phys. Soc. Jpn. **80** (2011) Suppl. A, SA134.
22) K. Oshiba and T. Hotta: J. Phys. Soc. Jpn. **80** (2011) 094712.
23) J. Bardeen, L. N. Cooper, and J. R. Schrieffer: Phys. Rev. **108** (1957) 1175.
24) E. Maxwell: Phys. Rev. **78** (1950) 477.
25) C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt: Phys. Rev. **78** (1950) 487.
26) S. Hoen, W. N. Creager, L. C. Bourne, M. F. Crommie, T. W. Barbee III, M. L. Cohen, and A. Zettl: Phys. Rev. B **39** (1989) 2269.
27) S. L. Drechsler and N. M. Plakida: Phys. Stat. Sol. **144** (1987) K113.
28) V. H. Crespi, M. L. Cohen, and D. R. Penn: Phys. Rev. B **43** (1991) 12921.
29) M. K. Crawford, M. N. Kunchur, W. E. Farneth, E. M. McCarron III, and S. J. poon: Phys. Rev. B **41** (1990) 282.
30) V. H. Crespi and M. L. Cohen: Phys. Rev. B **44** (1991) 4712.
31) A. B. Migdal: Zh. Eksp. Teor. Fiz. **34** (1958) 1438.
32) G. M. Eliashberg: Zh. Eksp. Teor. Fiz. **38** (1960) 966.
33) T. Hotta: J. Phys. Soc. Jpn. **78** (2009) 073707.
34) T. Hotta: J. Phys. Soc. Jpn. **77** (2008) 103711.
35) W. L. McMillan: Phys. Rev. **167** (1968) 331.
36) P. B. Allen and R. C. Dynes: Phys. Rev. B **12** (1975) 905.
37) T. Terashima, N. Kurita, A. Kiszandhi, E.-S. Choi, J. S. Brooks, K. Sato, J. Yamaura, Z. Hiroi, H. Harima, and S. Uji: Phys. Rev. B **85** (2012) 180503(R).