Dynamic Jahn-Teller Effect in a Rare-Earth Compound: $CeAl_2$

M. Loewenhaupt
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

and

B. D. Rainford
Blackett Laboratory, Imperial College, London SW7 2BZ, England

and

F. Steglich[a]
II. Physikalisches Institut, Universität zu Köln, D-5000 Köln 41, West Germany
(Received 26 December 1978)

Measurements of the neutron–energy-loss spectrum of $CeAl_2$, made using a triple-axis spectrometer, reveal the existence of two inelastic lines in the paramagnetic regime. Only a single line ($\Gamma_7 \rightarrow \Gamma_8$) is expected from the cubic symmetry of the crystal field. The origin of the two lines is attributed to the removal of the degeneracy of the excited Γ_8 electronic state by the action of the dynamic Jahn-Teller effect.

While for Fe-group compounds the dynamic Jahn-Teller effect (DJTE), which results in a lifting of orbitally degenerate $3d$ states by a vibronic strain, is familiar enough,[1] no convincing observation of DJTE is known for any rare-earth (RE) compound. This is usually explained by rather effective shielding of the electrostatic interaction between the localized $4f$ shell of the Re ion and its surrounding ions via the outer $6s$ and $5d$ valence electrons. In this Letter, we present data of the inelastic neutron scattering from $CeAl_2$ which provide the first experimental evidence for DJTE in a RE compound.

Previous experiments[2] on $CeAl_2$ and the pseudobinary alloys[3] $(Ce_xLa_{1-x})Al_2$ employed the time-of-flight (TOF) technique, with incident neutrons of low energy (3.53 meV). A well-resolved inelastic peak was observed at an energy transfer $\hbar\omega = 9$ meV in the energy-gain spectrum. This was attributed to the crystal-field (CF) transition between the Γ_7 doublet ground state and the Γ_8 quartet excited state of the Ce^{3+} ions which experience a CF of cubic symmetry. In addition, extra scattering intensity was observed at about twice this energy transfer, which could not be explained by trivial instrumental sources (e.g., multiple scattering, TOF frame overlap, etc.). From the dependence of the intensity on the wave-vector transfer $\vec{Q}$, it was inferred that this additional line originates in magnetic rather than phonon scattering.[4] The relative intensities of the first and second inelastic lines were found to be independent of Ce concentration in the $(Ce_xLa_{1-x})Al_2$ system, down to $x = 7$ at.%.[3,4] This suggests that *both* lines arise from a single-ion property of Ce^{3+}. The second line could be resolved completely in the energy-loss spectrum of $CeAl_2$ by extending the measurements to higher incident energies (thermal neutrons) at Grenoble,[5] and also at Brookhaven.[6] These preliminary results,[5,6] which were obtained using the triple-axis technique, have been interpreted controversially in terms of either trivalent or mixed-valent Ce ions. It was also a purpose of the present investigation to clarify this controversy.

The experiments were made on a large cylindrical $CeAl_2$ single crystal (20 mm diam × 70 mm) which was mounted with a (001) axis vertical to the scattering plane on the triple-axis spectrometer IN8 at the high-flux reactor of the Institut Laue-Langevin. The monochromator and analyzer crystals were pyrolitic graphite (002) and the spectrometer was operated with the scattered wave vector, $|k_f|$, fixed at 2.662 $Å^{-1}$. A pyrolitic graphite filter placed between the sample and analyzer eliminated higher-order contamination in the scattered beam. Typical energy resolutions [full width at half maximum (FWHM)] with this configuration were 1.2, 2.6, and 3.9 meV at energy transfers of 0, 10, and 20 meV, respectively. Scans were made with $\vec{Q}$ in the $(\xi, 0, 0)$ direction with $\xi = 2.3$, 2.5, 2.6, and 3.0, and in the $(\xi, \xi, 0)$ direction with $\xi = 1.6$, 1.7, and 1.8. The temperature was varied between 2 and 150 K.

Figures 1(a) and 1(b) show the energy spectra of paramagnetic $CeAl_2$ as measured at 5 K for $\vec{Q}$ in the $(\xi, 0, 0)$ and $(\xi, \xi, 0)$ directions. Since the spectra are essentially identical for different Q values in either direction, three scans have been added in Figs. 1(a) and 1(b) to improve statistics. Nuclear contributions to the scattering (i.e., elastic incoherent scattering and inelastic phonon

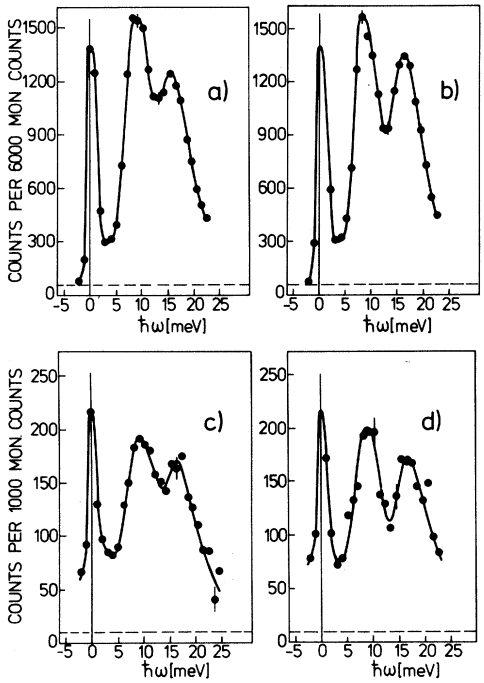

FIG. 1. Energy-loss spectrum of neutrons scattered from $CeAl_2$ at two different temperatures in constant Q scans. (a) $T = 5$ K, $Q = (\zeta, 0, 0)$ averaged for $\zeta = 2.3$, 2.5, and 2.6. (b) $T = 5$ K, $Q = (\zeta, \zeta, 0)$ averaged for $\zeta = 1.6$, 1.7, and 1.8. (c) $T = 60$ K, $Q = (2.5, 0, 0)$. (d) $T = 60$ K, $Q = (1.8, 1.8, 0)$.

scattering) are practically negligible for these values of $\vec{Q}$ and temperature.[4] The instrumental background is indicated by the dashed line. The excitation spectrum of $CeAl_2$ consists of a quasielastic line (centered at $\hbar\omega = 0$) due to paramagnetic scattering from the Γ_7 ground-state level and of two inelastic lines at $\hbar\omega = 8.9$ and 15.7 meV, respectively. Compared to the positions measured in the $(\xi, 0, 0)$ scans, a slight increase in the separation between the two inelastic lines is seen for the Q values in the $(\xi, \xi, 0)$ direction: The first line is shifted to lower energies, the second to higher energies.

As the temperature is raised the peak separation remains constant [see Figs. 1(c) and 2(d) for $T = 60$ K], but the linewidths increase. At the same time the intensity decreases, presumably because of the change in the population of the ground state. The *relative* intensity of the two peaks remains the same, however, as the temperature increases.

To convert the data into the form of the spectral function $S(Q, \omega)$ it was necessary to correct the counts, which were measured for a fixed number of monitor counts, to allow for the varying amount of second-order contamination incident on the monitor detector. The counts for energy transfer $\hbar\omega$ were multiplied by the factor R where $R = 1 + 7.465 \exp(-3E_i/18.2)$ and $E_i = \hbar\omega + E_f$ is the incident neutron energy in meV. This factor R has been determined from experiments on thermal beams,[7] with the same spectrometer configuration as used in the present experiments. Assuming a $1/v$ efficiency for the monitor detector, the corrected count rate is directly proportional to $S(Q, \omega)$. For the data in Fig. 1(a), the ratio of the corrected counts integrated over the inelastic region (4 to 24 meV) to those in the quasielastic region (−2 to 4 meV) was found to be 3.20 ± 0.20. This ratio agrees extremely well with the ratio of the dipole cross sections for $(\Gamma_7 \rightarrow \Gamma_8)$ and $(\Gamma_7 \rightarrow \Gamma_7)$, which equals 16/5. We conclude that the *whole* of the intensity in the inelastic region, comprising *both* inelastic peaks, corresponds to the transition between the crystal-field ground state and the excited state(s).

The effect of a CF of cubic symmetry acting on the $^2F_{5/2}$ term of the Ce^{3+} ion is to split the state into a doublet (Γ_7) and a quartet (Γ_8). All existing evidence[5] points to the ground state in $CeAl_2$ being the Γ_7 doublet. The inelastic neutron-scattering spectrum in this case should consist of a single quasielastic line (due to transitions within the Γ_7 and Γ_8 multiplets) and a single inelastic line in energy loss or energy gain (corresponding to transitions $\Gamma_7 \rightarrow \Gamma_8$ or $\Gamma_8 \rightarrow \Gamma_7$, respectively). There are several possible explanations for the occurrence of *two* inelastic lines as we have observed in $CeAl_2$, viz.: (i) An exchange splitting of the Γ_8 states. (ii) A spin-phonon coupling leading to an "anticrossing" or (iii) a static distortion of the crystal such that the point symmetry is lower than cubic at the rare-earth site, leading to a splitting of the $^2F_{5/2}$ state into three doublets rather than one doublet and one quartet. (iv) The degeneracy of the Γ_8 state is lifted by a DJTE. Possibilities (i)–(iii) can be excluded on the basis of available evidence, as will be discussed below.

Another possibility has been put forward by Parks *et al.*[6] Here, the first peak at 9 meV is attributed to the $\Gamma_7 \rightarrow \Gamma_8$ transition of Ce^{3+}, whereas the second peak at 17.5 meV is attributed to a transition between the $4f^1 5d^0$ and $4f^0 5d^1$ configurations of Ce^{3+} and Ce^{4+}, respectively. We think this explanation to be unlikely (albeit fascinating) for the following reasons: From the above discussion it is apparent that the intensity of the

first peak is much too small to be consistent with the $\Gamma_7 \rightarrow \Gamma_8$ cross section. Moreover, for the second peak, which would involve a transition to a continuum of final 5*d* conduction-band states, one would have to invoke a very rapidly decreasing electronic density of states $N(E)$ at the Fermi level E_F in order to yield a spectrum which cuts off so rapidly at the high-temperature side. However, from the thermoelectric power[8] of the homologous compounds $LaAl_2$ and $CeAl_2$ (+15 and 22 μV/K at 300 K) $N(E)$ is inferred to vary more weakly by one order of magnitude and to increase rather than decrease at E_F.[9] Finally, from recent susceptibility (χ) measurements on $CeAl_2$ performed up to 1000 K, there is no evidence of (thermally activated) Ce^{4+} ions; instead χ vs T can be well fitted by the $J=\frac{5}{2}$ and $\frac{7}{2}$ terms of Ce^{3+},[8] with a multiplet separation of 2500 ± 500 K.

Returning to the possibilities (i)–(iv) above, we would expect that any exchange splitting of the Γ_8 states would be of the order of $k_B T_N$, where $T_N \simeq 4$ K is the Néel temperature of $CeAl_2$. This is more than an order of magnitude smaller than the observed separation ($\simeq 100$ K) of the two inelastic peaks. Further, the TOF measurements showed the separation to be independent of dilution of Ce by La in the $(Ce_xLa_{1-x})Al_2$ alloys.[3,4]

The possibility of a spin-phonon interaction can be ruled out since the spectra measured in the $(\xi,0,0)$ and $(\xi,\xi,0)$ directions are essentially independent of $\vec{Q}$. There are no modifications in the position or line shape of the lower peak at points in the Brillouin zone where this excitation crosses the acoustic phonon branches. The upper peak lies at an energy in between the top of the acoustic phonon branches and the lowest lying of the optic phonon modes.

High-precision x-ray diffraction measurements have failed to show any evidence of a static distortion of the Ce environment.[8] Thus the time-averaged point symmetry of the Ce site appears to be cubic (at room temperature).

We are left with the possibility of the double-peaked structure in the spectrum arising from a dynamic, rather than a static, strain which couples to the excited Γ_8 quartet. The theory for the vibronic coupling of a Γ_8 state has been worked out for two cases,[10] i.e., coupling to a vibrational mode of τ_2 symmetry, and equal coupling to vibrational modes of τ_2 and ϵ symmetry.

The line shapes have been calculated for both cases by Pooler,[11] using parameters determined from the first four energy moments of our measured spectrum in Fig. 1(a). We have chosen to show in Fig. 2 the calculated line spectrum for the case $\Gamma_8 \otimes \tau_2$, while the corresponding parameters appear in the figure caption. The smoother curve in Fig. 2 represents the envelope of the line spectrum obtained by convoluting it with a Gaussian line shape of width 4.65 meV (FWHM). The envelope of the line spectrum for the cases $\Gamma_8 \otimes (\tau_2 \oplus \epsilon)$ is almost identical to the one shown, though the fitted parameters are a little different.

It can be seen that there is good agreement with the experimental line shape in Fig. 1(a). Discrepancies near the high-energy end of the spectrum may be partly due to the variation in the instrumental energy resolution with energy transfer; the calculated line shape assumes the energy resolution to be constant. The excellence of the fit, however, may be fortuitous since in some respects the theory[10] of the line shape is inadequate to describe the present situation. Thus it is assumed[10] that the electronic level lies well above the band of phonon states, and that the splitting of the Γ_8 state is small compared to the excitation energy. In contrast, in $CeAl_2$, the $\Gamma_7 \rightarrow \Gamma_8$ excitation lies *within* the band of phonon states, and the splitting of the Γ_8 level is roughly *equal* to the excitation energy. A proper theory should at least take account of the matrix elements of the strain between the Γ_7 and Γ_8 states in calculating the line shape. We note that the en-

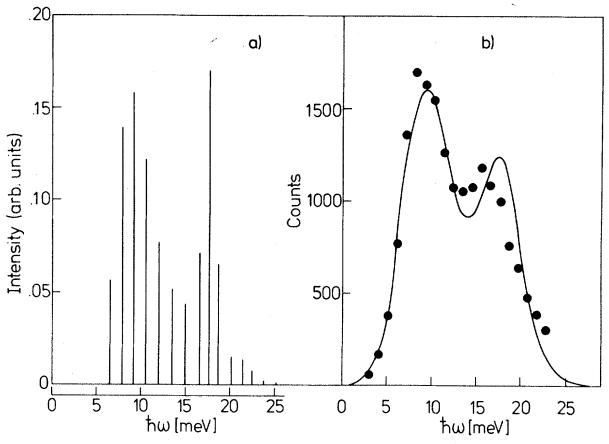

FIG. 2. Comarpison between measured and calculated $S(Q,\omega)$ for $CeAl_2$. (a) Vertical bars: line spectrum calculated by Pooler (Ref. 11) using the energy moments of the scan in Fig. 1(a), and the procedure outlined in Ref. 10. (b) Smooth curve: convolution of line spectrum with Gaussian. In the notation of Ref. 10, the parameters are $\hbar\omega = 1.24$ meV, $E_0 = 10.9$ meV, $E_{JT} = 2.57$ meV and $\alpha = 0.09$ meV^{-2}. Solid points, corrected experimental data corresponding to Fig. 1(a).

ergy of the vibrational mode $\hbar\omega = 1.2$ meV ($\simeq 14$ K) derived from the line-shape fit is much smaller than one would expect in this situation. For comparison the zone-center optic phonon mode of Γ_5 (τ_2) symmetry has an energy of about 21 meV. We do not have a physical explanation for the low energy of the vibrational mode.

A further drawback of the conventional approach to line-shape calculations for the DJTE is that it assumes vertical transitions between electronic levels (i.e., zero wave vector $\vec{Q}$). It will not be able, therefore, to account for the observed differences in the line shape for scans in the $(\xi, 0, 0)$ and $(\xi, \xi, 0)$ directions. Although the splitting of the Γ_8 quartet in $CeAl_2$ may appear unexpectedly large for a RE system at first glance, yet perhaps it is not too surprising since (i) the matrix elements of the quadrupole operator are large in this case and (ii) the magnetoelastic coupling constant may also be large because of the Stevens factor $\alpha_{5/2}$.[12] In addition the appreciable extent of the $4f^1$ wave function of Ce^{3+} may give rise to an enhancement of the magnetoelastic coupling via $4f$ hybridization with the conduction electrons.

To conclude, we believe that the most plausible explanation of the neutron scattering results presented here is the existence of a dynamical Jahn-Teller effect in the rare-earth compound $CeAl_2$. Further experimental and theoretical work is required to test this hypothesis. We plan to investigate other similar compounds, especially $CePt_2$.

We would like to thank Dave Pooler for kindly making available the results of his line-shape calculations, and Roger Pynn for valuable help with the experiment. Discussion with R. J. Elliot, M. C. M. O'Brien, B. Lüthi, R. Marx, E. Müller-Hartmann, R. D. Parks, and K. D. Schotte have been very helpful. This work was partially supported by Sonderforschungsbereich 125.

---

[a] Present address: Institut für Festkörperforschung (Experimentalphysik), Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany.

[1] R. Englmann, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972).

[2] M. Loewenhaupt and F. Steglich, Physica 86–88B, 187 (1977).

[3] M. Loewenhaupt and F. Steglich, in *Crystal Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum, New York, 1977), p. 198.

[4] M. Loewenhaupt and W. Schmatz, in *Neutron Inelastic Scattering 1977* (International Atomic Energy Agency, Vienna, 1978), Vol. II, p. 227.

[5] F. Steglich, C. D. Bredl, M. Loewenhaupt, and K. D. Schotte, in Proceedings of the International Conference on Metallic Rare Earths, St. Pierre de Chartreuse, 4–7 September 1978 (to be published).

[6] R. D. Parks, L. C. Kupferberg, M. A. Manheimer, S. M. Shapiro, and E. Gurewitz, in Proceedings of the International Conference on Metallic Rare Earths, St. Pierre de Chartreuse, 4–7 September 1978 (to be published).

[7] B. Lebech, B. Buras, and O. W. Dietrich, private communication.

[8] S. Horn, M. Loewenhaupt, F. Steglich, W. Franz, J. Aarts, F. R. de Boer, and G. Mair, to be published.

[9] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Taylor and Francis, London, 1972).

[10] D. R. Pooler and M. C. M. O'Brien, J. Phys. C 10, 3769 (1977).

[11] D. R. Pooler, unpublished.

[12] B. Lüthi, in *Magnetism and Magnetic Materials —1976* (Joint MMMM-Intermag Conference, Pittsburgh), AIP Conference Proceedings No. 34 (American Institute of Physics, New York, 1976), p. 4, and private communication.