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Thomas Dahm, Kazuo Ueda. Theoretical study of NMR relaxation due to rattling phonons. *Journal of Physics and Chemistry of Solids*, 2009, 69 (12), pp.3160. 10.1016/j.jpcs.2008.06.048 . hal-00594809

HAL Id: hal-00594809

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Submitted on 21 May 2011

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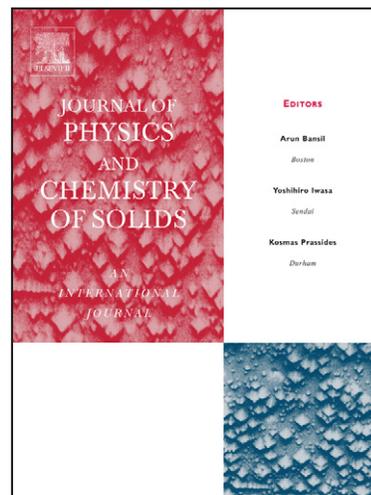
Author's Accepted Manuscript

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PII: S0022-3697(08)00264-3
DOI: doi:10.1016/j.jpcs.2008.06.048
Reference: PCS 5567

To appear in: *Journal of Physics and Chemistry of Solids*



www.elsevier.com/locate/jpcs

Cite this article as: Thomas Dahm and Kazuo Ueda, Theoretical study of NMR relaxation due to rattling phonons, *Journal of Physics and Chemistry of Solids* (2008), doi:10.1016/j.jpcs.2008.06.048

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Theoretical study of NMR relaxation due to rattling phonons

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Abstract

We calculate the NMR relaxation rate due to quadrupolar coupling of the nucleus to a local, strongly anharmonic phonon mode. As a model potential for a “rattling” motion we consider a square-well potential. We calculate the free phonon Green’s function analytically and derive the low and high temperature limits of the NMR relaxation rate. It is shown that the temperature dependence of the NMR relaxation rate possesses a peak in contrast to harmonic phonons but in qualitative agreement with a recent NMR study on KOs_2O_6 . We discuss the influence of phonon renormalization due to electron-phonon interaction.

Key words: NMR relaxation, anharmonic phonons, rattling, pyrochlore oxides

PACS: 76.60.-k, 63.20.Ry, 74.70.Dd

The new pyrochlore oxide superconductor KOs_2O_6 shows unusual behavior both in the normal as well as in the superconducting state. Density functional calculations have shown that the vibrations of the potassium ion are highly anharmonic, allowing large excursions from its equilibrium position within the surrounding Os-O cage [1], consistent with recent X-ray studies [2]. Such a situation, in which a small ion can move anharmonically within an oversized cage of surrounding atoms has been called “rattling” and also exists in other compounds [3–5]. The anharmonic dynamics of the potassium ion in KOs_2O_6 is currently being discussed as a possible origin for the anomalies seen in various experimental quantities, like e.g. specific heat [6], resistivity [7], thermal conductivity [8], and NMR relaxation [9].

Here we focus on recent NMR studies of KOs_2O_6 . In particular, the nuclear spin-lattice relaxation rate

$1/T_1T$ at the potassium site can directly probe the unusual potassium dynamics through quadrupolar coupling of the K nucleus to the electric field gradient, as has been shown recently [9]. The temperature dependence of the NMR relaxation rate $1/T_1T$ was found to be highly anomalous, increasing at low temperatures, reaching a peak value around ~ 14 K and decreasing again at higher temperatures. Such a behavior is inconsistent with the $1/T_1 \sim T^2$ behavior expected from harmonic phonons at high temperatures due to the two-phonon Raman process [10].

In a previous work we succeeded in describing this anomalous temperature dependence considering a strong anharmonicity of the vibration of the potassium ion [11]. We added a fourth order term to the harmonic potential and studied its influence within a self-consistent quasi-harmonic approximation. Within this model the effective phonon frequency becomes a strongly increasing function of temperature, modifying the higher temperature behavior of both NMR relaxation rate and resistivity [11], consistent with the experimental observations.

In the present work we are studying a square-well potential as a model for the potassium dynam-

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ics. This potential may seem less realistic and it also does not allow to “tune” the amount of anharmonicity. However, it can be regarded as the most extreme case of “rattling” and, more importantly, the square-well potential allows us to calculate the phonon spectral function analytically, without having to resort to the quasi-harmonic approximation. We wish to demonstrate that an anomalous temperature dependence of the NMR relaxation rate like the one found in Ref. [11] results, reinforcing our previous conclusion.

As the simplest possible model we consider the one-dimensional square-well potential with infinitely high walls. As is well known, the energy levels in this case are given by

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \quad \text{with} \quad n = 1, 2, \dots \quad (1)$$

Here, L is the size of the well and m the mass of the atom. It is an easy exercise to analytically calculate all the matrix elements of the positional operator x , giving

$$\langle n|x|m \rangle = \frac{2L}{\pi^2} \left[\frac{1}{(m+n)^2} - \frac{1}{(m-n)^2} \right], \quad (2)$$

if $m+n$ odd and 0 otherwise. The free, non-interacting phonon Green’s function $D_0(\omega)$ can be calculated quite generally from the expression [12]

$$D_0(\omega) = \frac{1}{Z} \sum_{m,n} \frac{(e^{-\beta E_m} - e^{-\beta E_n}) |\langle n|x|m \rangle|^2}{(\omega - E_n + E_m) |\langle 1|x|2 \rangle|^2} \quad (3)$$

Here, $Z = \sum_n e^{-\beta E_n}$ is the partition function and $\beta = 1/T$ the inverse temperature and we have normalized $D_0(\omega)$ to the lowest energy excitation $\langle 1|x|2 \rangle$.

In the superconducting state the NMR relaxation rate at the potassium site exhibits a sudden decrease. As has been pointed out in Ref. [9] this suggests that the rattling phonon must be strongly coupled to the conduction electrons. Following Ref. [11] we therefore introduce a finite phonon self energy $\Pi(\omega)$ due to coupling to the conduction electrons. Then, the interacting phonon Green’s function $D(\omega)$ can be calculated from Dyson’s equation

$$D(\omega) = \frac{1}{D_0^{-1}(\omega) - \Pi(\omega)} \quad (4)$$

The phonon spectral function $A(\omega)$ is obtained from

$$A(\omega) = -\frac{1}{\pi} \text{Im} D(\omega + i0^+) \quad (5)$$

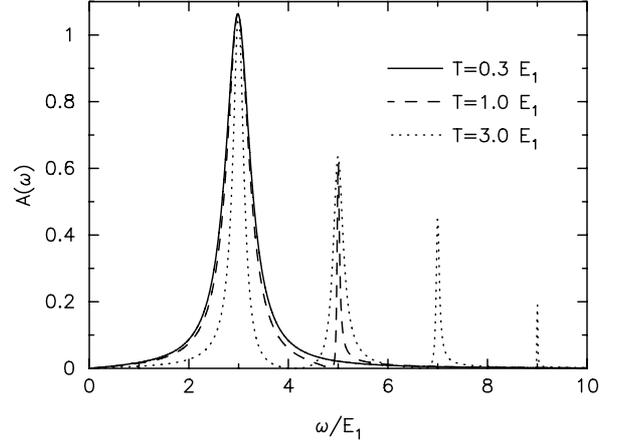


Fig. 1. Phonon spectral function $A(\omega)$ for the square well potential at three different temperatures $T = 0.3E_1$ (solid line), $T = 1.0E_1$ (dashed line), and $T = 3.0E_1$ (dotted line). With increasing temperature, spectral weight is shifted gradually away from the main peak at $3E_1$ to the higher energy peaks.

Because the electronic energy scale is much larger than the phononic energy scale, we can make a low energy expansion of the phonon self energy and write

$$\Pi(\omega) \approx -\Pi_1 - i\alpha\omega \quad (6)$$

where Π_1 and α are positive real constants describing the interaction of the phonon with the conduction electrons. Here, Π_1 is the renormalization of the phonon frequency and α determines the phonon damping rate.

As can be seen from Eq. (3) the non-interacting phonon Green’s function consists of a sum of poles at the transition energies $E_n - E_m$. For a harmonic oscillator these poles all fall on top of each other, resulting in a single, temperature independent pole. However, for the present square-well potential the allowed transition energies are different and the corresponding spectral function consists of a series of peaks at the positions $\delta_n = \frac{\hbar^2 \pi^2}{2mL^2} (2n+1)$. The relative weight of these peaks is temperature dependent. With increasing temperature spectral weight is gradually transferred to higher energies, because higher energy transfers become possible. In Fig. 1 we show the energy dependence of the spectral function $A(\omega)$ calculated from Eqs. (1)-(5) at three different temperatures $T = 0.3E_1$ (solid line), $T = 1.0E_1$ (dashed line), and $T = 3.0E_1$ (dotted line). Here, $E_1 = \frac{\hbar^2 \pi^2}{2mL^2}$ is the ground state energy of the square well potential. For illustration, no phonon frequency renormalization $\Pi_1 = 0$ and a small phonon damping of $\alpha = 0.1$ has been chosen. The influence of

these two parameters on the NMR relaxation rate will be discussed below. Fig. 1 illustrates how the spectral weight is shifted away from the lowest energy peak at $3E_1$ to the higher energy peaks, when temperature is increasing.

Within the quasi-harmonic approximation of Ref. [11] this gradual transfer of spectral weight to higher energies appears as a temperature increase of the effective phonon frequency. We wish to emphasize that the peak positions do not change as a function of temperature. Only their intensities do. The effective phonon frequency of Ref. [11] therefore corresponds to an effective average frequency and should not be associated with an energy level distance. For example, a neutron scattering experiment is expected to observe a temperature dependent intensity of a series of phonon peaks and will not be able to directly observe the effective average frequency.

Once the phonon spectral function is known, the NMR relaxation rate $1/T_1$ from quadrupolar interaction of the potassium nucleus to the local electric field gradient can be calculated. In Ref. [11] we have shown that the two-phonon Raman process is dominating over the direct process, because of the small number of phonon states available at the Larmor frequency [10]. Therefore, here we will focus on the two-phonon Raman process. In this case $1/T_1$ is given by

$$\frac{1}{T_1} \propto \int_{-\infty}^{\infty} d\omega A^2(\omega) [n(\omega) + 1] n(\omega) \quad (7)$$

neglecting higher order vertex corrections due to electron-phonon coupling. Here, $n(\omega)$ is the Bose distribution function. In Fig. 2 we show a numerical evaluation of Eq. (7) using the spectral function from Eq. (5). Again, $\Pi_1 = 0$ and $\alpha = 0.1$ has been chosen. It is immediately apparent that the NMR relaxation rate $1/T_1 T$ possesses a peak as a function of temperature near $T = 5E_1$, in contrast to harmonic phonons. The behavior is qualitatively similar to the experimental data from Ref. [9]. At low temperatures $1/T_1 T$ varies like T^2 due to the linear behavior of the spectral function at low energies seen in Fig. 1. At high temperatures we can show that $1/T_1 T$ varies like $1/\sqrt{T}$ (see below). This is in contrast to harmonic phonons, where $1/T_1 T \sim T$ at high temperatures, but it is also different from the fourth order potential result where $1/T_1 T \sim \text{const}$ was found [11]. Apparently the high temperature be-

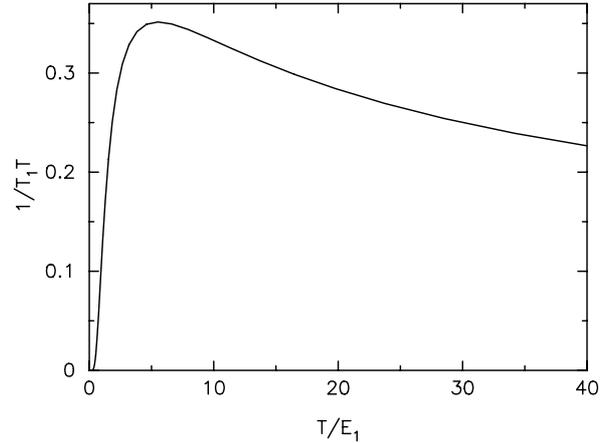


Fig. 2. Temperature dependence of the NMR relaxation rate $1/T_1 T$ from the two-phonon Raman process for the square-well potential.

havior depends somewhat on the type of potential chosen.

In order to derive the high temperature limiting behavior we assume that the damping parameter α is small enough such that the poles appearing in Eq. (3) remain well separated. Generally we can write $D_0(\omega)$ as a series of poles:

$$D_0(\omega) = \sum_n \frac{a_n(T)}{\omega - \delta_n} \quad (8)$$

where $a_n(T)$ are the temperature dependent weights of the poles. Because the matrix elements $|\langle n|x|m \rangle|^2$ quickly decrease with increasing distance $n - m$, to a good approximation we can only keep the nearest neighbor terms $m = n \pm 1$. Then we have

$$a_n(T) = \frac{e^{-\beta E_{n\pm 1}} - e^{-\beta E_n}}{Z(T)} \quad (9)$$

The partition function $Z(T) = \sum_n e^{-\beta E_1 n^2}$ varies like \sqrt{T} at high temperatures because the number of terms contributing significantly to the sum increases as \sqrt{T} . If the poles are well separated, the full phonon Green's function becomes

$$D(\omega) \approx \sum_n \frac{a_n(T)}{\omega - \delta_n - a_n(T) \Pi(\omega)} \quad (10)$$

and the spectral function can be written in the form

$$A(\omega) \approx \frac{1}{\pi} \sum_n \frac{a_n(T) \Gamma_{n,eff}}{[\omega - \delta_n + a_n(T) \Pi_1]^2 + \Gamma_{n,eff}^2} \quad (11)$$

with $\Gamma_{n,eff} = \alpha a_n(T) (\delta_n - a_n(T) \Pi_1)$. Using Eq. (11) and evaluating each pole separately, we find from Eq. (7)

$$\frac{1}{T_1} \approx \frac{1}{2\pi} \sum_n \frac{a_n(T)}{\alpha \Omega_n} [n(\Omega_n) + 1] n(\Omega_n) \quad (12)$$

where $\Omega_n = \delta_n - a_n(T) \Pi_1$ are the renormalized phonon frequencies. Apparently, $1/T_1$ scales like $1/\alpha$ for all temperatures and small values of α . This means that the parameter α has no large influence on the temperature dependence of the NMR relaxation rate, but only on its absolute values.

In the high temperature limit we find from Eq. (9)

$$a_n(T) \approx \frac{\beta(E_n - E_{n\pm 1})}{Z(T)} \sim T^{-3/2} \quad (13)$$

Using $n(\Omega_n) \sim T/\Omega_n$ we finally arrive at

$$\frac{1}{T_1 T} \propto \frac{1}{\alpha \sqrt{T}}. \quad (14)$$

We can estimate an absolute value of the expected peak position of the NMR relaxation rate by choosing the potassium mass for m in Eq. (1) and a size of the well of $L \approx 1 \text{ \AA}$, as suggested by both bandstructure calculations [1] and X-ray studies [2]. Then we find $E_1 \approx 6.1 \text{ K}$, which would suggest the NMR peak position to appear around $5E_1 \approx 30 \text{ K}$. However, the peak in the experimental data appears near 14 K and also the peak is somewhat more sharp than the one in Fig. 2. A possible explanation for these differences could be the influence of a sizeable phonon renormalization due to electron-phonon interaction, as given by the parameter Π_1 in Eq. (6). To illustrate the influence of the parameter Π_1 , in Fig. 3 we show the temperature dependence of $1/T_1 T$ for four different values of Π_1 , keeping $\alpha = 0.1$ fixed. With increasing Π_1 the peak becomes more sharp and the peak position moves to lower temperatures easily softening the peak position by more than a factor of 2. Thus, a better agreement with the NMR data on KOs_2O_6 could be obtained for a value of $\Pi_1 \approx 0.5E_1$.

To summarize we have calculated the NMR relaxation rate due to quadrupolar coupling to a local, strongly anharmonic phonon mode considering the two-phonon Raman process. We have calculated the free phonon Green's function analytically for a square-well potential. Including phonon renormalization due to electron-phonon interaction we were able to show that the temperature dependence of the NMR relaxation rate $1/T_1 T$ possesses a peak as a function of temperature, in stark contrast to harmonic phonons. The position and height of this peak depends on the strength of the phonon renormalization. We also derived the high and low temperature

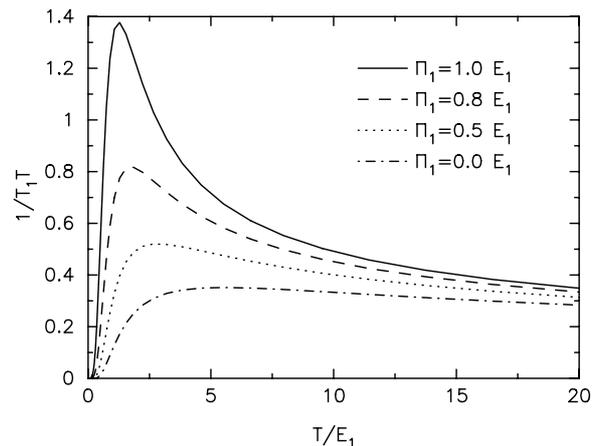


Fig. 3. Temperature dependence of the NMR relaxation rate $1/T_1 T$ from the two-phonon Raman process for different values of the real part of the phonon self-energy: $\Pi_1 = E_1$ (solid line), $\Pi_1 = 0.8E_1$ (dashed line), $\Pi_1 = 0.5E_1$ (dotted line), and $\Pi_1 = 0$ (dashed-dotted line).

limiting behaviors. These results reinforce our previous approximate treatment of a fourth order potential.

We would like to thank Z. Hiroi, K. Ishida, Y. Matsuda, T. Shibauchi, and M. Takigawa for valuable discussions.

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Accepted manuscript