Probing the Coulomb Interaction of the Unconventional Superconductor $PuCoGa_5$ by Phonon Spectroscopy

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The phonon dispersion curves of the 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 description of the phonon spectrum is obtained only when a local Coulomb repulsion $U \approx 3$ eV among $5f$ electrons is taken into account.

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The discovery of superconductivity in the plutonium based intermetallic compound $PuCoGa_5$ came as a surprise with regard to the high transition temperature $T_c = 18.5$ K for an actinide material [1]. The analogy with the isostructural heavy fermion superconducting compound $CeCoIn_5$ ($T_c = 2.3$ K) strongly suggests a magnetic mechanism for the electron pairing [2]. Nuclear magnetic resonance (NMR) measurements [3] underline the presence of magnetic fluctuations above T_c, as well as an overall behavior below T_c that is compatible with d-wave pairing. $PuCoGa_5$ seems thus to be similar to other heavy fermion superconductors (HFS) except for its high T_c and rather low linear specific heat coefficient $\gamma = 77$ mJ/mol K^2 ($\gamma = 1000$ mJ/mol K^2 for $CeCoIn_5$). A moderate γ implies a high characteristic temperature of spin fluctuations, $T_{sf} \propto \gamma^{-1}$, that leads to high values of T_c in the theory of magnetically mediated superconductivity. $PuCoGa_5$ thus somehow bridges a gap between the canonical HFS ($T_c \simeq 0.5$ K, $T_{sf} \approx 10$ K) and the high-T_c cuprates ($T_c \simeq 100$ K, $T_s \approx 1000$ K) [3].

However, this unified picture is still not perfect since there is no conclusive evidence of magnetically mediated superconductivity both for HFS and for high-T_c cuprates. For example, the role of phonons for the pairing mechanism of the latter family of compounds with respect to magnetic fluctuations is still under debate [4]. 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). For these reasons and in view of the emergence of a global picture of unconventional superconductivity, the study of the phonon spectrum of $PuCoGa_5$ is of crucial importance. The understanding of strongly correlated electron systems beyond this phenomenological approach, based on similarities between several families of systems (HFS, high-T_c cuprates) and on consistencies in energy scales, asks for microscopic input. The dual nature of the f electrons (itinerant vs localized), the strong correlations among them, and the hybridization with conduction electrons in f electron based intermetallic compounds has always been a challenge for theoretical methods of band structure calculations. However, the recent advances in this field are tremendous and allow one to consider precise experimental confrontation.

In this Letter we show that the phonon spectrum of $PuCoGa_5$, determined by inelastic x-ray scattering (IXS), is sensitive to details of the electronic distribution and is therefore influenced by the on-site Coulomb repulsion U between f electrons. 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 [5]. By comparing the IXS data with a density functional theory (DFT) calculation [6], using the generalized gradient approximation with finite U (GGA + U) method, we conclude that the inclusion of Coulomb interaction U of approximately 3 eV is essential to describe quantitatively the lattice dynamics of $PuCoGa_5$.

$PuCoGa_5$ crystallizes in the tetragonal $P4/mmm$ space group with the lattice parameters $a = 4.232$ Å and $c = 6.786$ Å. 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 [001] direction normal to the platelet in reflection and transmission geometry and one with the [100] direction normal to the platelet in transmission geometry. The dimensions of these samples are $1.3 \times 0.55 \times 0.33$ mm^3, $0.5 \times 1 \times 0.04$ mm^3, and $0.5 \times 0.15 \times 0.02$ mm^3. 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. The IXS measurements were carried out on the

undulator beam line ID28 at the European Synchrotron Radiation Facility, Grenoble. The incident beam was monochromatized by a perfect plane silicon crystal working in extreme backscattering geometry at the (11,11,11) reflection (21.747 keV). The monochromatic beam was focused onto the sample position by a toroidal mirror into a 250×80 μm^2 spot. The scattered photons were analyzed by a bank of five spherically bent high-resolution silicon analyzers placed on a 7 m long horizontal arm. The analyzers are held one next to the other with a constant angular offset and operate in backscattering geometry at the same reflection order. The energy scans were performed by varying the monochromator temperature while keeping the analyzer crystals at fixed temperature. The nominal instrumental energy resolution achieved in this configuration is 1.5 meV. The three encapsulated samples allow one to investigate all the phonon modes along the [100], [110], and [001] directions. The measured sample mosaicity was typically 0.03–0.1°. For the low energy 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 phonon frequencies were calculated [6] using the *ab initio* direct method [8] that is summarized below. The crystal and electronic structures were optimized using the projector augmented-wave GGA potentials [9]. Two parameters characterizing on-site Coulomb interactions of the Pu ($5f$) electrons were included: intraorbital repulsion U and Hund's exchange J. The calculations were performed for two different 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 at finite U. A $2 \times 2 \times 1$ supercell was used to relax the atomic positions. The obtained lattice parameters $a = 4.246$ Å and $c = 6.917$ Å for $U = 3$ eV show good agreement with the experimental data. Using this *ab initio* input, the force constants and dynamical matrices were obtained from nine atomic displacements equal to 0.02 Å.

Representative spectra are shown in Fig. 1 for transverse acoustic (TA) and transverse optic (TO) modes for $\mathbf{Q} = (0, 4, 3 - q)$ and $\mathbf{Q} = (0, 4, 1 - q)$ [q is expressed in reciprocal lattice units (r.l.u.)]. The choice of the Brillouin zone was guided by the dynamical structure factor calculation of the model taking into account the geometrical constraints of the spectrometer. The calculated intensities are generally found to be in qualitative agreement with the data. In particular, the model reproduces the fact that the TA and TO peaks have similar intensities for $\mathbf{Q} = (0, 4, 0.6)$ while only the TA mode is observed for $\mathbf{Q} = (0, 4, 0.5)$ (See Fig. 1). Prior to comparing the obtained dispersions with the theoretical predictions, we classify the

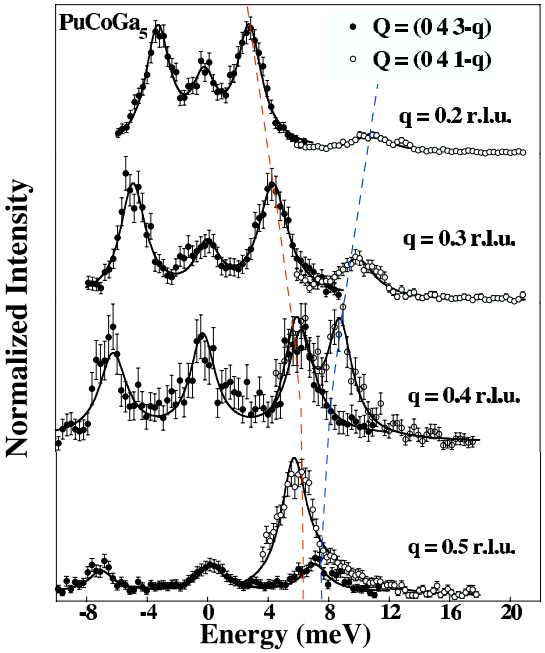

FIG. 1 (color online). IXS phonon spectra of $PuCoGa_5$ measured at $T = 297$ K. The full symbols correspond to mode measured at $\mathbf{Q} = (0, 4, 3 - q)$ and the empty symbols at $\mathbf{Q} = (0, 4, 1 - q)$. The dashed lines indicate the dispersion of the corresponding TA and TO modes.

phonon branches according to the irreducible representations to which they belong [10]. The decomposition of the 21 phonon branches along the [100] direction is $\Delta = 7\Delta_1 + 2\Delta_2 + 7\Delta_3 + 5\Delta_4$ and the one along [001] is $\Lambda = 5\Lambda_1 + 2\Lambda_4 + 7\Lambda_3$.

In the definition used here [10], the longitudinal acoustic (LA) modes are included in the representation with subscript 1. The representation Δ_3 contains the TA modes with polarization along the c axis and the Δ_4 one those polarized along the b axis. No acoustic modes correspond to the representation Δ_2. The representation Λ_3 contains the TA modes with polarization along the a axis. This representation is of second order in relation to the degeneracy between the a and b axis. No acoustic modes correspond to the representation Λ_4. The compatibility relations between the zone center Γ point (for which the decomposition is given in Ref. [6]) and the [100] and [001] directions are given in Table I. They express how an irreducible representation at the Γ point is further reduced along a less symmetric direction.

The comparison of the experimental data with the *ab initio* calculation for $U = 0$ and $U = 3$ eV is shown in Fig. 2 for the direction [100] and in Fig. 3 for [001]. For the [100] direction (Fig. 2), none of the TO modes in the Δ_3 and Δ_4 representations is reproduced for the calculation with $U = 0$, while the model with $U = 3$ eV describes well the lowest TO (Δ_3) mode polarized along the c axis. All three TO modes in Δ_4 are also in rather good agreement. For this direction the $U = 3$ eV model is clearly superior, even if one TO mode in Δ_3 is not so well repro-

TABLE I. Compatibility relations between the Γ point [6] and the [100] and [001] directions [10].

Γ	A_{1g}	B_{1g}	E_g	A_{2u}	B_{2u}	E_u
[100]	Δ_1	Δ_1	$\Delta_2 + \Delta_3$	Δ_3	Δ_3	$\Delta_1 + \Delta_4$
[001]	Λ_1	Λ_4	Λ_3	Λ_1	Λ_4	Λ_3

duced and if a small discrepancy remains for the higher energy part of the TA mode in Δ_3. The agreement between experiment and theory using $U = 3$ eV is also very satisfactory for the longitudinal optic and TO modes along the [001] direction (Fig. 3), while the TO modes do not agree with the calculations performed with $U = 0$. A somewhat worse agreement for the high energy part of the LA mode may be partly due to the larger discrepancy of about 2% between the theoretical and experimental lattice parameter for the c axis, while it is only 0.3% for the a axis [6]. Altogether, the data shown in Figs. 2 and 3 for [100] and [001] directions clearly demonstrate that the GGA + U calculations with $U = 3$ eV provides an accurate description of the lattice dynamics of $PuCoGa_5$. This conclusion is basically drawn from the lowest energy TO modes that are the most sensitive ones to electron redistribution due to a finite Coulomb repulsion. The same conclusion is made for a comparison (not shown) of the data to the different models for the [110] direction. The comparison of all the collected data with the model with $U = 3$ eV is shown in Fig. 4.

The overall softening of phonon frequencies for $U > 0$ results from reduced force constants due to modification of crystal geometry and electronic structure. However, the U dependence cannot be simply related to an increase in lattice constants and interatomic distances; the changes in lattice constants are very small (<2%)—while the differences in phonon frequencies approach even 30%. This demonstrates that force constants are strongly influenced by charge redistribution of the $5f$ states. Indeed, the

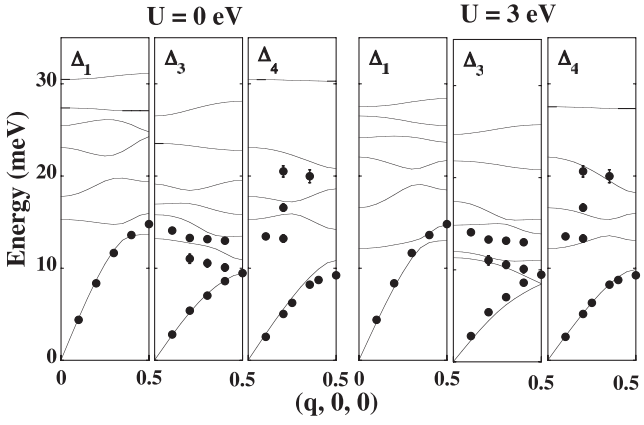

FIG. 2. Dispersion relations for the [100] direction. The experimental data (full circles) are compared with *ab initio* calculations for $U = 0$ and 3 eV. Branches are classified according to the irreducible representations along [100].

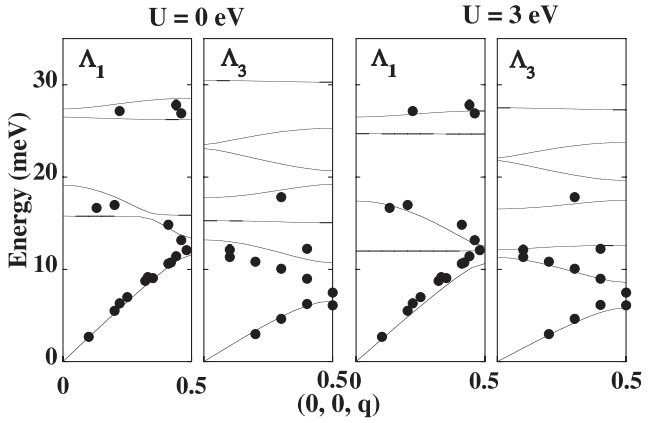

FIG. 3. Dispersion relation for the [001] direction. The experimental data (full circles) are compared with *ab initio* calculation for $U = 0$ and 3 eV. Branches are classified according to the irreducible representations along [001].

largest changes in force constants between $U = 0$ and $U = 3$ eV are observed for Ga atoms, located in Pu-Ga planes [6]. This explains a strong effect of U on the lowest TO modes with Λ_3 and Δ_3 symmetries, corresponding to in-plane and out-of-plane vibrations of Pu and Ga atoms, respectively. We also note that the measurements were done at room temperature, and the quantitative agreement between experiment and theory obtained here for $U = 3$ eV, may in reality require a somewhat different value of U. However, one expects that phonon frequencies will harden by not more than a few percent at low temperature (except for possible phonon anomalies at T_c), so that the main conclusion concerning the importance of local Coulomb interactions remains valid.

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

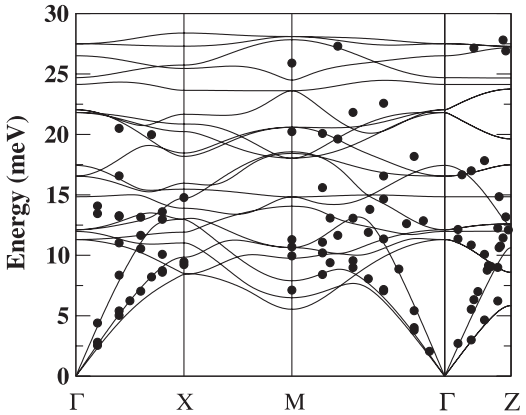

FIG. 4. Measured (full circles) and calculated (lines) phonon dispersion relations with $U = 3$ eV along the principal symmetry directions for $PuCoGa_5$.

$PuCoGa_5$ deduced from the temperature dependence of the magnetic susceptibility [1], as well as from DFT calculations which found a magnetically ordered ground state [6,11]. This demonstrates that purely DFT methods, such as local density approximation (LDA) or GGA, that neglect strong electron interactions are insufficient. In 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 [12]. One can resolve this difficulty within the GGA + U method which includes the electron correlations in a mean-field way, similar to LDA + U [13]. In magnetic systems, local f electron degrees of freedom can be well controlled in local spin density approximation with finite U (LSDA + U) which gives in the case of $PuCoGa_5$ [11] better results than LSDA calculation [14].

The present work offers an alternative way of probing information on electronic properties. The elegance of the method lies in the fact that IXS is a bulk sensitive weak perturbation probe as opposed to other methods that involve intermediate excited states like photoemission. Another recent work on plutonium enlightens the tremendous progress in lattice dynamics calculations for strongly correlated electron systems [15]. In that case it was shown that the dynamical mean-field theory (DMFT) method must be used beyond DFT (including LDA + U) to explain quantitatively [16] both the equilibrium properties [17] and the lattice dynamics of δ Pu [15]. 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.

While our work clearly addresses the case of $PuCoGa_5$, it is highly desirable to investigate the magnitude and 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. Preliminary inelastic neutron scattering studies of $UCoGa_5$ are already reported [18] and show that a similar *ab initio* but purely itinerant GGA approach with $U = 0$ provides a good description of the phonon spectrum. While $UCoGa_5$ and $PuCoGa_5$ have rather similar lattice parameters, the difference in lattice dynamics of the two compounds 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 [19], indicating that the localized f degrees of freedom are absent.

The relevance of the phonon spectrum for the superconductivity of $PuCoGa_5$ cannot be addressed here. It has to be postponed until the present study is extended to low temperatures $T < T_c$. The estimation of the superconducting transition temperature from the electron-phonon coupling constant [6], and the recent NMR results [3] tend to restrict the role of phonons for the superconductivity of $PuCoGa_5$, but this issue still remains open. For instance, a complete theory of magnetically mediated superconductivity would have to explain why $UCoGa_5$ is not superconducting while $CeCoIn_5$ and $PuCoGa_5$ are.

To summarize, the phonon spectrum of $PuCoGa_5$ measured by IXS was 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 confrontation between theory and experiment emphasizes the recent progress in lattice dynamics calculation based on DFT calculation in line with recent equivalent work performed on δ Pu using DMFT calculations.

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