Raman Scattering from Coupled Phonon and Electronic Crystal-Field Excitations in $CeAl_2$

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Raman scattering in $CeAl_2$ probes the interacting phonon ($\tilde{\Gamma}_6$) and crystalline–electric-field-split $\tilde{\Gamma}_7$-$\tilde{\Gamma}_8$ excitations. The observed 109-cm^{-1} Raman peak due to $\tilde{\Gamma}_6$ and the 71-cm^{-1} peak (at 5 K) due to $\tilde{\Gamma}_7 \to \tilde{\Gamma}_{8(2)}$ are in very good agreement with the recent theoretical bound-state model for $CeAl_2$.

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Electronic Raman scattering from crystalline-electric-field (CEF) excitations in metals has not so far been observed. $CeAl_2$ appears to be a good test case for observing such excitations, because of the strong magnetoelastic coupling.[1] Recently Thalmeier and Fulde[2] have suggested that the strong interaction between CEF levels and a Raman-active phonon in $CeAl_2$ leads to a bound state and that it explains the two-peak structure found in inelastic magnetic neutron-scattering studies.[3] In this study we have performed Raman-scattering measurements on $CeAl_2$ and find strong support for the phonon and CEF levels proposed by Thalmeier and Fulde.[2] We have also performed Raman scattering in several other RAl_2 compounds and have observed the Γ_{25}' (T_{2g}) Raman-active phonon. We will present these results and discuss the case of $CeAl_2$ in particular.

The rare-earth (R) intermetallics RAl_2 crystallize in the cubic Laves ($C15$) phase structure with two formula units per unit cell. The R atoms occupy diamond lattice sites giving rise to a Γ_{25}' Raman-active phonon. Raman-scattering measurements were performed on freshly fractured polycrystals or single crystals, in vacuum. The 5145-Å Ar^+ laser line was focussed (with a microscope) onto single-crystalline facets, exposed after fracture of the polycrystalline material. In the case of $CeAl_2$ we have also measured freshly fractured single-crystal samples. The loss of crystal orientation after fracturing, as well as the unknown orientation of the facets, did not permit polarized Raman studies.

The Raman spectra of RAl_2 (R = La, Ce, Eu, Gd, Tb, Dy, Yb) have been measured at room temperature, with a spectral resolution of 4 cm^{-1}. Figure 1 shows the spectra for these materials, with the exception of $TbAl_2$. A mode in the frequency range from 95 cm^{-1} ($YbAl_2$) to 118 cm^{-1} ($GdAl_2$) is identified as the Γ_{25}' phonon. The phonon peaks exhibit a full width at half maximum (FWHM) of 4 cm^{-1} for $EuAl_2$ and $GdAl_2$, 5 cm^{-1} for $LaAl_2$ and $DyAl_2$, 7 cm^{-1} for $CeAl_2$, and 10 cm^{-1} for mixed-valent $YbAl_2$. The latter shows the softest and most strongly broadened phonon in the series.

$LaAl_2$ might be considered as a reference compound for $CeAl_2$. On the basis of the general trend for $R^{3+}Al_2$, the Γ_{25}' phonon frequency in $CeAl_2$ should be slightly higher than its reference compound $LaAl_2$. However, the opposite is the case, and the lower frequency of the excitation

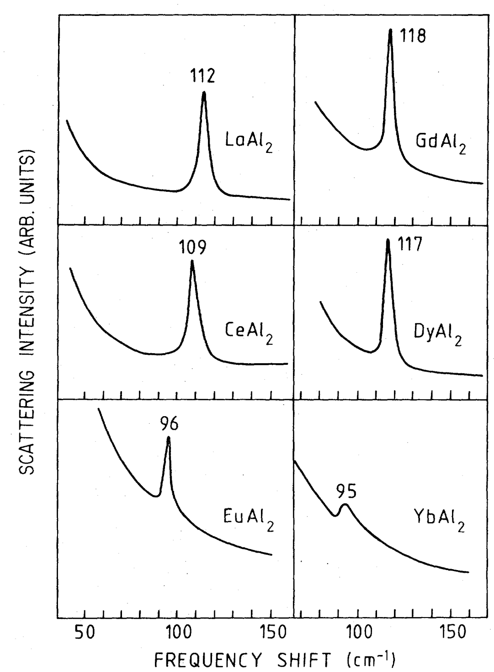

FIG. 1. Unpolarized Raman spectra of RAl_2 at 300 K.

in $CeAl_2$ is thus anomalous.

We have performed Raman-scattering measurements as a function of temperature down to 5 K to ascertain the temperature dependence of the excitation energies in $CeAl_2$, as well as to see if the levels proposed by Thalmeier and Fulde[2] become observable at very low temperatures. The results are shown in Fig. 2 and may be summarized as follows: The Raman peak near 109 cm^{-1} at 300 K does not show a significant shift upon cooling to 5 K. The decrease in intensity upon cooling from 300 to 5 K is in good agreement with the Bose-Einstein factor. The width (FWHM) of the phonon increases from 300 to 5 K by about 15%. Upon cooling below 77 K, a new peak emerges near 71 cm^{-1} (8.9 meV) with FWHM = 15 cm^{-1}. This additional peak is not observed in the reference compound $LaAl_2$, suggesting that it is connected with the CEF levels in $CeAl_2$, for there is no CEF level in $LaAl_2$.

We present in Fig. 3 a qualitative level scheme for the uncoupled and magnetoelastically coupled excitations for $CeAl_2$, which is essentially the same as proposed by Thalmeier and Fulde. We may note here that in $CeAl_2$ only the coupled system is accessible to the experimental probes.

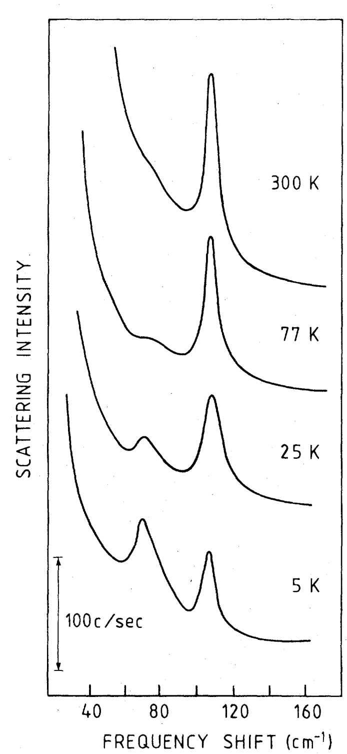

FIG. 2. Temperature dependence of the unpolarized Raman scattering of $CeAl_2$.

According to the Thalmeier and Fulde model, the Γ_{25}' phonon in $CeAl_2$ interacts strongly with the CEF and splits the Γ_8 into two sublevels. The positions of these levels, designated $\tilde{\Gamma}_{8(1)}$ and $\tilde{\Gamma}_{8(2)}$, follow from the neutron data. These levels are not pure states but have admixtures of phononic and electric parts in them. The level shown as $\tilde{\Gamma}_6$ coincides with the Γ_{25}' of the uncoupled system, but it should be noted that it is not the same as the latter. It is a vibronic eigenstate of the coupled system, arising out of the phonon-CEF interaction mentioned above.

The Raman peak near 71 cm^{-1} in Fig. 2 coincides with the lower sublevel $\tilde{\Gamma}_{8(2)}$ of the split Γ_8 CEF level, observed in neutron scattering near 8.9 meV. However, we do not see any feature in Raman scattering corresponding to the $\tilde{\Gamma}_{8(1)}$ sublevel observed in neutron scattering near 15.7 meV (126 cm^{-1}) of Fig. 3. This result suggests that the phononic admixture in the $\tilde{\Gamma}_{8(2)}$ excitation is substantially greater than in the $\tilde{\Gamma}_{8(1)}$. Given the signal-to-noise ratio of our experiment, we estimate $\tilde{\Gamma}_{8(2)}$ to have at least 4 to 5 times more phononic character than $\tilde{\Gamma}_{8(1)}$. Hence we have labeled them with the "phononic" in front of $\Gamma_{8(2)}$ and "electronic" in front of $\Gamma_{8(1)}$ to suggest this dominance. We believe that the Raman cross section for pure electronic Raman scattering from CEF levels is small. It must be the strong phononic admixture which gives rise to the observable Raman cross section in the

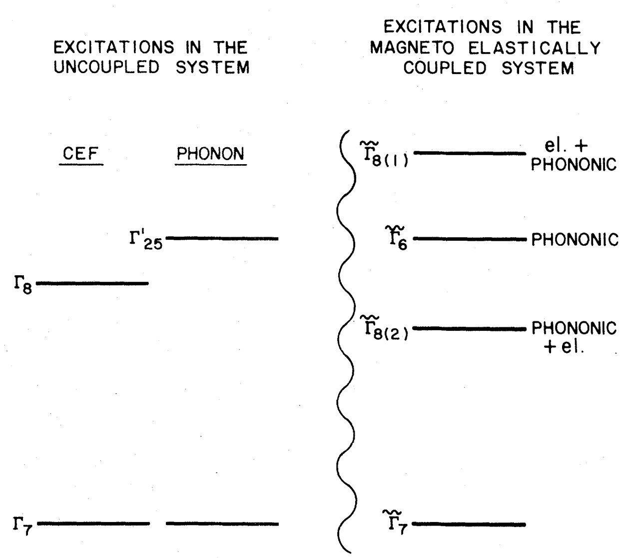

FIG. 3. A qualitative level scheme for phononic and CEF-split electronic excitations in $CeAl_2$, following the model proposed in Ref. 3.

case of $\tilde{\Gamma}_{8(2)}$ excitation. Thus we interpret the Raman peak near 71 cm^{-1} in Fig. 2 as the one that corresponds to the bound state $\tilde{\Gamma}_{8(2)}$ of Fig. 3. The 109-cm^{-1} peak very nicely agrees with the suggested $\tilde{\Gamma}_6$ phononic level in Fig. 3. Thus the Raman-scattering measurements give strong support to the theoretical model proposed by Thalmeier and Fulde to explain the anomalous Γ_8 splitting.

However, there are some puzzling aspects. The nearly temperature-independent frequency of the 109-cm^{-1} Raman peak in the 300- to 5-K range is in contrast to what one would expect from the 20% softening of the c_{44} elastic constant, and in particular is contrary to the 25% softening of the inelastic peak near 13.4 meV observed in very recent neutron-scattering measurements in the same temperature range.[4] This excitation was assigned to the Γ_{25}' phonon close to the zone center. From this we note that there is a difference between Raman and neutron scattering, in observing the interacting phonon-CEF levels in $CeAl_2$. It should be pointed out here that the calculations by Thalmeier and Fulde are for $T = 0$. At nonzero temperatures, when the levels are thermally populated, some renormalization may be expected. This may result in the shift of $\tilde{\Gamma}_6$ as well as $\tilde{\Gamma}_8$ sublevels. However, the Raman probe does not seem to sense these changes. This difference in behavior might be connected with the probing times involved in the two techniques on the one hand and the dynamical aspect of the interaction on the other.

In conclusion we point out that our Raman results are in very good agreement with the model of Thalmeier and Fulde with its novel feature of a "bound state." $CeAl_2$ is especially a favorable case for observing the CEF levels through Raman scattering, because of the strong magnetoelastic coupling.

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