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Dynamic coupling of crystal-field and phonon states in $YbPO_4$

C.-K. Loong
Argonne National Laboratory, Argonne, Illinois 60439-4814

M. Loewenhaupt
Technische Universität Dresden, Dresden, Germany

J. C. Nipko
Argonne National Laboratory, Argonne, Illinois 60439-4814

M. Braden
Institut für Nuklear Festkörperphysik, Karlsruhe, Germany

L. A. Boatner
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056

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The dynamic response of $4f$-electron-lattice interactions in $YbPO_4$ was characterized by neutron spectroscopy using single-crystal specimens. The Yb^{3+}:$^2F_{7/2}$ ground multiplet shows broadened and overdamped energy levels. A coupling of the upper Γ_6 and Γ_7 states with optic phonons was observed throughout the Brillouin zone, resulting in a strong renormalization of the bare crystal-field and phonon excitation spectra over the 15 to 475 K temperature range. A mechanism involving monopolar fluctuations of the Yb f orbital is proposed. [S0163-1829(99)50642-5]

The splitting of the f-electron energy levels belonging to rare-earth ions situated on specific crystallographic sites of a crystalline solid is a well-known phenomenon. When the energy separation between the states within the Hund's-rule ground multiplet are comparable with the energies of thermal and zero-point motion of the lattice, a coupling of the two subsystems may give rise to complex thermodynamic properties. The situation becomes less complex, in principle, for insulating materials since mediation by the conduction electrons can be ignored. A treatment of the ion-lattice interaction within the framework of cooperative Jahn-Teller (JT) effects points to either an onset of a (static) lattice distortion at low temperature or continuous (dynamic) fluctuations between energetically equivalent configurations of the crystal-field (CF) and phonon states.[1,2] The former situation arises from a cooperative coupling of the electronic states to long-wavelength acoustic phonons (bulk strain modes) or optic phonons at the Brillouin zone center, and manifests itself in anomalous static properties such as structural changes, magnetostriction, or softening of the elastic moduli near the transition temperature (T_D). The latter situation is more complex, and depends on the matrix elements of the CF-phonon interactions (which in general depend on the phonon wave vector) and its manifestation relies on the energy-transfer mechanism in specific dynamic properties.

The CF-lattice interactions in a family of insulator RMO_4 (R=rare earths, M=P, V, and As), which crystallize in the zircon structure (space groups $I4_1/amd$), have been studied by a number of workers. Most of the observed JT effects belong to the static cooperative JT phase transition which involves a lattice distortion at a low temperature, e.g., T_D $=2.3$, 33, 25.5, 13.8, 11.2, 2.2 and 6.1 K for $TbPO_4$,[3–5] $TbVO_4$,[6] $TbAsO_4$,[7,8] $DyVO_4$,[9] $DyAsO_4$,[10,11] $TmVO_4$,[12,13] and $TmAsO_4$,[14] respectively. Evidence of dynamic JT effects in these materials, on the other hand, is expected to be less conspicuous as compared to the static JT phase transition or long-range magnetic ordering. In order to detect these effects, the dynamic properties have to be examined over a wide range of wave vectors and temperatures.

A candidate for studies of the dynamic nature of the JT effect is $YbPO_4$. Becker *et al.*[15] reported the mixing of two Yb^{3+} CF states at 32 and 43 meV with an E_g phonon mode at 37 meV from 4.2 to 295 K revealed by Raman-scattering data. The outstanding features that are not understood include: (i) the unusually large coupling strength [an order of magnitude larger than those of previously reported systems such as $CeAl_2$,[16] PrF_3,[17] $LiTbF_4$,[18] $PrAlO_3$,[19] and $R(OH)_3$ (R=Nd, Gd, and Tb)[20]], (ii) the asymmetric linewidths, and (iii) the wide range of temperatures involved. Nipko *et al.*[21] reported an ~20% softening of the $(C_{11}-C_{12})/2$ elastic constant with decreasing temperature from 300 to 10 K but no structural phase transition occurred. The CF excitation spectra obtained from neutron time-of-flight spectroscopy using polycrystalline samples revealed broad and asymmetric CF peaks down to 10 K. The relative intensities of these CF transitions cannot be explained quantitatively by a single-ion CF model. Furthermore, the CF peaks become overdamped as soon as the temperature rises above ~100 K.

A quantitative characterization of the CF-lattice interactions in $YbPO_4$ requires single-crystal neutron experiments that are capable of differentiating the wave-vector–dependent contributions. Additionally, phonon data from an isostructural, nonmagnetic reference compound are needed for comparison. The latter were obtained recently by measur-

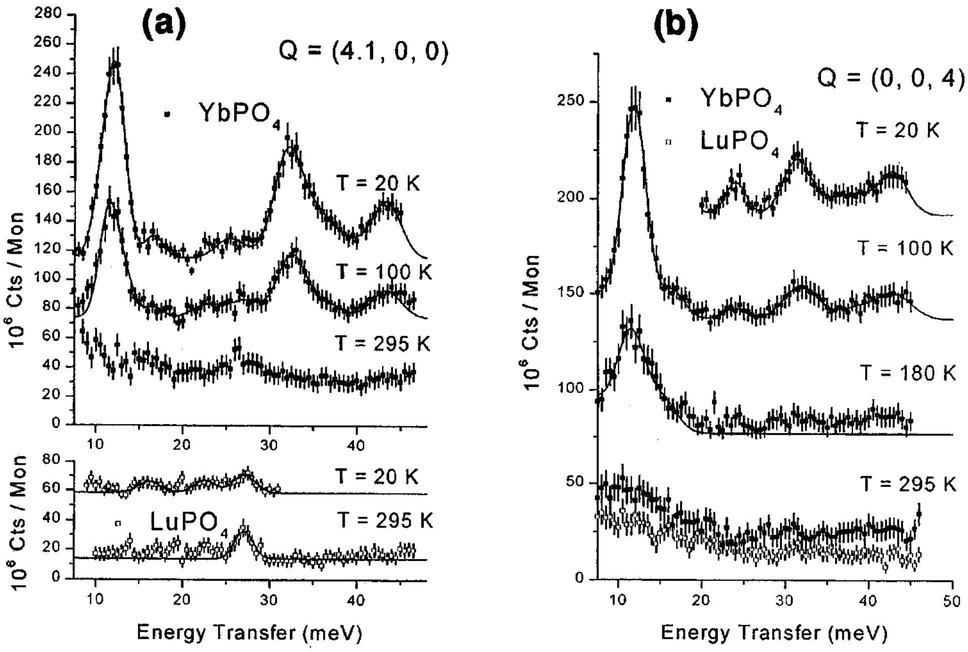

FIG. 1. The excitation spectra of YbPO$_4$ and LuPO$_4$at constant **Q**: (a) $\mathbf{Q}=(4.1,0,0)$ and (b) $\mathbf{Q}=(0,0,4)$. The LuPO$_4$data show the phonon background for comparison. For clarity, each data set was shifted vertically by a constat interval. A sharp peak centered at 12 meV was observed in YbPO$_4$ at 20 K at (0, 0, 4) in a separate scan but was not shown here in (b).

ing the major phonon-dispersion curves of LuPO$_4$ using neutron triple-axis spectroscopy.[22] In this paper, we present the results of single-crystal measurements of YbPO$_4$, showing evidence of dynamic JT effects that may involve monopolar fluctuations of the Yb ions over a wide range of temperatures. The nature of this ion-lattice interaction appears to be unique to the class of RMO$_4$ materials.

The single crystals of YbPO$_4$ (~0.5 cm^3)and LuPO$_4$ (~0.75 cm^3) were grown using a flux technique described previously.[23] The neutron-scattering experiment was performed using the triple-axis spectrometer at the Laboratoire Leon Brillouin in Saclay, France. The ground multiplet $^2F_{7/2}$ of Yb^{3+}ions in YbPO$_4$ is split into four Kramers doublets Γ_6, Γ_7, Γ_6, and Γ_7 at 0, 12, 32, and ~43 meV, respectively.[21] They overlap with the acoustic and the first six optic phonon branches which comprise the substantial motion of the Yb ions. We have measured a majority of these phonon branches as well as the CF transitions along the $[x,0\,0]$, $[x,x,0]$, and $[0,0,x]$ symmetry directions at 20 and 295 K. Additional data were taken at 100, 180, and 475 K in order to examine the temperature dependence of the CF-phonon excitations.

A majority of the phonon energies of YbPO$_4$, as measured from reciprocal lattice points that provide favorable intensities according to structure factor calculations, follow closely the corresponding phonon data of LuPO$_4$.[22] We find no clear evidence of drastic phonon energy shifts and splitting or softening of any phonon branches. However, in the 30–50 meV region, the phonon intensities are smeared out by the superposition of two broad CF peaks around 32 and 43 meV that correspond to transitions from the ground state to the upper Γ_6 and Γ_7 CF states, respectively. If the CF-phonon interaction is small, the CF linewidths would be comparable to the instrumental resolution. This is the case for other RPO$_4$ compounds (R=Tb to Tm).[24,25] Since polarized neutrons were not employed in the measurements, the relative contributions from magnetic (CF) and nuclear (phonon) scattering intensity cannot be assigned accurately. Nevertheless, the magnetic intensities can be seen clearly from scans taken from reciprocal vectors (**Q**) where the phonon structure factors are small. Figures 1(a) and 1(b) show the energy for YbPO$_4$ and LuPO$_4$ at $\mathbf{Q}=(4.1,0,0)$ and (0, 0, 4), respectively. For YbPO$_4$ at 20 K, CF excitations from the ground state give rise to three peaks at 12, 32, and ~43 meV. The superimposed weak features of phonon origin can be seen from the corresponding spectra of LuPO$_4$. Normally, the observed intensity of a transition between two CF states, say $|\Gamma_a\rangle$ and $|\Gamma_b\rangle$, is proportional to the square of the matrix element $\langle\Gamma_a|J_\perp|\Gamma_b\rangle$ (where $J_\perp$is the angular momentum operator perpendicular to **Q**) multiplied by the (square of) the magnetic form factor of the Yb^{3+} ion. Therefore, these scans permit a comparison of the data with the calculated intensity obtained from a single-ion CF model. Using the CF parameters (in units of cm^{-1} and the convention of the spherical-tensor formalism,[26] $B_0^2=333$, $B_0^4=-171$, $B_4^4=-641$, $B_0^6=-615$, and $B_4^6=175$) derived independently from a previous neutron experiment,[21] we find very good agreement between the observed anisotropic intensities and the calculations. For example, at $T=100$ K the ratios of the observed intensities between the (0, 0, 4) and (4.1, 0, 0) scans (Fig. 1), after normalization according to the form-factor dependence, for the 12- and 32-meV peaks are 1.96±0.2 and 0.518±0.06, respectively. The ratios of the corresponding matrix element $(J_x^2+J_y^2)/(J_y^2+J_z^2)$ are 2.0 and 0.502. Therefore, in a (**Q**, T) region where CF transitions do not interfere with phonons, the magnetic intensity can be descried by a single-ion CF model.

In spite of the qualitative agreement between the CF data and model calculation, there are a number of peculiarities. First, the CF lines (particularly the 32 and 43 meV peaks) are unusually broad. Second, the profile of the 32-meV peak is highly asymmetric. Third, all the CF transitions damp out with increasing temperature much more rapidly than the expected behavior based on the population factor of four CF lines. Fourth, the origin of a small peak at ~24 meV [Fig. 1(b)] is not understood. In general, these CF characteristics, except for the extra peak at 24 meV, were observed throughout the reciprocal space.

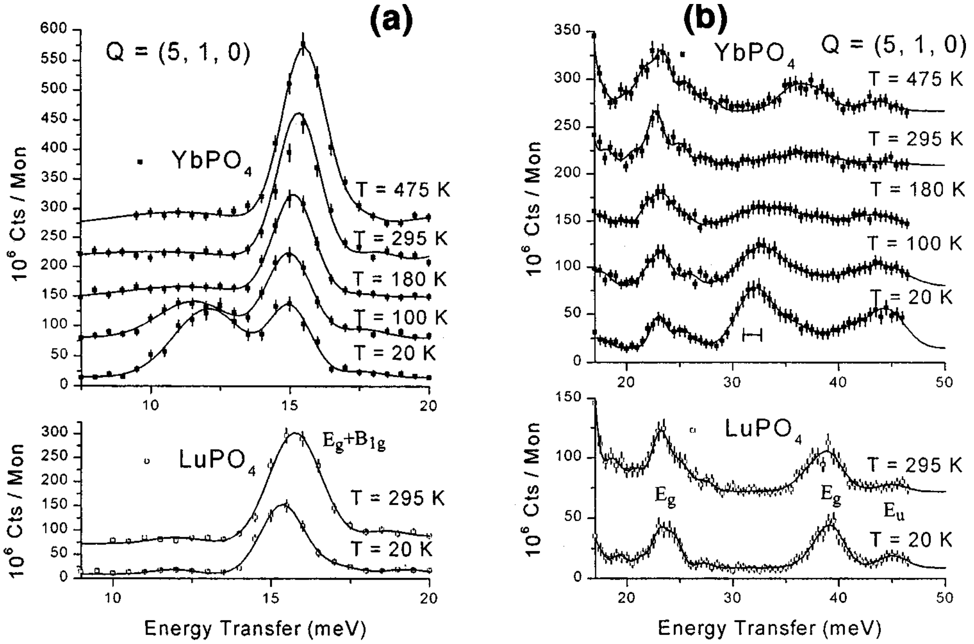

FIG. 2. Constant-**Q** scans for $YbPO_4$ and $LuPO_4$ at selected temperatures in the (a) low- and (b) high-energy region. For clarity, each data set was shifted vertically by a constant interval. The horizontal bar in (b) represents the energy resolution (full width at half maximum).

The CF-phonon indirection was investigated by taking extensive energy scans at many **Q** vectors guided by the ''bare-phonon'' intensities estimated from the $LuPO_4$ data and a lattice-dynamics shell model.[22] We find the most intense CF-phonon coupling occurs in the 30 to 50 meV region where phonons in $YbPO_4$ are strongly renormalized by CF excitations. Figures 2(a) and 2(b) show the constant-**Q** scans at (5, 1, 0) over a wide range of energies and temperatures for $YbPO_4$ and $LuPO_4$. At low energies [Fig. 2(a)], a phonon peak for the combined E_g+B_{1g} modes at 15.5 meV and 20 K (15.8 meV at 295 K) is clearly seen in $LuPO_4$. While its intensity increases according to the Bose-Einstein statistics, the slight increase in energy with increasing temperature is unexpected. This phonon peak and the similar energy shift are also observed in $YbPO_4$. In addition, the CF peak at ~12 meV is clearly evident in $YbPO_4$ at 20 K, and it quickly broadens and dissipates at higher temperatures. However, the CF peak does not affect the intensity or the line shape of the nearby phonon. At high energies [Fig. 2(b)], the $LuPO_4$ scans show two strong E_g phonons at approximately 23 and 39 meV as well as weak ones around 19, 24, and 45 meV. In $YbPO_4$ the phonons below 30 meV, which do not overlap with any CF excitations from the ground state, closely resemble those of $LuPO_4$. Above ~30 meV, the spectrum at 20 K is dominated by two broad CF peaks around 32 and 45 meV. The E_g phonon at 39 meV is either suppressed or shifted to ~35 meV and mixed with the CF peak at 32 meV. The CF peaks broaden and weaken to become almost unrecognizable at 180 K, and at the same time, a gradual recovery of the phonon intensities centered around 37 meV can be seen as the temperature increases. At 475 K, two broad phonon peaks are seen at about 37 and 43 meV. These phonons, comparing with the corresponding E_g (~38 meV) and E_u (~45 meV) phonons in $LuPO_4$, have slightly lower energies. The spectra in Fig. 2 are consistent with the Raman-scattering data reported by Becker *et al.*.[15]

The present experiment provided clear evidence of CF-lattice interactions in $YbPO_4$ that are unique among the $R\mathrm{PO}_4$ family. Although the Yb^{3+}:$^2\mathrm{F}_{7/2}$ ground multiplet splits into four Kramers doublets of Γ_6 (0 meV), Γ_7 (12 meV), Γ_6(~32 meV), and Γ_7(~43 meV) following the point symmetry at the rare-earth site, the anomalous linewidths and transition strengths of CF excitations clearly indicate energy-transfer processes between the magnetic ions and the host lattice. First, any further splitting of the Kramers doublets would require the breaking of time-reversal symmetry, such as from an electromagnetic field, rather than by local or global structural distortions. Indeed, at zero energy transfer, the elastic line corresponding to the transition within the Γ_6 ground doublet observed from both the polycrystalline[21] and single-crystal experiment shows negligible broadening. Therefore, the severe broadening and indications of splitting in the excitations of the ground-to-upper Kramers doublets (Figs. 1 and 2) confirm the dynamic nature of the CF-lattice interactions from 15 K to ambient temperature. Second, an interpretation of the evolution of mixed CF and phonon intensities in the 30–50 meV region would require a full diagonalization of a Hamiltonian properly including the magnetic and crystal lattices and their interactions. Third, coupling of the upper Γ_6 and Γ_7 CF states with phonons occurs in the entire Brillouin zone rather than involving phonons of specific symmetries. The interactions are strongest in the 200–400 K temperature range because of the relatively high CF energies.

The strong CF-lattice interactions in $YbPO_4$ indicate the presence of a fluctuating component associated with the Yb^{3+} ions. Based on the above observations and a multipolar expansion of the $4f$ orbitals, we may explore the nature of the fluctuations relevant on the CF-phonon coupling in $YbPO_4$ following previous arguments used by Yamada[27] and Sinha.[28] In general, coupling of the anisotropic quadruple moment of the low-lying CF states with certain symmetry-compatible strain modes (phonons in the long-wavelength limit) usually results in magnetostrictive effects. In the extreme case, the ''freeze out'' of the coupled CF-strain modes at low temperatures may induce a static cooperative JT phase transition. In fact, magnetostriction in terms of anomalous thermal expansion has been observed in $R\mathrm{PO}_4$ (R=Tm, Ho and Dy) and RVO$_4$ (R=Tm, Ho, Dy and Yb),[29–34] and a JT-like lattice distortion has been found in TbPO$_4$, TbVO$_4$, DyVO$_4$, and TmVO$_4$.[3–5,6–9,12,13] In YbPO$_4$, however, except for a small (∼20%) softening of the $(C_{11}-C_{12})$elastic constants, neither magnetostriction nor lattice distortion was observed. A CF model employing the second- (quadrupole), fourth-, and sixth-order coefficients provides a fair description of the transition strengths observed at **Q** vectors where phonons are weak. Therefore, the quadrupole (and the higher-order) moment of Yb^{3+} ions in YbPO$_4$ is quite stable. Instead, the data suggest a large fluctuating component associated with the monopole term whereby coupling of the CF states, particularly the upper Γ_6 and Γ_7 doublets, with phonons of comparable strengths and energies. The coupling to the monopole term does not require the compatible symmetry of specific phonon modes such as in the case for CeAl$_2$.[16] In YbPO$_4$, strong CF-phonon mixing was observed throughout the Brillouin zone as long as their energies and transition strengths are comparable. This feature concerning the matrix elements of the CF-phonon interactions is unique among all the RMO$_4$ compounds of zircon structure studied thus far.

Strong fluctuating rare-earth monopolar components are known to be the driving force of mixed-valence phenomena observed in a variety of Ce, Yb, and Sm intermetallic compounds.[27] In these materials the predominant interaction is f-d hybridization in conjunction with strong electron correlations between the 4f moments, and these effects manifest themselves in terms of an onset of non-Fermi-liquid behavior below a characteristic Kondo temperature. The effect of monopolar fluctuations in rare-earth insulators is expected to be more subtle due to the absence of conduction electrons and the larger distances between rare-earth ions. The present study suggests that a fluctuating monopolar component in YbPO$_4$ may give rise to a dynamics coupling of the CF and phonon states that is distinct from other RMO$_4$ members. Since these materials exhibit interesting fundamental properties (e.g., JT effects, magnetostriction, and antiferromagnetic ordering)[1,35,36] and potential applications (e.g., as luminescent materials, magnetic refrigerants, and interphase media in toughened ceramic composites),[37–40] they deserve further systematic study.

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