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Observation of crystal twinning of LaF_3 with Raman heterodyne detection of NMR in Pr^{3+}:LaF_3

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By examining the spatial dependence of the Raman heterodyne signals of nuclear coherent transients of ^{141}Pr nuclei in Pr^{3+}:LaF_3 in the presence of a static magnetic field (~100 Oe) we found evidence directly indicating that the crystal structure of LaF_3 is $D_{3d}^4(P\bar{3}c1)$ twinned on a macroscopic scale.

The Pr^{3+}:LaF_3 crystal is one of the most thoroughly studied impurity ion solids. A number of optical and optical-rf double resonance experiments have been performed on this system to examine optical and magnetic properties of Pr^{3+} ions.[1] However, the crystal structure of LaF_3 has been the subject of considerable controversy because different types of experiments lead to different conclusions.[2]

The x-ray and neutron-diffraction investigations by different workers lead to different results. Among the proposed space group the most probable one was thought to be D_{3d}^4. However, the EPR and nuclear quadrupole resonance (NQR) experiments on (rare earth)$^{3+}$:LaF_3 systems show that the existence of six magnetically inequivalent sites of the guest ions, which is inconsistent with the D_{3d}^4 space group. Raman and ir reflection spectroscopies of phonons of LaF_3 support the D_{3d}^4 space group. A microtwinning has been assumed[2-4] to resolve this inconsistency between the D_{3d}^4 space group and the number of sites observed. For the final settlement of this problem more decisive experimental evidence is necessary.

We examined Raman heterodyne signals (RHS) (Ref. 5) of nuclear-spin echoes and transient nutation of ^{141}Pr ($I=\frac{5}{2}$) in Pr^{3+}:LaF_3 at 2 K in the presence of a static magnetic field H_0 of about 100 Oe, and found anomalous behavior of the signals that has not been reported so far. In this Rapid Communication we describe the phenomenon and show that it clearly indicates the twinning of the LaF_3 crystal with symmetry $D_{3d}^4(P\bar{3}c1)$. High spatial resolution achieved by using a laser beam and phase-sensitive characteristics of the Raman heterodyne detection technique enabled us to derive this conclusion.

The experimental procedure for the detection of the RHS is essentially the same as that in Ref. 5. As shown in Fig. 1 the sample crystal (0.1 mol%, 4×4×2 mm, supplied by OPTOVAC) is irradiated with a linearly polarized light propagating along the C_3 axis from a dye laser (spectral width ~3 MHz) tuned to the $^3H_4$-$^1D_2$ transition (592.52 nm). The C_3 axis is perpendicular to the 4×4 mm plane of the sample. The laser beam is focused with a lens (focal length ~50 cm) and the beam diameter at the sample is about 300 μm. In order to simplify the experimental condition, the light beam is gated. At first a pump light pulse (~50 ms, ~5 mW) is applied to create population differences between ground-state sublevels with optical pumping. After a time much longer than the relaxation times (~0.5 ms) of the optical transition, rf pulses are applied to generate spin echoes or transient nutation in the ground state. The rf field H_1 is parallel to the C_3 axis. A probe light pulse is applied at the echo time or during the transient nutation, and the signals are detected as heterodyne beats of the induced Raman and the probe lights. Signals are phase sensitively detected and the phase of the reference signal is adjusted so that the maximum bell-shaped echo signal is obtained.

Anomalous behavior of the signals was found at first for the RHS of spin echoes for the $I_z=-\frac{3}{2}\leftrightarrow-\frac{5}{2}$ transi-

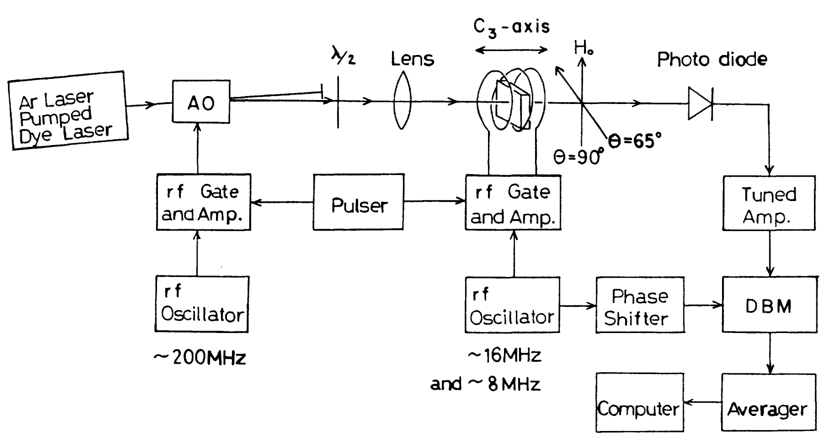

FIG. 1. Experimental setup. AO is an acousto-optic modulator.

tions (at about 16 MHz) at $\theta = 90°$, where θ is an angle between H_0 and the C_3 axis. According to the recent NQR experiment[4] on Pr^{3+}:LaF_3, there are six magnetically inequivalent sites (referred to as A_1, B_1, A_2, B_2, A_3, and B_3) of Pr^{3+} ions. The directions of the principal axes (X, Y, and Z) of the ground-state quadrupole coupling tensors are known and two of them (for the sites A_1 and B_1) are shown in Fig. 2. Those for the other four sites are obtained by rotations about the C_3 axis by $\pm 2\pi/3$. The angle between X_A and X_B axis is about 17°. The sites A_1 and B_1 interchange by a 180° rotation about the C_3 axis or a mirror reflection perpendicular to that axis. It is also known that resonance frequencies of the $(-\frac{3}{2} \leftrightarrow -\frac{5}{2})$ transitions for the sites A_i and B_i ($i = 1-3$) coincide at $\theta = 90°$.[4] Therefore, three $(-\frac{3}{2} \leftrightarrow -\frac{5}{2})$ transitions are expected corresponding to the sites 1, 2, and 3. We separately detected spin-echo signals for these transitions by choosing the frequency of the rf field and the polarization of the laser beam. Observed resonance frequencies were 15.64, 16.14, and 16.11 MHz at $H_0 = 100$ Oe, which are in good agreement with calculated values obtained by using the parameters in Ref. 4.

The anomalous spatial dependence of the signals was observed for all these transitions. A typical experimental result for the site 1 signal (at 15.64 MHz) is shown in Fig. 3. Figure 3(a) shows a positive maximum signal obtained by adjusting the light path through the sample. As the light path is shifted with the beam direction fixed, the signal changes continuously from positive maximum to negative maximum through zero as shown in Figs. 3(a)-3(e). The amplitudes of the maximum signals are nearly the same and the shape of the signal is practically unchanged. The positive and negative signals are 180° out of phase with each other. The same change as in Fig. 3 was observed by moving the position of the sample instead of that of the laser beam, which indicates that the phenomenon is not spurious due to the instrumental effect such as birefringence of the Dewar windows. The observed echo envelope decay times were equal (~25 μs) for the positive and negative signals. By scanning the beam position we obtain a map like Fig. 4, where "+", "−", and "0" indicate positions where the signal is positive maximum, negative maximum, and zero. The distribution of "+", "−", and "0" is rather regular. The average distances between "+", and "−" are about 1 mm. It is remarkable that the maps drawn for the signals from the sites 1, 2, and 3 were practically the same; strong and zero signals always appeared at the definite beam positions. When the phase of the reference signal was shifted by 180°, the positions "+" and "−" were interchanged. No signal was observed when the phase shift was 90°.

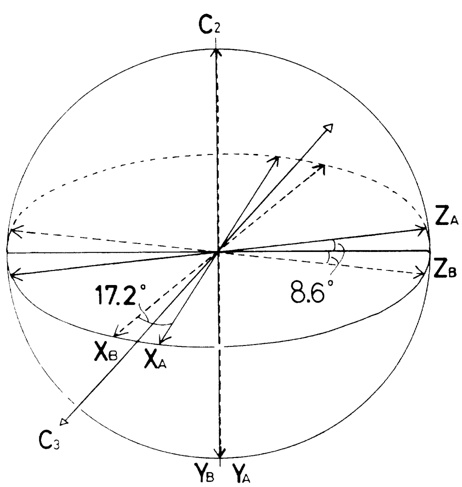

FIG. 2. Directions of the principal axes of the quadrupole coupling tensor in the ground state. There are six sites of Pr^{3+} ions in LaF_3. Two of the directions (for the A_1 and B_1 site) are shown. Those for the other four sites are obtained by rotations about the C_3 axis by $\pm 2\pi/3$.

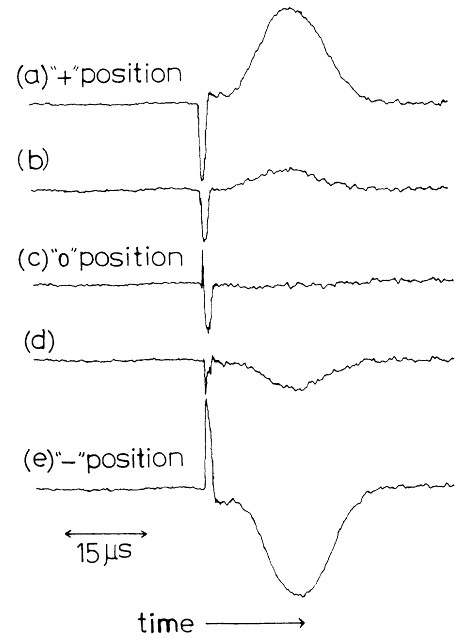

FIG. 3. RHS of spin echoes for the $^3H_4$ $(I_z = -\frac{3}{2} \leftrightarrow -\frac{5}{2})$ transition (at 15.64 MHz for site 1) at various beam positions. $H_0 = 100$ Oe and $\theta = 90°$. The signals change from positive to negative through zero continuously from (a) to (e). rf pulse widths are 4 and 8 μs and the separation is 15 μs. The switching transients of the probe pulse are shown as spikes after the second rf pulse. Signals are averaged over eight shots.

These experimental results were obtained without scanning the laser frequency,[5] and scanning at a rate ~1 GHz/min did not affect the experimental results. The results were essentially the same when the cw irradiation (as in Ref. 5) was used instead of the gated irradiation. No signal was observed at the zero positions even when the experimental conditions, such as the optical pumping, polarization of the laser beams, phase of the reference signal, were changed.

It is probable that the anomalous dependence is due to the macroscopic inhomogeneous distributions of impurity ions and/or the macroscopic inhomogeneous broadening as in ruby.[6] So we measured absorption rates at different beam positions, but did not find any differences.

In order to examine the origin of the anomalous behavior we tried to observe A and B site signals separately by

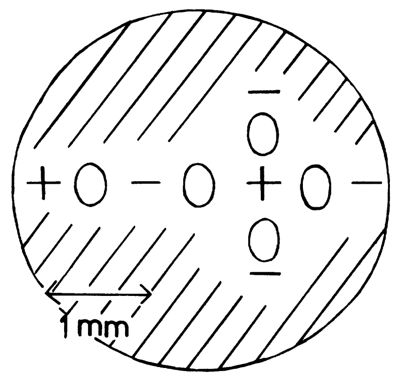

FIG. 4. A map schematically showing the position dependence of the signals (see text). Average distances between "+" and "−" positions are about 1 mm. A rather regular distribution of "+", "−", and "0" is recognized. The outer region of the circle is invisible. In the shaded region signals could not be observed because the light beam was blocked or scattered by the radiation shield of the Dewar, etc.

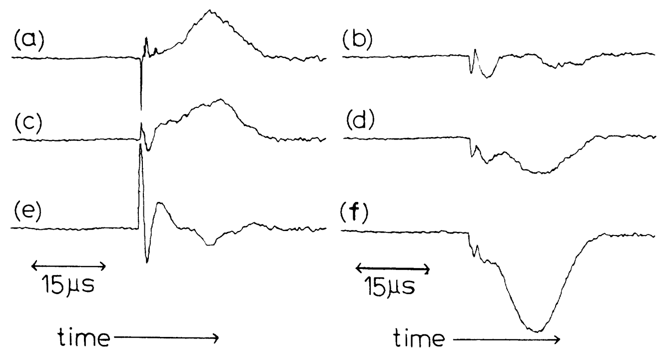

FIG. 5. RHS of spin echoes for the $^3H_4$ ($I_z=-\frac{3}{2}\leftrightarrow-\frac{5}{2}$) transition from the A_1 and B_1 site ions at $\theta=65°$ at three beam positions "+" [(a),(b)], "0" [(c),(d)], and "−" [(e),(f)]. Resonance frequencies of the A_1 and B_1 site ions at 15.63 and 15.74 MHz ($H_0=100$ Oe). (a), (c), and (e) show signals at 15.64 MHz, and (b), (d), and (f) show those at 15.74 MHz. The small signals in (b) and (e) are due to the off-resonant excitation of the A and B site ions, respectively. The rf and probe light pulses are the same as those in Fig. 3. Signals are averaged over eight shots.

shifting θ from 90°. We observed two signals for site 1 at 15.63 and 15.74 MHz when $\theta=65°$. By using the parameters in Ref. 4 these are identified as signals from site A_1 and B_1 (we assign the signal at 15.63 MHz to the site A_1). These signals also exhibit an anomalous spatial dependence, but in a different way from that in Fig. 3. As shown in Fig. 5, the signal from site A_1 (or B_1) is maximum and that from site B_1 (or A_1) practically disappears at the "+" (or "−") position where the original (at $\theta=90°$) signal is positive (or negative) maximum. The signs of A_1 and B_1 signals do not change and are opposite to each other. Both signals become smaller and have nearly equal amplitudes at the "0" position where the original signal disappears. In our experimental condition the difference of resonance frequencies of the A_1 and B_1 signals is not so large compared with the linewidth (~100 kHz). The weak signals in Figs. 5(b) and 5(e) are due to an inevitable off-resonant excitation.

Comparison of the behaviors of the signals at $\theta=90°$ and $\theta=65°$ shows that the original ($\theta=90°$) signal is a superposition of the A_1 and B_1 signals. It turns out that the signal mostly comes from the A_1 (or B_1) site ions at the "+" (or "−") position, and the A_1 and B_1 signals cancel each other at the "0" position because of the interference. Generally the amplitudes of A_1 and B_1 signals depend on the beam position though the sum of the absolute amplitudes is almost constant. Since no more interference effect is expected for the single-site signal, one obtains important information about the spatial distribution of A and B site ions as follows. Namely, ions existing in the light path through the "+" (or "−") position are mostly A (or B) site ions, and nearly the same number of ions exist in that through the "0" position. Generally, the relative concentration of A and B site ions existing in the light path depends on the beam position though the total number of the ions is almost constant.

The fact that no interference effect exists for the single-site signal was confirmed experimentally by observing transient nutation signals at $\theta=65°$ as changes of the transmitted light intensity.[7] Although the detection sensitivity is lower than that in the Raman heterodyne method, signals thus obtained are free from phase cancellation characteristics of the RHS and provide a measure of the ion density. The observed signals exhibited a behavior which supports the above conclusion on the ion distribution.

The same spatial distribution of the ions was derived from the examination of the spin-echo signals for the $+\frac{3}{2}\leftrightarrow+\frac{5}{2}$ transitions and also signals from the sites 2(A_2 and B_2) and 3(A_3 and B_3). We also observed that the position dependences of the RHS of transient nutation at $\theta=90°$ and $\theta=65°$ were essentially the same as those of the spin echoes.

The anomalous distribution of A and B site ions cannot be explained by assuming a single crystal with six inequivalent sites. The origin of the anomalous distribution is the twinning of the LaF_3 crystal. A composite structure of the twinned crystal is discriminated by a fine laser beam. The ions in the light path through the "+" (or "−") position are mostly those in the component single crystal with sites A_1, A_2, and A_3 (or B_1, B_2, and B_3). Generally a mixture of these single crystals are observed. Considering various types of experiments and discussions published so far, our explanation is quite natural. The twinning plane is perpendicular to the C_3 axis or the twinning axis is parallel to the C_3 axis. The fact that the average distance of 1 mm between "+" and "−" positions indicates that the twinning occurs on a rather macroscopic scale.

The effect of crystal twinning was also observed on the signals for the $\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ transitions (8 MHz transitions), but in a different form from that for the $\pm\frac{3}{2}\leftrightarrow\pm\frac{5}{2}$ transitions (16 MHz transitions). We observed 8 MHz signals simply by changing the rf frequency. In contrast to the 16 MHz signals, (1) the signs of the

A and B site signals at $\theta = 65°$ were the same, and (2) no path dependence was observed at $\theta = 90°$. However, the amplitudes of the A and B site signals changed nearly in the same way as in Fig. 4 indicating the effect of the twinning. The sum of the A and B signals was practically independent of the beam position, which is a reason why the path dependence at $\theta = 90°$ is absent.

We performed experiments for another sample crystal. The crystal twinning was also recognized. Thus we conclude that the LaF_3 crystal structure is $D_{3d}^4(P\bar{3}c1)$ twinned on a rather macroscopic scale. We believe that the LaF_3 crystals examined by other authors[2] are generally twinned and the inconsistency between their experimental results is now resolved.

The twinning was not detected in our x-ray-diffraction experiment probably because of the low accuracy of the intensities estimated from the films as was the case in the previous experiments.[2]

Finally, we will briefly discuss the signs of RHS. We observed that the signs of the RHS of A and B site ions are different for the 16-MHz transitions, and the same for the 8-MHz transitions. It is equivalent to the known experimental fact[5] that the signs of A and B signals for 16-MHz transitions are inverted and those for 8-MHz transitions remain unchanged when the direction of H_0 is reversed. We actually observed such sign reversals. The equivalence is easily understood at $\theta = 90°$ by considering the geometrical symmetry that the B (or A) site is transferred to the A (or B) site when the direction of H_0 is reversed. We have theoretically derived a symmetry law and explained sign-reversal characteristics observed so far. Details of the derivation of the symmetry law and its application will be described elsewhere.

In summary we have experimentally confirmed, for the first time, that the LaF_3 crystal structure is $D_{3d}^4(P\bar{3}c1)$ twinned on a rather macroscopic scale by examining Zeeman effects of NMR of Pr^{3+} in LaF_3. We believe that the twinning of the LaF_3 crystal for other guest impurity ions and that of tysonite crystal in general can be detected by this technique.

[1]See, for example, R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Crystals Containing Rare Earth Ions,* edited by A. A. Kaplyanskii and R. M. Macfarlane (North-Holland, Amsterdam, 1987).

[2]Historical and comprehensive reviews are given in M. Dahl and G. Schaack, Z. Phys. B **56**, 279 (1984), and references therein.

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