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Probing the Coulomb interaction of $PuCoGa_5$ by phonon spectroscopy

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Abstract

The phonon dispersion curves of the unconventional superconductor $PuCoGa_5$ were studied by inelastic X-ray scattering at room temperature. The experimental data agree well with *ab initio* lattice dynamics calculations. An accurate theoretical description of the phonon spectrum is obtained only when a local Coulomb repulsion $U \approx 3$ eV among 5f electrons is taken into account. This implies partial localization of the 5f electrons in this compound. A comparison made with the phonon spectrum of $UCoGa_5$ suggests that the latter compound is better described with a fully itinerant f electrons model.

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Keywords: Superconductivity; Phonon spectrum; *Ab initio* calculation

1. Introduction

Given its characteristic energy scales (Sommerfeld coefficient, $\gamma = 77$ mJ/mol K^2; superconducting transition temperature, $T_c = 18.5$ K), the unconventional superconductor $PuCoGa_5$ is playing the central role of a missing link between the canonical heavy fermion (HF) superconductors and the high-T_c cuprates [1]. The understanding of its physical properties could thus allow one to make progress in the global understanding of unconventional superconductivity. While a magnetic mechanism for the electron pairing is strongly suggested, the study of the phonon spectrum is nonetheless of interest. The first reason is that there is no definitive conclusive evidence of magnetically mediated superconductivity for this compound as well as for other HF materials and high-T_c cuprates [2]. It is also worthwhile to note that the high value of T_c in $PuCoGa_5$ is in the range of conventional superconductors like Nb_3Sn ($T_c = 18$ K) or MgB_2 ($T_c = 39$ K). The second interest in determining the lattice dynamics of $PuCoGa_5$ stems from the tremendous recent progress in band structure calculations that allow one to compute accurately phonon spectrum of actinide based strongly correlated electron systems [3,4]. In Ref. [5], a comparison between the phonon spectrum of $PuCoGa_5$ determined by inelastic X-ray scattering (IXS) with an *ab initio* density functional theory (DFT) calculation [4], using the generalized gradient approximation with finite U (GGA + U) method, emphasizes the fact that the phonon spectrum is sensitive to details of the electronic structure. In particular, it is influenced by the on-site Coulomb repulsion U between f electrons.

In the present paper, we review the outcome of Ref. [5] that shows that the inclusion of Coulomb interaction U of approximately 3 eV is essential to describe quantitatively the lattice dynamics of $PuCoGa_5$. Further details on the experimental method used are given in the present paper with more detailed analysis of the phonon intensities. Finally, a discussion of the localization of the f electrons is made together with a comparison with the phonon spectrum of $UCoGa_5$ determined by inelastic neutron scattering [6].

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2. Experimental details

$PuCoGa_5$ crystallizes in the tetragonal $P4/mmm$ space group with the lattice parameters $a = 4.232$ Å and $c = 6.786$ Å. The Brillouin zone is shown in Fig. 1. The ^{242}Pu-based single crystals were grown at the Institute for Transuranium Elements by the Ga flux method as described elsewhere [7], and encapsulated in order to comply with safety regulations. Three rectangular shaped samples were investigated: two with the [0 0 1] direction normal to the platelet in reflection and transmission geometry and one with the [1 0 0] direction normal to the platelet in transmission geometry. The dimensions of these samples are: 1.3 mm × 0.55 mm × 0.33 mm, 0.5 mm × 1 mm× 0.04 mm, and 0.5 mm × 0.15 mm × 0.02 mm, respectively. The samples in transmission geometry have thus a thickness of about 30 μm that is approximately the optimal value given the X-ray absorption by Pu for the incident energy that was used (21.747 keV). The IXS measurements were carried out on the undulator beamline ID28 at the European Synchrotron Radiation Facility, Grenoble. IXS is a powerful method to determine the lattice dynamics of single crystals whenever these are only available in small quantities or when high hydrostatic pressure conditions are needed [8]. For the present experiment, details of the beamline setup are given in Ref. [5]. The corresponding nominal instrumental energy resolution was 1.5 meV. The three encapsulated samples allow one to investigate all the phonon modes along the [1 0 0], [1 1 0] and [0 0 1] directions. The measured sample mosaicity was typically 0.03–0.1°. For the low energy (ω) modes both the energy-loss (Stokes) and energy-gain (anti-Stokes) part of the IXS spectra were recorded. For the higher energy modes, only the Stokes side was measured with the central line of the neighboring scan serving as a reference for the zero-point of the energy scale. This elastic line corresponds to background arising mostly from the diffuse elastic scattering of the Kapton coating of the samples. The one-phonon X-ray scattering cross section for a phonon of wavevector $\mathbf{q}$ in branch j with energy $\omega_j(\mathbf{q})$ [9] is proportional to the scattering function $S_j(\mathbf{Q}, \omega)$ that is the product of the dynamical structure factor $G_j(\mathbf{Q}, \mathbf{q})$ and a spectral weight function $F_j(\omega, \omega_j(\mathbf{q}), T)$ with :

$$G_j(\mathbf{Q}, \mathbf{q}) = \left| \sum_{\mathrm{d}}^{\text{unit cell}} f_{\mathrm{d}}(\mathbf{Q}) \mathrm{e}^{-W_{\mathrm{d}}(\mathbf{Q})} [\mathbf{Q} \cdot \mathbf{e}_{\mathrm{d},j}(\mathbf{q})] M_{\mathrm{d}}^{-1/2} \, \mathrm{e}^{i\mathbf{Q}\mathbf{R}_{\mathrm{d}}} \right|^2 \quad (1)$$

$$F_j(\omega, \omega_j(\mathbf{q}), T) = \frac{\langle n_j \rangle + (1/2) \pm (1/2)}{\omega_j(\mathbf{q})} \delta(\omega \mp \omega_j(\mathbf{q})) \quad (2)$$

Here F_j is written for undamped phonons, $f_{\mathrm{d}}(\mathbf{Q})$ the atomic form factor of atom d with mass M_{d} at position $\mathbf{R}_{\mathrm{d}}$, $\mathbf{e}_{\mathrm{d},j}(\mathbf{q})$ is the normalized eigenvector for atom d in branch j, $\mathrm{e}^{-W_{\mathrm{d}}(\mathbf{Q})}$ the Debye–Waller factor and $\langle n_j \rangle$ is the Bose population factor. The momentum transfer, $\mathbf{Q}$, is $\mathbf{Q} = \boldsymbol{\tau} + \mathbf{q}$, where $\boldsymbol{\tau}$ is a Brillouin zone center. In this paper q is expressed in reciprocal lattice units (r.l.u.).

The choice for measuring the phonon branches was guided by two factors: the possible experimental geometry (governed by the maximum available scattering angles, the dead angles of the sample capsules, the possible contamination of analyzers by strong Bragg peaks) and the intensity calculation provided by the lattice dynamics model. A typical accessible area of reciprocal space in the (a, b) plane is shown in Fig. 2. The dashed line corresponds to a path Γ-M-Γ-M-Γ in reciprocal space for which intensity calculation is shown in Fig. 3. Representative scans along this path are shown in Fig. 4. All the phonon spectra were found to be resolution limited excluding thus, within the resolution achieved, the discussion of possible broadening effects. Consequently, the data were analyzed by using a Lorentzian that reproduces the ID28 experimental resolution function for the δ function in Eq. (2).

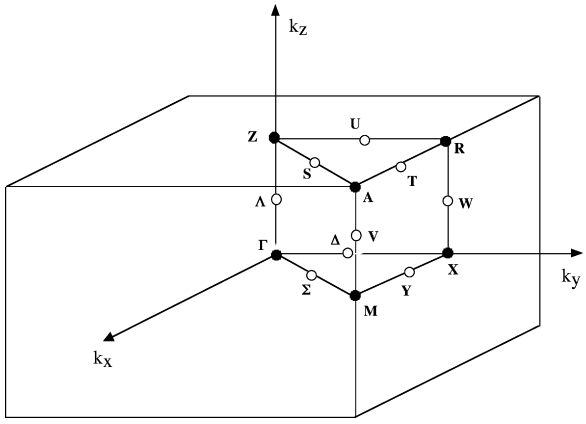

Fig. 1. Brillouin zone of the $P4/mmm$ space group.

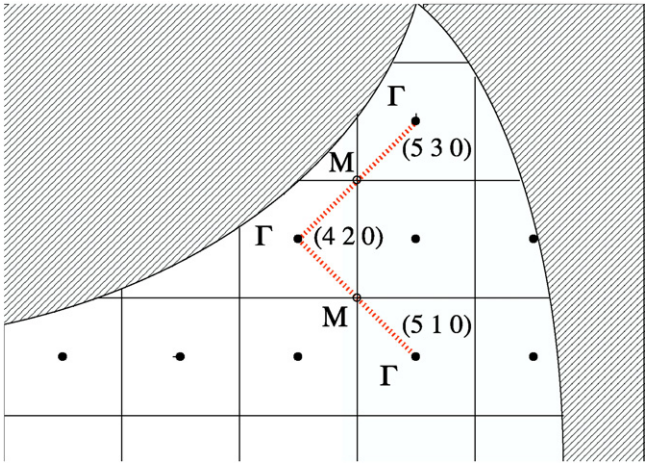

Fig. 2. Example of accessible measurement zone in the (a, b) plane. The hatched area corresponds to forbidden zone due to the experimental setup. The dashed line corresponds to a path in reciprocal space for which intensity calculation is provided in Fig. 3.

3. Lattice dynamics calculation

The phonon frequencies calculation within the *ab initio* direct method [10] is developed in Ref. [4] and summarized below. The crystal structure was optimized using the projector augmented-

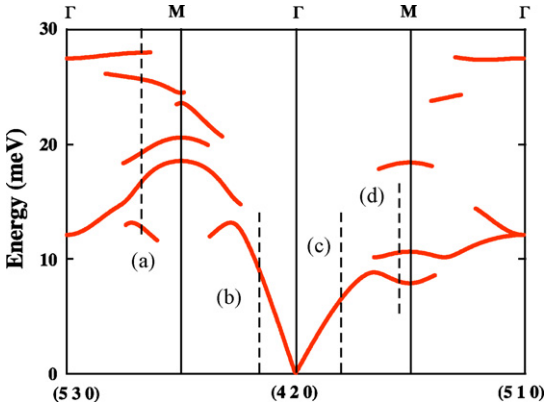

Fig. 3. Modes with strong dynamical structure factors (see text) from *ab initio* lattice dynamics model with $U = 3$ eV for the path in reciprocal space Γ-M-Γ-M-Γ shown in Fig. 2.

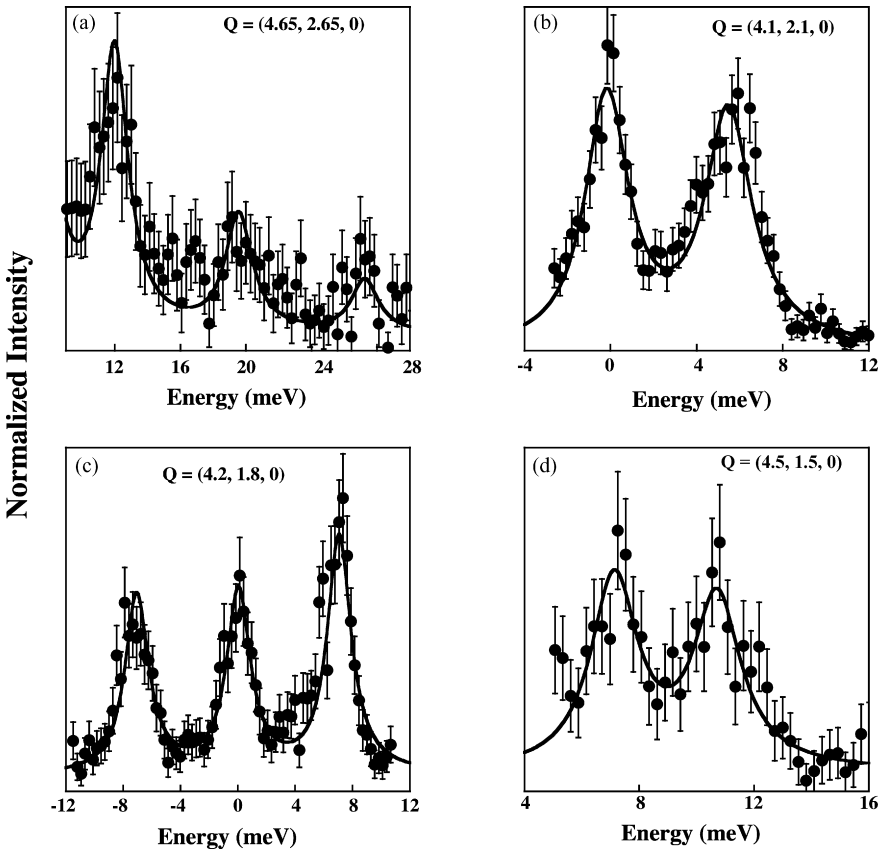

Fig. 4. IXS phonon spectra of $PuCoGa_5$ measured at $T = 297$ K. The four panels correspond to scans shown in Fig. 3, the dashed line on that figure being their ω range.

wave GGA potentials [11]. Two parameters characterizing on-site Coulomb interactions of the Pu(5f) electrons were included: Coulomb element U and Hund's exchange J. The calculations were performed for two electronic ground states: nonmagnetic state for $U = J = 0$ and a ferromagnetic state for $U = 3$ eV and $J = 0.7$ eV. The latter state simulates the formation of local moments at Pu ions for finite U. The lattice parameters $a = 4.246$ Å and $c = 6.917$ Å obtained for $U = 3$ eV show good agreement with the experimental data [4]. Using this *ab initio* input, the force constants and dynamical matrices were computed by using the software PHONON [12]. Fig. 3 shows the modes with strongest dynamical structure factors $G_j(\mathbf{Q}, \mathbf{q})$ calculated from the model with $U = 3$ eV. On this graph, a single color represents all the modes having intensities above 15% of the maximum intensity for the line Γ-M-Γ-M-Γ of the (a, b) plane drawn in Fig. 2. In the calculation $f_d(\mathbf{Q})$ is replaced by the atomic number Z_d, its $Q = 0$ limit. Comparison with measured intensities is given below.

4. Phonon spectra

Representative spectra are shown in Fig. 4. The panels correpond to the cut (a–d) of Fig. 3 for the wavevectors $\mathbf{Q} = (4.65, 2.65, 0)$, $\mathbf{Q} = (4.1, 2.1, 0)$, $\mathbf{Q} = (4.2, 1.8, 0)$ and $\mathbf{Q} = (4.5, 1.5, 0)$ that allow one to measure predominantly LO, LA, TA and TO modes, respectively. The comparison between the measured intensities and the calculated ones (with $U = 3$ eV) is shown in Table 1. The experimental structure factor is determined from the measured peak intensity, I_{meas}, after background subtraction by $I_{meas} \times \omega_j(\mathbf{q})/(\langle n_j \rangle + 1)$. The experimental data are normalized to the calculated value for the TA mode at $\mathbf{Q} = (4.2, 1.8, 0)$ and 7.1 meV. There is relatively good agreement between measured and calculated values given the experimental error bars. Discrepancy occurs for the highest LO mode at $\mathbf{Q} = (4.65, 2.65, 0)$ and 27.3 meV that is barely measurable.

The intensity calculation provided by the *ab initio* model in conjunction with a group theory analysis of the data (see Ref. [5]) allow a straightforward assignment of the phonon branches. Details of the comparison of the measured phonon spectra and the *ab initio* calculations with $U = 0$ and 3 eV are given in Ref.

Table 1
Comparison between measured and calculated dynamical structure factors with $U = 3$ eV for the data shown in this paper

$\mathbf{Q}$	$\mathbf{q}$	$\omega_j(\mathbf{q})$	$G_j^{calc}(\mathbf{Q}, \mathbf{q})$	$G_j^{exp}(\mathbf{Q}, \mathbf{q})$
(4.65, 2.65, 0)	0.35	11.6(4)	23.33	34(10)
(4.65, 2.65, 0)	0.35	19.6(7)	39.85	32(10)
(4.65, 2.65, 0)	0.35	27.3(8)	59.76	22(15)
(4.1, 2.1, 0)	0.1	5.42(13)	124.05	88(20)
(4.2, 1.8, 0)	0.2	7.1(1)	113.64	113(20)
(4.5, 1.5, 0)	0.5	7.1(4)	27.44	24(10)
(4.5, 1.5 , 0)	0.5	11.3(6)	45.85	43(20)

$\omega_j(\mathbf{q})$ is the experimental value in meV. Normalized calculated ($G_j^{calc}(\mathbf{Q}, \mathbf{q})$) and experimental ($G_j^{exp}(\mathbf{Q}, \mathbf{q})$) structure factors are given in arbitrary units.

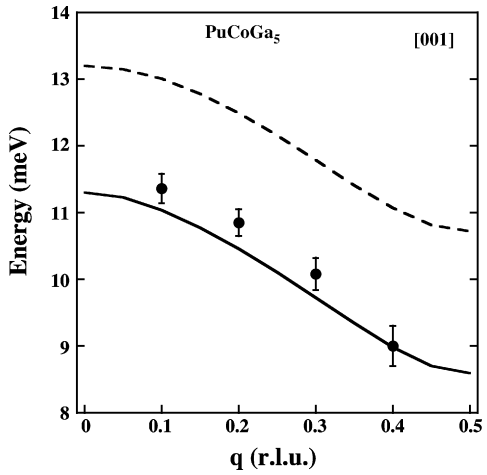

Fig. 5. Dispersion of the TO mode propagating along [0 0 1] and polarized along [1 0 0] for $PuCoGa_5$ at 297 K. The solid (dashed) line corresponds to the *ab initio* calculation with $U = 3$ eV ($U = 0$ eV).

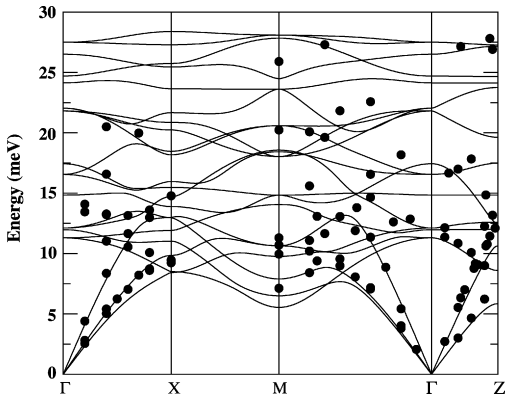

Fig. 6. Measured (full circles) and calculated (lines) phonon dispersion relations with $U = 3$ eV along the principal symmetry directions for $PuCoGa_5$.

[5]. It is unambiguously concluded from this comparison that the model with $U = 3$ eV better describes the data. This conclusion is basically drawn from the lowest energy TO modes that are the most sensitive ones to electron redistribution due to increasing Coulomb repulsion. Such an effect is shown in Fig. 5 in the [0 0 1] direction for the lowest energy TO mode with polarization along [1 0 0]. The experimental points are the IXS data and the full (resp. dashed) line is the calculation with $U = 3$ eV (resp. $U = 0$ eV). Much better agreement is obtained for $U = 3$ eV. This conclusion is also supported by other modes in the [0 0 1], [1 0 0] and [1 1 0] directions [5].

The changes in phonon frequencies induced by U can be explained by two mechanisms. The stronger electron repulsion leads to larger lattice constants and lower phonon energies. This effect, however, cannot explain large changes observed for some TO modes. The other mechanism is connected with the modification of electronic states on Pu atoms. With increasing U, the f states becomes partially localized, and this directly influences interatomic forces. A significant reduction of force constants, observed for Ga atoms located in the Pu–Ga planes, induces further softening of the lowest TO modes; in particular the one propagating along the [1 0 0] direction with polarization along [0 0 1] [4]. The overall dispersion of the branches together with the *ab initio* calculation with $U = 3$ eV is shown in Fig. 6.

5. Discussion

The satisfactory agreement between the full experimental phonon spectrum determined by IXS and the *ab initio* lattice dynamics calculation proves that electron correlation effects between nearly localized 5f electrons due to finite $U = 3$ eV are essential. This further supports the evidence for localized 5f degrees of freedom in $PuCoGa_5$ deduced from the temperature dependence of the magnetic susceptibility [13], as well as from DFT calculations which found a magnetically ordered ground state [4,14]. Therefore, we conclude that purely DFT methods, such as local density approximation (LDA) or GGA, that neglect strong electron interactions are insufficient. To this respect, photoemission data underline the existence of two separate regions of 5f electron spectral intensity corresponding to localized and itinerant degrees of freedom that cannot be described by an itinerant GGA method [15]. One can resolve this difficulty within the GGA + U method which includes the electron correlations in a mean-field way, similar to LDA + U [16]. Other possible description of the photoemission data is provided by the mixed level model (MLM) that assumes explicitly two types of electrons from the beginning [15].

Note that in magnetic systems, local f electron degrees of freedom can be well controlled in local spin density approximation (that includes spin polarization and spin–orbit interaction) with finite U (LSDA + U). In the case of $PuCoGa_5$ [14], it gives better results than LSDA calculation [17]. While LSDA + U takes into account static correlations between f electrons, further refinement is provided by including the dynamical correlations due to local Coulomb interaction within the dynamical mean-field theory (DMFT) [18].

DMFT was also sucessfully used recently beyond DFT to explain quantitatively the equilibrium properties and the measured phonon spectrum of δ-plutonium [3,19]. In particular, the lattice model describes fairly well a kink in the lowest TA branch along [0 1 1] and the softening of the TA branch near the [1 1 1] zone boundary. The need of using here a DMFT approach rather than LDA + U (or GGA + U) stems from the complexity of δ-Pu that lies in the vicinity of a Mott transition. The present study shows that $PuCoGa_5$ is a simpler system owing to its rather conventional phonon spectrum. Another case of complex phonon spectrum arising in actinides is the one α-uranium [20] with low temperature softening ($T < 43$ K) associated with the formation of charge density wave and high temperature effects associated either with electronic properties [21] ($T > 50$ K) or new localized mode ($T \approx 450$ K) [22]. *Ab initio* lattice dynamics calculation for this compound is presented using density functional perturbation theory (DFPT) in the present proceedings [23]. The case of α-uranium emphasizes that temperature effects can be very important for actinides. Such an issue for $PuCoGa_5$ is postponed for further studies to be performed however rather at low temperature in the superconducting phase.

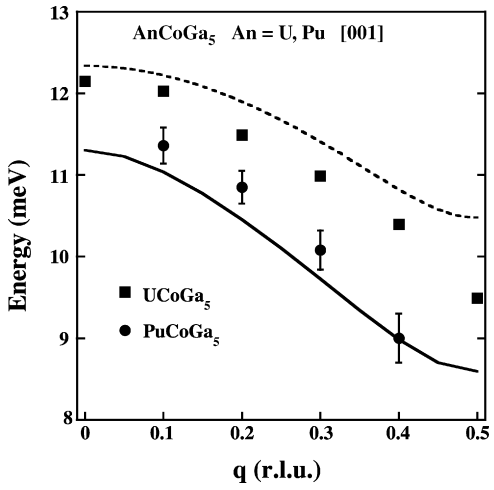

Fig. 7. Dispersion of the TO mode propagating along [0 0 1] and polarized along [1 0 0] for $PuCoGa_5$ (circles) and $UCoGa_5$ (squares) at 297 K. The solid (dashed) line corresponds to the *ab initio* calculation for $PuCoGa_5$ with $U = 3$ eV ($UCoGa_5$ with $U = 0$ eV).

6. Comparison with $UCoGa_5$

Because of the well-known localization transition that occurs within the actinide series between Pu and Am [24], it is highly desirable to tighten our determination of the role of the Coulomb interaction by a systematic study of the lattice dynamics of the $AnCoGa_5$ series with $An = U$, Np, Am in relation to the different physical properties of each compound. To achieve this goal, the phonon spectrum of $UCoGa_5$ was measured by inelastic neutron scattering [6]. It was shown that a similar *ab initio* calculation but with a purely itinerant GGA approach with $U = 0$ provides a good description of the phonon spectrum. A comparison of the lowest TO branch propagating along [0 0 1] and polarized along [1 0 0] is shown in Fig. 7 for $PuCoGa_5$ and $UCoGa_5$ together with the two corresponding *ab initio* calculations that better describe the data.

While $UCoGa_5$ and $PuCoGa_5$ have rather similar lattice parameters, the lattice dynamics of the two compounds is distinct and stems from their remarkably different electronic properties. Indeed, in contrast to $PuCoGa_5$, $UCoGa_5$ is an itinerant electron paramagnet with a weak temperature dependence of the magnetic susceptibility and a low Sommerfeld coefficient, $\gamma \approx 10$ mJ/mol K^2 [25], indicating that the localized f degrees of freedom are absent. This itinerant nature is also supported by photoemission spectroscopy on $UCoGa_5$ [26] that even suggests the proximity to a valence instability. Angle resolved photoemission spectroscopy performed on the similar compound $UFeGa_5$ ($\gamma = 40$ mJ/mol K^2) also suggests an itinerant behavior for this latter compound with a description of the spectra at the LDA level [27]. While taking $U \approx 0$ for $UCoGa_5$ is suprising at first sight, values of U quite different from the "atomic-like" value could be found in itinerant systems due to enhanced screening. This emphazises the idea that 5f electrons exhibit metallic behavior in uranium, while they are more localized in plutonium compounds. The values of U determined in the present study must be taken with caution since the calculation does not consider spin–orbit coupling. With the present method, including such a term leads to instability in the phonon spectrum calculation. The importance of spin–orbit coupling for Pu with respect to the problem of 5f electron localization is pointed in X-ray absorption and electron energy-loss spectroscopy studies [28,29]. Spin–orbit should affect phonon spectra in a similar way than U. This issue deserves future development of the present calculation method.

7. Conclusion

The phonon spectrum of $PuCoGa_5$ measured by IXS is accurately described by a direct force constant method that starts from an *ab initio* GGA + U electronic structure calculation. The comparison of experimental data with this calculation validates a model with a Coulomb interaction $U = 3$ eV. This conclusion is primarily drawn from the sensitivity of the lowest TO modes to the Coulomb repulsion. This result implies that a certain amount of localization of f electrons in $PuCoGa_5$ in contrast to the itinerant nature of the f electron inferred for $UCoGa_5$ by using the same comparison between lattice dynamics and GGA calculation. In this way the dual nature, localized versus itinerant, of f electrons is demonstrated. This observation is further supported by photoemission data.

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