PHYSICAL REVIEW B **83**, 195124 (2011)

Anharmonic effects in the mixed 4*f*-electron lattice excitations of Pr skutterudites

Peter Thalmeier
Max Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

(Received 19 November 2010; revised manuscript received 18 March 2011; published 13 May 2011)

The structure of Pr skutterudites provides large cages for the anharmonic rattling motion of the rare-earth guest atom. For suitable composition, their frequency may be nearly degenerate with low-energy crystalline electric-field excitations of localized 4*f* states. In this case, the anharmonic oscillation of Pr is supplemented by nonadiabatic or vibronic effects due to 4*f*-electron–phonon coupling. This affects the temperature dependence of the effective phonon frequency and the rattling phonon-Raman contribution to NMR and nuclear quadrupole resonance relaxation. Furthermore, dispersive 4*f*-quadrupole excitations originating from intersite quadrupole coupling may exhibit typical anomalies due to mixing with the phonons. A model of anharmonic rattling phonons together with dispersive 4*f* excitations is introduced to study these effects. It is of particular relevance to $\mathrm{Pr(Os_{1-x}Ru_x)_4Sb_{12}}$, where the degeneracy of 4*f* excitations and rattling phonons has been identified before.

DOI: 10.1103/PhysRevB.83.195124 PACS number(s): 63.20.kd, 63.20.Ry, 71.70.Ch, 76.60.−k

I. INTRODUCTION

Filled rare-earth-based skutterudite compounds have been intensely investigated, mostly because of their exotic superconducting and hidden-order phases due to strongly correlated 4*f* electrons.[1–3] In particular, it was shown[4,5] that in $\mathrm{PrOs_4Sb_{12}}$ and $\mathrm{Pr(Os_{1-x}Ru_x)_4Sb_{12}}$, low-energy crystalline electric-field (CEF) excitations play a crucial role in the superconducting mechanism. Furthermore, in these compounds, the rare earth can be viewed as guest ions in a cage formed by the $\mathrm{Sb_{12}}$ icosahedrons of the host. The cage potential may have considerable anharmonicity, which leads to low-energy "rattling" phonons with temperature-dependent effective phonon frequency. The rattling phonons can be viewed as dispersionless (local) optical modes of the guest atom lying deep in the continuum of the acoustic-phonon branch of the host.[6] This is quite similar to the anharmonic rattling of alkaline-earth atoms in the cages of pyrochlore superconductors such as $\mathrm{KOs_2O_6}$.[7] For this class of compounds, a model involving only lattice degrees of freedom was investigated by Dahm and Ueda[8] and, e.g., in Refs. 9 and 10. In particular, an effective temperature dependence of guest phonon frequency and its Raman contribution to NMR relaxation was found.[8] Such effects should also be present in skutterudites and have been studied in Refs. 11 and 12. Experimentally, evidence for the rattling in skutterudites has been suggested from ultrasonic[13] neutron diffraction,[14] as well as from NMR and nuclear quadrupole resonance (NQR) experiments.[17]

In previous theoretical investigations, the guest rattling motion has been treated purely as a lattice problem. However, recently an interesting situation has been found in $\mathrm{Pr(Os_{1-x}Ru_x)_4Sb_{12}}$.[18] It was shown from specific-heat analysis that around $x \approx 0.65$, a crossing of the x-independent guest mode frequency $\omega_e^0 \simeq 45$ K and the $\Gamma_1 - \Gamma_4^{(2)}$ singlet-triplet CEF excitation $\Delta(x)$, which increases monotonously with x from $\Delta(0) = 8$ K to $\Delta(0) = 84$ K, takes place. In this case, one not only has to expect purely anharmonic lattice effects but also nonadiabatic or vibronic effects coming from the resonant 4*f*-phonon interaction. The latter have been studied in Ref. 5, in particular in hindsight of the superconducting $T_c(x)$ concentration dependence found in Ref. 19. However, harmonic phonons and dispersionless CEF excitations without intersite coupling were assumed in this analysis.

For a fully self-consistent treatment of the problem, one first has to include the dispersion effects of CEF excitations shown to exist in Ref. 20, and second, both anharmonic lattice coupling and nonadiabatic 4*f*-electron–phonon coupling have to be treated on the same footing. This demands a further extension of the theory given in Ref. 5. The aim is to investigate nonadiabatic effects in the temperature-dependent anharmonic rattling phonons and anharmonic effects in the mixed 4*f*-phonon mode dispersion. The latter can be investigated with inelastic neutron scattering (INS). Furthermore, it should be clarified to what extent the 4*f*-phonon coupling leaves its signature in the Raman-phonon contribution to NMR and NQR relaxation, which was proposed for the anharmonic pyrochlore compound.

In Sec. II, we will introduce the generalized model Hamiltonian for coupled rattling phonons and CEF excitations. In the quasiharmonic approximation, this model will first be diagonalized without the dispersive effects in Sec. III, and the influence of the vibronic mode splitting on the phonon-Raman NMR and NQR will be discussed in Sec. IV. Then the typical signature of anharmonicity in the vibronic mixed-mode dispersions will be discussed in Sec. V by considering the dynamic and momentum-dependent dipolar spectral function relevant for INS experiments. Finally, Sec. VI gives the conclusions.

II. MODEL FOR ANHARMONIC RATTLING PHONONS AND DISPERSIVE 4*f* EXCITONS

For the present purpose, the microscopic model presented in Ref. 5 for the interaction of rattling phonons and 4*f* CEF excitations in Pr skutterudites needs to be extended in two essential ways: (i) the anharmonicity of the rattling phonons has to be included explicitly and (ii) the intersite quadrupolar interactions should be included to describe the observed dispersion effects of $4f$ excitations.[20] This leads us to an extended model Hamiltonian given by

$$\begin{aligned} H = \sum_{ni} \Big[& \frac{1}{2}\omega_0(b_n^\dagger b_n + b_n b_n^\dagger) + \frac{1}{2}\Delta(a_n^\dagger a_n + a_n a_n^\dagger) \\ & + i\hat{g}_0(b_n a_n - b_n^\dagger a_n^\dagger + b_n^\dagger a_n - b_n a_n^\dagger)\Big]_i \\ & - \frac{1}{2}\tilde{D}\sum_{\langle ij\rangle,n}(a_{ni} - a_{ni}^\dagger)(a_{nj} - a_{nj}^\dagger) \\ & + \frac{B}{4}\left(\frac{\hbar}{2M\omega_e}\right)^2 (b_{ni} + b_{ni}^\dagger)^4. \end{aligned} \tag{1}$$

Here the first three terms were introduced before,[5] describing guest harmonic phonons (bare frequency ω_0), CEF excitations [singlet-triplet splitting $\Delta(x)$], and their vibronic interaction (coupling constant $\hat{g}_0$), respectively, while the remaining terms are treated in this work. The third term describes the quadrupolar next neighbor intersite coupling with strength $\tilde{D}$, and is written in bosonic $(a,a^\dagger)$ variables.[21,22] The last term is the quartic anharmonic potential $V_a(\mathbf{r}) = (B/4)\sum_n x_n^4$, where $\mathbf{r} = (x_1,x_2,x_3)$ describes the distance from the equilibrium position of the guest atom in the host cage and B gives the anharmonic potential strength. We assume that the guest atom is in a centered equilibrium position at all temperatures, as suggested by neutron diffraction.[14,15] As a first step, we only add the anharmonic term. The dispersive (fourth) term will be included later.

Before we proceed, we discuss an essential difference to the rattling motion in the pyrochlore superconductors like KOs_2O_6. In the latter, the site symmetry of the rattling K host atom is T_d,[10] which does not contain the inversion with respect to the K site. Therefore, in these compounds, there are additional anharmonic potential terms $\sim(x_1,x_2,x_3)$ of the third order in the guest atom displacement $\mathbf{r}$. Such terms cannot be treated within the quasiharmonic approximation, as discussed in Ref. 10. However, in the present case of filled skutterudite, the Pr host atom resides in the center of the Sb_{12} cage where the site symmetry is T_h,[16] which contains the inversion symmetry with respect to the Pr site. Therefore the anharmonic potential of the latter does not include terms of the third (odd) order in the displacement coordinates x_n, as these are strictly forbidden by inversion. Consequently, we can safely apply the quasiharmonic treatment of rattling motion including only the above fourth-order anharmonicity term in the following.

III. QUASIHARMONIC THEORY OF COUPLED VIBRONIC STATES

In this section, we investigate the effect of anharmonic terms on the local vibronic (coupled $4f$ rattling phonon) spectrum. This will be done in a quasiharmonic approximation, which was used before in Refs. 8 and 9 for the pyrochlore superconductor AOs_2O_6 where the third-order terms were neglected. In the pyrochlore case, however, there are no $4f$ electrons and therefore no vibronic excitations; it rather is a pure phonon problem. In the present case of Pr skutterudites, the self-consistent quasiharmonic theory has to be extended by including the effect of the vibronic coupling term. In the quasiharmonic approximation, the anharmonic guest potential is approximated by a harmonic one with an effective temperature-dependent coefficient leading to

$$V_a(\mathbf{r}) \simeq \frac{B}{2}\langle x^2\rangle \sum_n x_n^2, \tag{2}$$

$$\omega_e(T) = \omega_0^2 + \frac{B}{M}\langle x^2\rangle. \tag{3}$$

Here, $\langle x^2\rangle = \langle x_n^2\rangle$ is the mode-independent (Cartesian polarization directions $n = 1$–3), mean-square displacement, and $\omega_e(T)$ is the renormalized rattling frequency of the guest (Pr) atom, which depends on temperature via the self-consistency in Eq. (3). Like the unrenormalized ω_0, $\omega_e(T)$ is threefold degenerate (independent of n) due to the tetrahedral symmetry. The temperature dependence of the effective quasiharmonic frequency results from the nonequidistant level spacing of the true anharmonic oscillator spectrum. The average level spacing corresponding to $\omega_e(T)$ will then depend on the thermal occupation of those levels and therefore on temperature. Without the dispersive term, the quasiharmonic vibronic Hamiltonian then reduces to

$$\begin{aligned} H = \sum_{ni}\Big[& \frac{1}{2}\omega_e(T)(b_n^\dagger b_n + b_n b_n^\dagger) + \frac{1}{2}\Delta(a_n^\dagger a_n + a_n a_n^\dagger) \\ & + i\hat{g}_0(b_n a_n - b_n^\dagger a_n^\dagger + b_n^\dagger a_n - b_n a_n^\dagger)\Big]_i . \end{aligned} \tag{4}$$

Formally this is now the same model as in Ref. 5 except for the replacement $\omega_0 \to \omega_e(T)$, where the T-dependent anharmonic $\omega_e(T)$ has to be determined self-consistently. For that purpose, we diagonalize the model as in Ref. 5 and obtain

$$H = \sum_n \Omega_\phi(T)\left(\phi_n^\dagger\phi_n + \frac{1}{2}\right) + \sum_n \Omega_\psi(T)\left(\psi_n^\dagger\psi_n + \frac{1}{2}\right). \tag{5}$$

Here, ϕ,ψ are the vibronic normal-mode coordinates, and the triply degenerate $(n = x,y,z)$ and temperature-dependent, normal-mode frequencies $\Omega_s^n = \Omega_s$ $(s = \phi,\psi)$ are given by $(\gamma \equiv \frac{1}{4}\hat{g}_0)$,

$$\begin{aligned} \Omega_s(T) = 2\Bigg\{ & \frac{1}{2}\left(\frac{\omega_e(T)^2}{4} + \frac{\Delta^2}{4}\right) \pm \frac{1}{2}\Bigg[\left(\frac{\omega_e(T)^2}{4} - \frac{\Delta^2}{4}\right)^2 \\ & + \frac{1}{4}\gamma^2\omega_e(T)\Delta\Bigg]^{\frac{1}{2}}\Bigg\}^{\frac{1}{2}}. \end{aligned} \tag{6}$$

For vanishing vibronic coupling $(\gamma = 0)$, the purely phononic self-consistency equation for the guest displacement is given by

$$\langle x_n^2\rangle = \left(\frac{\hbar}{2M\omega_e}\right)(2n_e + 1), \quad n_e = (e^{\omega_e/T} - 1)^{-1}. \tag{7}$$

For the present nonzero coupling to the Pr CEF excitations $(\gamma \neq 0)$, this has to be generalized: The averaged squared displacement $\langle x_n^2\rangle$ must now be calculated with respect to the new normal coordinates. Using $x_n = (\hbar/2M\omega_e)^{\frac{1}{2}}(b_n + b_n^\dagger)$ and the transformation

$$b_n + b_n^\dagger = u_{r\phi}(\phi - \phi^\dagger) + u_{r\psi}(\psi - \psi^\dagger), \tag{8}$$

with coefficients (independent of mode n) given by[5]

$$u_{rs}^2 = \frac{\omega_e}{\Omega_s}\,\frac{\gamma^2\Delta\omega_e}{\left(\omega_e^2-\Omega_s^2\right)^2+\gamma^2\Delta\omega_e}, \tag{9}$$

the self-consistency equation now reads

$$\langle x_n^2\rangle = \left(\frac{\hbar}{2M\omega_e}\right)\sum_s u_{rs}^2(2n_s+1), \quad n_s = (e^{\Omega_s/T}-1)^{-1}. \tag{10}$$

Inserting this expression into Eq. (3), we obtain, after some algebra, a self-consistent equation for the renormalized Pr guest rattling frequency under the presence of vibronic coupling to $4f$ CEF excitations:

$$\begin{gathered}\left(\frac{\omega_e}{\omega_e^0}\right)^2_{T\gamma} = 1+\beta_r\left(\frac{\omega_e^0}{\omega_e}\right)\left[\bar{n}+\frac{1}{2}-\frac{1}{2}\frac{\omega_e}{\omega_e^0}\right],\\ \beta_r(T,\gamma) = \beta\sum_s u_{rs}^2, \quad \bar{n} = \sum_s n_s u_{rs}^2\Big/\sum_s u_{rs}^2.\end{gathered} \tag{11}$$

Here we defined $\omega_e^0 = \omega_e^0(T=0)$ as the low-temperature limit of the rattling frequency and $\beta = \hbar B/M^2(\omega_e^0)^3$ as a dimensionless anharmonic potential strength. This is the generalization of the corresponding equation in Ref. 8 to the case where the rattling motion of guest atoms is coupled to virtual CEF excitations. It contains three parameters: The effective low temperature ω_e^0 and the anharmonic and vibronic coupling constants β,γ, respectively. It should be noted that $\omega_e^0 \simeq 45$ K is the experimentally determined low-temperature rattling frequency.[18] It is equal to ω_0 only when the anharmonic coupling is neglected ($\beta = 0$), as was done previously.[5] Furthermore, the singlet-triplet splitting $\Delta(x)$ is interpolated between the boundary values $\Delta(0) \simeq 8$ K and $\Delta(1) \simeq 84$ K.[5]

The temperature dependence of $\omega_e(T)$ obtained from Eq. (11) and its variation with coupling parameters is shown in Fig. 1. We estimate β as follows: From INS,[23] one obtains the ratio $\omega_e(300\text{ K})/\omega_e^0 \simeq 1.4$ for $\mathrm{PrOs_4Sb_{12}}$. Using $\omega_e^0 = 45$ K to stay consistent with Refs. 5,18, this ratio is obtained for $\beta \simeq 0.3$. Thus, in Pr skutterudite, the anharmonicity is quite moderate and it is not comparable to the strongly anharmonic case ($\beta \gg 1$) of the pyrochlore compounds, where values $\beta \simeq 6$–7 have been proposed.[8,9] In the weakly anharmonic case, $\omega_e(T)$ roughly increases $\sim T$, except at the lowest temperatures. This is shown in Fig. 1 corresponding to $x = 0$ by the dashed line without vibronic coupling ($\gamma = 0$). When γ is turned on (dash-dotted and solid lines), the low-energy CEF excitation at $\Delta(x)$ acquires a partly phononic character; this in turn increases the anharmonic effect via the self-consistency relation in Eq. (11). Therefore, $\omega_e(T)$ increases more rapidly with T and the linear T regime is enlarged (for fixed $\beta < 1$), as shown in Fig. 1. For larger x, the splitting $\Delta(x)$ increases, which diminishes the effect of vibronic coupling in $\omega_e(T)$. In the crossing region $x \approx 0.65$, where $\omega_e^0 \simeq \Delta(x)$, only a small γ dependence of $\omega_e(T)$ remains.

In the crossing region, a different effect due to anharmonicity may be observed: The dipolar spectral function has a double-peak structure caused by the vibronic coupling,[5] which will now depend considerably on temperature because the resonant condition $\omega_e^0(T) \simeq \Delta(x)$ will change with temperature for $\beta > 0$. Therefore, a shift and intensity transfer of the split vibronic modes due to anharmonic effects may be expected, as illustrated in Fig. 2.This prediction may be checked by INS experiments.

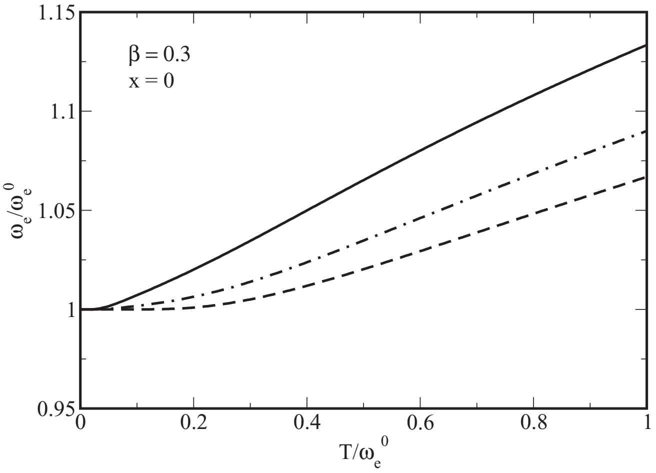

FIG. 1. Temperature dependence of quasiharmonic rattling phonon frequency for $4f$-phonon coupling constant $\gamma = 0$ (dashed line), 0.15 (dash-dotted line), and 0.3 (solid line). The anharmonic coupling β is defined in Sec. III.

IV. VIBRONIC EXCITATIONS IN THE NMR AND NQR RELAXATION

It is known from the pyrocholore cage compounds[8,24] that guest rattling leads to a NMR relaxation with unusual temperature dependence. It was attributed to the specific anharmonic features in the two-phonon Raman process, which dominates

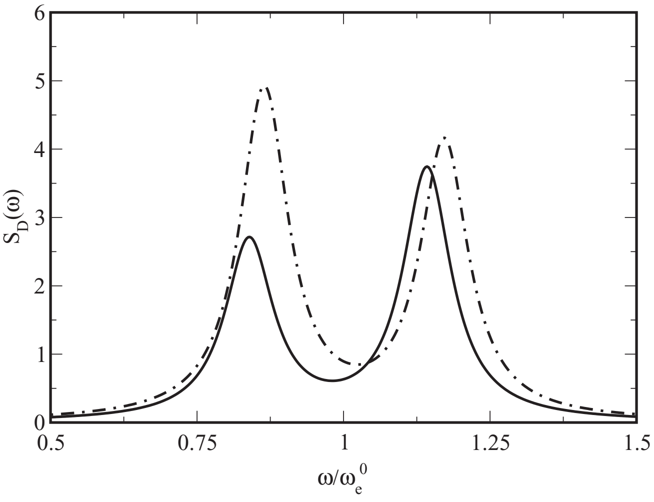

FIG. 2. Dipolar dynamical structure function (in units of b_D^2) for resonant case ($x \approx 0.654$) for $T = 0$ (solid line) and $T/\omega_0^e = 0.8$ (dash-dotted line). Here we used $\beta = 0.3$, $\gamma = 0.2$, and linewidth $\Gamma = 0.2$ (in units of ω_e^0). The anharmonic increase of rattling mode frequency $\omega_e^0(T)$ with temperature leads to a shift of mixed-mode peaks and redistribution of their spectral weight.

the relaxation mechanism.[8] The quadrupolar relaxation rate of the Raman process is given by[25]

$$\frac{1}{T_1^R} = V_2^2 \sum_n \int_{-\infty}^{\infty} dt e^{i\omega_L t} \langle x_n^2(t) x_n^2(0) \rangle = \left(\frac{3\hbar V_2^2}{2M\omega_e} \right) R(\omega_L), \qquad (12)$$
$$R(\omega_L) = \int_{-\infty}^{\infty} dt e^{i\omega_L t} \langle B(t)^2 B(0)^2 \rangle.$$

Here we defined $B = b + b^\dagger$, with b denoting any ($n = x,y,z$) of the triply degenerate rattling mode displacements. The constant V_2 is proportional to the derivative of the electric-field gradient, and ω_L is the nuclear Lamor frequency. In the Pr skutterudites, in contrast to pyrochlores, the correlation function in the integral for $\frac{1}{T_1^R}$ is not only determined by the lattice dynamics but also by the coupling to $4f$ excitations. Using the transformation to vibronic coordinates in Eq. (8), and defining $\Phi = \phi - \phi^\dagger$ and $\Psi = \psi - \psi^\dagger$, we obtain

$$\langle B_n(t)^2 B_n(0)^2 \rangle = F^2(0) + 2F^2(t), \qquad (13)$$
$$F(t) = u_{r\phi}^2 \langle \Phi(t)\Phi(0) \rangle + u_{r\psi}^2 \langle \Psi(t)\Psi(0) \rangle.$$

The Fourier transform of $F(t)$ is then given by

$$F(\omega) = -2\pi \sum_s u_{rs}^2 [n(\omega) + 1] A_s(\omega), \qquad (14)$$
$$A_s(\omega) = -\frac{1}{\pi} D_s(\omega) = \frac{4\Omega_s \Gamma_s \omega}{\left(\omega^2 - \Omega_s^2\right)^2 + 2\Gamma_s^2\left(\omega^2 + \Omega_s^2\right) + \Gamma_s^4}.$$

Here, $A_s(\omega)$ is the spectral function of the bosonic propagator $D_s(\omega)$ for the normal mode with energy Ω_s and phenomenological linewidth Γ_s ($s = \phi,\psi$). For $\Gamma_s \ll \Omega_s$, the denominator may be approximated by $(\omega^2 - \Omega_s^2)^2 + 4\Gamma_s^2\Omega_s^2$. The relaxation function in Eq. (12) may now be expressed as

$$R(\omega_L) = 2\pi F^2(0)\delta(\omega_L) + \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega F(\omega) F(\omega - \omega_L). \qquad (15)$$

Then for $\omega_L \to 0$, we obtain the Raman relaxation rate due to vibronic excitations as

$$\frac{1}{T_1^R} = \frac{4\pi V_2^2 3\hbar}{2M\omega_e(T)} \sum_{ss'} u_{rs}^2 u_{rs'}^2$$
$$\times \int_{-\infty}^{\infty} n(\omega)[n(\omega) + 1] A_s(\omega) A_{s'}(\omega)\, d\omega. \qquad (16)$$

We separate the (temperature-dependent) prefactor and define the normalized relaxation rate $\frac{1}{\hat{T}_1^R T}$ by

$$\frac{1}{T_1^R T} = \left(\frac{6\pi\hbar V_0^2}{M\Gamma\omega_e^{02}} \right) \left(\frac{\Gamma\omega_e^{02}}{\omega_e(T)} \right) \frac{1}{\hat{T}_1^R T}, \qquad (17)$$

where the product of the last two factors is dimensionless and almost independent of the linewidth Γ. We can split the normalized relaxation rate into direct and cross contributions according to $1/\hat{T}_1^R = 1/\hat{T}_{1D}^R + 1/\hat{T}_{1C}^R$, as given by

$$1/\hat{T}_{1D}^R = 2 \int_0^{\infty} n(\omega)[n(\omega) + 1]\left[u_{r\phi}^4 A_\phi^2(\omega) + u_{r\psi}^4 A_\psi^2(\omega)\right] d\omega, \qquad (18)$$
$$1/\hat{T}_{1C}^R = 2 \int_0^{\infty} n(\omega)[n(\omega) + 1] u_{r\phi}^2 u_{r\psi}^2 \left[2A_\phi(\omega) A_\psi(\omega)\right] d\omega.$$

The direct contribution simply sums up the individual terms coming by two distinct vibronic normal modes, ϕ,ψ. Their integrands in Eq. (19) consist of their respective spectral function (Eq. (15)) and their weight factors (Eq. (9)) squared at a given frequency. However, the additional cross terms are determined by the overlap of spectral functions and weight functions for the two normal modes. This overlap and the associated cross contribution will be sizable only when their frequencies are not too different. This is the case in the anticrossing region of rattling phonons and the singlet-triplet CEF excitations of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, which lies around a critical Ru concentration of $x \simeq 0.65$.

The temperature dependence of the total Raman relaxation rate and its contributions are shown in Fig. 3 for various parameters. For harmonic phonons, $1/T_1^R T$ would be linear in T,[8] where the small anharmonicity leads to a slightly sublinear behavior which is shown in the pure phonon ($\gamma = 0$) reference (solid upper line). The vibronic coupling has a sizable effect only for the region $x \approx 0.65$, where the mode splitting occurs and strongly affects the normalized relaxation rates in Eq. (19). The experimental NMR and NQR relaxation rate[17,26] in the normal state of PrOs$_4$Sb$_{12}$ and La-substituted compounds is dominated by the localized magnetic fluctuations of thermally excited $\Gamma_4^{(2)}$ triplet states and the Korringa relaxation from quasiparticles. It is difficult to directly extract the anharmonic phonon-Raman contribution in these systems.[17] One should investigate the x dependence of the difference of the total relaxation rates $(T_1T)_x^{-1} - (T_1T)_{x=0}^{-1}$ taken at temperatures scaled with $\Delta(x)$ to subtract out the former contributions. The difference as a function of x should have an anomaly in the crossing region $x \simeq 0.65$ due to the vibronic coupling effect in the Raman contribution.

V. DISPERSIVE EFFECTS DUE TO QUADRUPOLAR EXCITONS

In the previous sections and also in Ref. 5, only isolated Pr $4f$ states were considered. It is known, however, that the singlet-triplet CEF excitations in PrOs$_4$Sb$_{12}$ acquire a considerable dispersion of ~30% (Ref. 20) resulting from effective intersite interactions between Pr quadrupole moments, and therefore form a band of quadrupolar excitons. In fact, the field-induced softening of the latter at x-point wave vector $\mathbf{k} = (2\pi/a, 0, 0)$ of the body-centered cubic Brillouin zone are responsible for the transition to the antiferroquadrupolar (AFQ) order above $H = 4.5$ T. These observations have been explained within a mean-field random phase approximation theory of the AFQ order.[21,22] It is expected that dispersive effects are present throughout the whole Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ series, even though the AFQ order eventually vanishes because the CEF splitting energy $\Delta(x)$ or center of $\Gamma_1 - \Gamma_4^{(2)}$

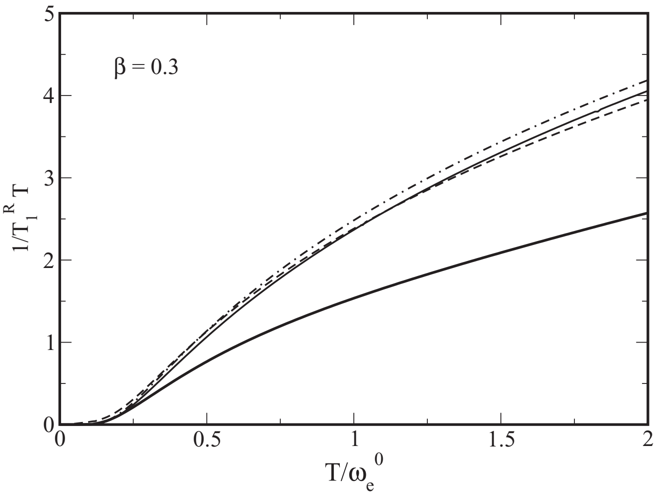

FIG. 3. Temperature dependence of the rattling phonon contribution to the Raman relaxation rate [unit is the first prefactor in Eq. (17)]. The three upper curves correspond to arbitrary x, $\gamma = 0$ (solid thin line); $x = 0$, $\gamma = 0.2$ (dashed line); and $x = 1$, $\gamma = 0.25$ (dash-dotted line). The lower curve corresponds to the resonant case ($\Delta = \omega_e^0$) with $x = 0.65$, $\gamma = 0.3$. Only close to $x \simeq 0.65$ does the vibronic coupling γ have a large influence on the Raman relaxation rate.

quadrupolar exciton band becomes larger for increasing the Ru content x. In the anticrossing region of singlet-triplet excitation and rattling phonon, one definitely would expect that the dispersive effects of the former described by the fourth term in the Hamiltonian of Eq. (2) should become important. In this section, we extend the previous theory[5] for isolated $4f$ states to the case of dispersive excitons coupled to anharmonic phonons.

The full model Hamiltonian in Eq. (2) in a quasiharmonic approximation, and using momentum representation, is given by

$$
\begin{aligned}
H = \sum_{\mathbf{k}} \Big[& \frac{1}{2}\omega_e(T)(b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + b_{\mathbf{k}} b_{\mathbf{k}}^\dagger) + \frac{1}{2}(\Delta + A_{\mathbf{k}})(a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + a_{\mathbf{k}} a_{\mathbf{k}}^\dagger) \\
& + i\hat{g}_0(b_{\mathbf{k}} a_{-\mathbf{k}} - b_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger + b_{\mathbf{k}}^\dagger a_{\mathbf{k}} - b_{\mathbf{k}} a_{\mathbf{k}}^\dagger) \\
& - \frac{1}{2} A_{\mathbf{k}}(a_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger + a_{-\mathbf{k}} a_{\mathbf{k}}) \Big], \qquad (19)
\end{aligned}
$$

where the quadrupolar exciton dispersion enters through

$$
\begin{aligned}
A_{\mathbf{k}} &= \tilde{D}_Q z \gamma_{\mathbf{k}}, \\
\gamma_{\mathbf{k}} &= \frac{1}{z}\sum_{\delta} \exp(i\hat{\mathbf{k}}) = \cos\frac{\hat{k}_x}{2}\cos\frac{\hat{k}_y}{2}\cos\frac{\hat{k}_z}{2}, \qquad (20)
\end{aligned}
$$

with δ denoting summation over next neighbors in the Pr sublattice, and where the normalization $\hat{\mathbf{k}} = (2\pi/a)\mathbf{k}$ has been chosen. The bilinear Hamiltonian of Eq. (20) can be diagonalized by a generalized Bogoliubov transformation in the same manner as was described in Ref. 5 for the dispersionless model. The details will not be repeated here. The eigenvalues in the dispersive model are simply obtained by replacing the local singlet-triplet energy by the dispersive quadrupolar exciton according to $\Delta \to \Delta_{\mathbf{k}}$, with

$$\Delta_{\mathbf{k}} = [\Delta(\Delta + 2A_{\mathbf{k}})]^{\frac{1}{2}}. \qquad (21)$$

This leads to the dispersive and T-dependent vibronic mode energies given by

$$
\begin{aligned}
\Omega_{\mathbf{k}s}(T) = 2\Bigg\{ & \frac{1}{2}\left(\frac{\omega_e(T)^2}{4} + \frac{\Delta_{\mathbf{k}}^2}{4}\right) \pm \frac{1}{2}\Bigg[\left(\frac{\omega_e(T)^2}{4} - \frac{\Delta_{\mathbf{k}}^2}{4}\right)^2 \\
& + 4\hat{g}_0^2\omega_e(T)\Delta\Bigg]^{\frac{1}{2}}\Bigg\}^{\frac{1}{2}}. \qquad (22)
\end{aligned}
$$

Note that in the last term, the *bare* Δ has to appear. The effective temperature dependence of normal-mode energies enters through that of the effective anharmonic rattling frequency $\omega_e(T)$, which is still determined by the self-consistency relation of Eq. (11). However, the anharmonic parameter and occupation function $\beta_r, \bar{n}$, respectively, are now given by the following more general relation that also involves summation over momentum in addition to mode indices:

$$\beta_r(T,\gamma) = \beta\frac{1}{N}\sum_{\mathbf{k}s} u_{r\mathbf{k}s}^2, \bar{n} = \sum_{\mathbf{k}s} n_{\mathbf{k}s} u_{r\mathbf{k}s}^2 \Big/ \sum_{s\mathbf{k}} u_{r\mathbf{k}s}^2. \qquad (23)$$

The transformation coefficients $u_{r\mathbf{k}s}$ and occupation numbers $n_{\mathbf{k}s}$ are obtained from Eqs. (9) and (10) simply by substituting $\Omega_s \to \Omega_{\mathbf{k}s}$. For the numerical calculations, as long as the dispersion is moderate and far from the soft-mode regime, the effective $\omega_e(T)$ may still be calculated from the dispersionless expression in Eq. (11).

Using the previous results, we can now discuss the anharmonic and dispersive effects in the vibronic spectrum as they should appear in the dipolar or phonon-scattering cross section. The former is given by the response function (mode index n suppressed i.f.),

$$\chi_D(\mathbf{k},\omega) = ib_D^2\int_{-\infty}^{\infty} dt e^{i\omega t}\langle[(a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger)_t,(a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger)_0]\rangle\theta_H(t). \qquad (24)$$

Here, b_D is the dipolar singlet-triplet matrix element and θ_H is the Heaviside function. In complete analogy to the dispersionless case, the corresponding spectral function $S(\mathbf{k},\omega) = 2(1 - e^{-\beta\omega})^{-1}\chi_D(\mathbf{k},\omega)''$ may be computed by transforming to the normal coordinates according to

$$a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger = u_{D\mathbf{k}\phi}(\phi_{\mathbf{k}} + \phi_{-\mathbf{k}}^\dagger) + u_{D\mathbf{k}\psi}(\psi_{\mathbf{k}} + \psi_{-\mathbf{k}}^\dagger), \qquad (25)$$

with the dipolar spectral weights of modes $s = \phi,\psi$ given by

$$u_{D\mathbf{k}s}^2 = \frac{\Omega_{\mathbf{k}s}}{\Delta}\frac{\left(\omega_e^2 - \Omega_{\mathbf{k}s}^2\right)^2}{\left(\omega_e^2 - \Omega_{\mathbf{k}s}^2\right)^2 + \gamma^2\Delta\omega_e}. \qquad (26)$$

For positive frequencies, the spectral function is explicitly given by

$$
\begin{aligned}
S_D(\mathbf{k},\omega) = 2\pi b_D^2 \sum_s & \frac{\Omega_{\mathbf{k}s}}{\Delta}\frac{(n_{\mathbf{k}s} + 1)\left(\omega_e^2 - \Omega_{s\mathbf{k}}^2\right)^2}{\left(\omega_e^2 - \Omega_{s\mathbf{k}}^2\right)^2 + \gamma^2\Delta\omega_e} \\
& \times \frac{\Gamma_s/\pi}{\left(\omega - \Omega_{\mathbf{k}s}\right)^2 + \Gamma_s^2}. \qquad (27)
\end{aligned}
$$

Here it is assumed that the phenomenological mode broadening Γ_s does not appreciably depend on momentum

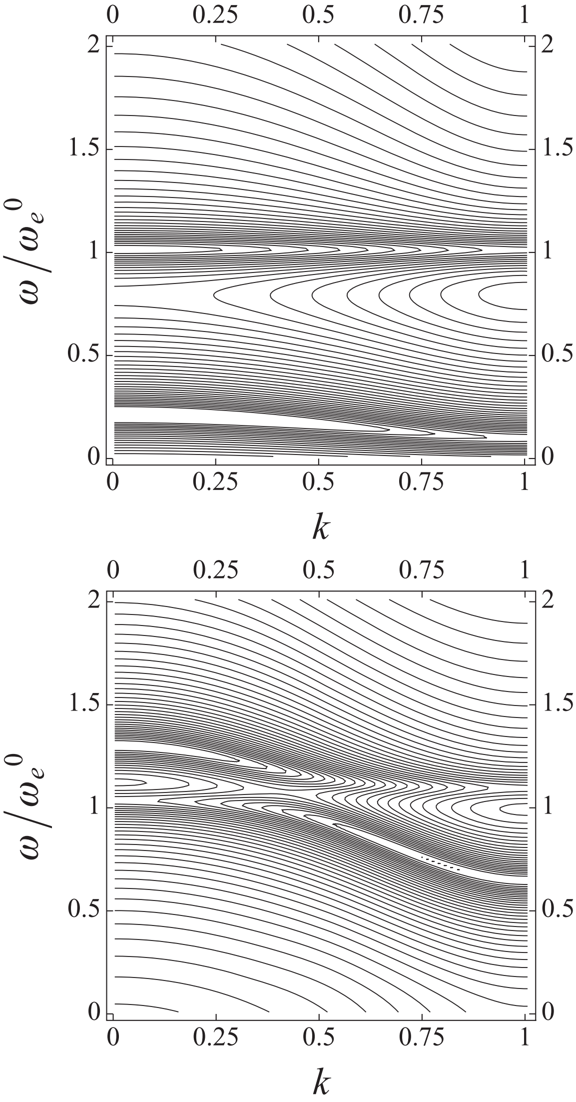

FIG. 4. Contour plot of the *logarithm* of the dynamical structure function $S_D(\mathbf{k},\omega)$ (in units of b_D^2) for $\mathbf{k} = (k,0,0)$ with $\beta = 0.3$, $\gamma = 0.2$, $\Gamma/\omega_e^0 = 0.05$, and k in units of $2\pi/a$. (a) Off-resonant case $x = 0$, $T = 0$: quadrupolar exciton band is located around $\omega/\omega_e^0 \simeq 0.2$ and small spectral weight is shifted to $T = 0$ phonon energy ω_E^0. (b) Resonant case $x = 0.65$ and $T/\omega_e^0 = 1$: Vibronic mode splitting around anharmonic $\omega_e(T) > \omega_e^0$ occurs. For $T > 0$, the anticrossing point is therefore shifted to $k < 0.5$.

k and mode index s. The temperature dependence of $S_D(\mathbf{k},\omega)$ appears explicitly through the Bose factors in the above expression and through the effective $\omega_e(T)$, and also via $\Omega_{\mathbf{k}s}(T)$ given by Eq. (22), which is caused by the anharmonic term in the Hamiltonian. The rattling phonon propagator is associated with a similar and complementary spectral function.

The dipolar spectral function relevant for INS is shown in Figs. 4 (in logarithmic scale) for the pure $\mathrm{PrOs_4Sb_{12}}$ ($x = 0$) off-resonant case and the resonant case with $\omega_e^0 = \Delta(x)$ ($x \approx 0.65$). In the former, one has the low-lying quadrupolar exciton band around $\omega/\omega_e^0 \simeq 0.2$ found in Ref. 20. Due to the finite vibronic coupling γ, a small part of the spectral weight is shifted to the rattling phonon frequency, which is exactly at ω_e^0 because of $T = 0$. In the latter (resonant case at $x \simeq 0.65$), the mode mixing of phonons and singlet-triplet excitations caused by $\gamma > 0$ is evident. It is assumed that the intersite interaction $\tilde{D}_Q$ scales with Δ. For this case, the anticrossing of vibronic modes when $\gamma > 0$ is exactly halfway in the Brillouin zone at $\mathbf{k} = (\pi/a,0,0)$ when $T = 0$. When T increases, $\omega_e(T) > \omega_e^0$ is increasing due to the anharmonic effect of nonzero β, therefore the vibronic coupling becomes slightly off-resonant. Consequently, the anticrossing point will shift to a smaller k vector. If this effect were identified in INS experiments, it would be direct evidence for the importance of anharmonic coupling in the mixed-mode spectrum. It would be much more dramatic with a complete vanishing of the mode splitting for a larger β.

VI. CONCLUSION AND OUTLOOK

We have investigated the simultaneous effects of anharmonic rattling phonons, the vibronic phonon–4f-electron interactions in Pr skutterudites, $\mathrm{Pr(Os_{1-x}Ru_x)_4Sb_{12}}$ and the 4f-intersite-quadrupolar interactions. This work presents a unified and self-consistent treatment of all terms that have been considered only separately in previous analyses.

It was found that the temperature dependence of effective quasiharmonic phonon frequency is considerably influenced by the coupling to CEF excitations, in particular for moderate x when the singlet-triplet splitting is small, and therefore the mixed-mode phononic spectral function obtains a low-energy contribution. The latter can be tuned by the 4f-phonon interaction leading to pronounced effects in the effective phonon frequency. This effect is diminished for larger x when the CEF splitting increases.

The same holds true for the γ dependence of the phonon-Raman contribution to the NMR and NQR relaxation rate. Because the anharmonicity parameter $\beta = 0.3$ is quite moderate in $\mathrm{PrOs_4Sb_{12}}$, the rate $1/T_1^R T$ still increases with temperature and is far from the saturation limit of the strongly anharmonic case.[8] However, β is already large enough to observe distinct deviations from the $\sim T$ behavior of the purely harmonic phonon-Raman contribution. Furthermore, in the resonance region, it consists of two contributions, namely, the direct and cross parts due to the vibronic mode splitting. It should be noted that the phonon-Raman contribution in $\mathrm{PrOs_4Sb_{12}}$ is difficult to extract because the total relaxation is dominated by the local-moment fluctuation part and the Korringa part from the heavy itinerant electrons.

The low-lying CEF singlet-triplet excitations in $\mathrm{PrOs_4Sb_{12}}$ have a distinct dispersion due to intersite quadrupolar interactions found in INS,[20] which may also be expected to exist in the mixed $\mathrm{Pr(Os_{1-x}Ru_x)_4Sb_{12}}$ compounds. For $x \approx 0.65$ close to the resonance condition of singlet-triplet and rattling phonon energy, the nonadiabatic or vibronic effects will lead to a typical splitting of these dispersive modes as a function of the wave vector **k**. The observation of this effect and of the temperature dependence of the anticrossing point (Fig. 4) and redistribution of the spectral shape (Fig. 2) by INS would be the most direct confirmation of the coupling of anharmonic rattling phonons and 4f CEF interactions in rare-earth skutterudites.

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