Raman Heterodyne Interference of Inequivalent Nuclear Sites

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(Received 21 December 1983)

A novel interference effect that is unique to the recently introduced technique of Raman heterodyne detection of NMR is illustrated for the impurity-ion crystal Pr^{3+}:$YAlO_3$. Experiments confirm theoretical arguments that the two inequivalent Pr nuclear sites in the host lattice generate coherent Raman signals of opposite sign that interfere. A necessary requirement, which can now be examined in detail, is that the principal nuclear quadrupole Z axis of Pr be incongruent in the ground and optically excited electronic states.

PACS numbers: 42.65.−k, 76.60.−k

An optical heterodyne technique based on the coherent Raman effect was demonstrated recently for detecting nuclear-magnetic resonance (NMR) and coherent spin transients of impurity-ion solids.[1,2] The Raman process, indicated in Fig. 1, employs a coherent radio-frequency field (ω) that resonantly excites the nuclear transition $1 \rightarrow 2$ and an optical-frequency field (Ω) that excites the electronic transition $2 \rightarrow 3$. An optical field at the sum frequency ($\Omega' = \Omega + \omega$) is thereby created and generates with the incident optical field at a photodetector a heterodyne beat signal of frequency $\omega = |\Omega - \Omega'|$, that reflects the NMR transition. The method is extremely sensitive and has the virtue of yielding NMR spectra and coherent spin transients in both ground and excited electronic states with kilohertz precision.

While the basic Raman heterodyne technique can be understood by a three-level perturbation calculation, two fundamental characteristics have been puzzling.[1,2] First, in the crystals studied thus far, Pr^{3+}:LaF_3 and Pr^{3+}:$YAlO_3$, the signals only appear in the presence of an external Zeeman field, and second, the line shapes are anomalous, resembling the second derivative of a Gaussian. This Letter identifies that both phenomena are a manifestation of inequivalent nuclear sites that generate Raman signals of opposite sign and thus can interfere when their frequencies match, as they do at low magnetic fields. For this to occur, we show that for nuclei possessing an electric quadrupole moment, such as Pr, the principal quadrupole axes in ground and excited electronic states must be incongruent, a condition easily satisfied in practice. While this Letter describes a Raman interference due to inequivalent nuclear sites, it may be only one of a broad class of Raman coherence phenomena. For example, interference of Raman-detected nuclear Zeeman transitions is observed for the case of a single site as well and will be covered elsewhere.[3] This work therefore reveals a new aspect of coherent Raman scattering of solids.

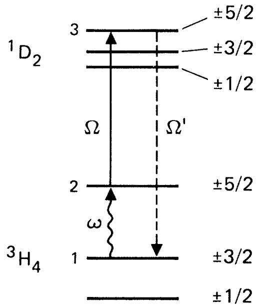

FIG. 1. Hyperfine energy-level diagram in the absence of state mixing for the 610.5-nm $^3H_4 \rightarrow {}^1D_2$ transition of Pr^{3+}:$YAlO_3$ showing the coherent Raman process (not to scale) for levels labeled 1, 2, and 3.

In contrast to most other optical spectroscopic methods where the signal is a function of the *square* of the relevant transition matrix elements, $|\mu_{ij}|^2$, the Raman heterodyne beat signal

$$S \sim \mu_{12}\mu_{23}\mu_{31} \tag{1}$$

exhibits a *linear* dependence in each of the three transition matrix elements associated with Fig. 1.[1,2] A consequence of (1), which has gone unnoticed until now, is that such a detection scheme has a potential for measuring the phase of a matrix element as well as its magnitude. Thus, the sign of the Raman heterodyne signal can vary among inequivalent impurity ion sites even if they are related by rotational symmetry. As a clear example, we discuss the case of Pr^{3+}:$YAlO_3$ which undergoes the optical transition $^3H_4 \rightarrow {}^1D_2$ of Fig. 1 and possesses two Pr^{3+} sites with twofold rotational symmetry as shown in Fig. 2, Z being the principal nuclear quad-

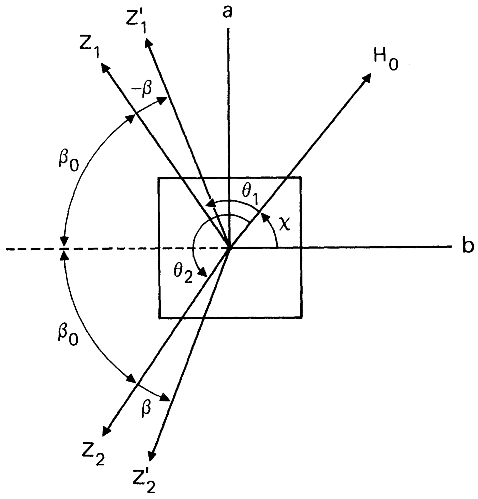

FIG. 2. The principal nuclear quadrupole Z axis of Pr lies in the a-b plane of $YAlO_3$ where the two inequivalent sites for $^3H_4$ ($Z_{1,2}$) or $^1D_2$ ($Z'_{1,2}$) make equal angles with the b axis. A static magnetic field H_0 also in the a-b plane deviates by the angle χ from the b axis, by θ_1 from Z_1, and by θ_2 from Z_2.

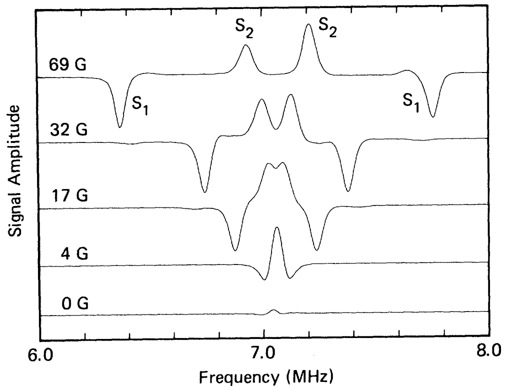

FIG. 3. Observed Raman heterodyne beat spectrum in absorption for the $^3H_4$ $|\pm\frac{3}{2}\rangle \leftrightarrow |\pm\frac{1}{2}\rangle$ transitions of 0.1-at.% Pr^{3+}:$YAlO_3$ as a function of $H_0(\chi=33.6°)$ where the sign reversal in S_1,S_2 for the two sites is evident.

rupole axis of quantization of Pr ($I=\frac{5}{2}$). We now show that the two sites corresponding to the $Z_{1,2}$ axes yield Raman signals of opposite sign as well as interference phenomena as observed in Fig. 3.

First, consider the case of a zero static external magnetic field, $H_0=0$. The three relevant transition matrix elements are given by

$$\mu_{ij}=\langle\phi_i m_i|\mu|\phi_j m_j\rangle$$

$$=\begin{cases}\langle\phi_{1,2}|\mu|\phi_3\rangle\langle m_{1,2}|m_3\rangle, & \text{(2a)}\\ \langle m_1|\mu|m_2\rangle, & \text{(2b)}\end{cases}$$

with the assumption that the Pr^{3+} electronic $|\phi\rangle$ and nuclear $|m\rangle$ wave functions are separable, where μ is an electric (2a) or a magnetic (2b) dipole operator and $\phi_1=\phi_2$. For the case of a nonaxial electronic field gradient at the Pr nucleus, the nuclear quadrupole functions[4]

$$|\pm m_i\rangle=\sum_m a_m^{(i)}\psi_m,\quad m=\pm\tfrac{3}{2},\ \mp\tfrac{1}{2},\ \mp\tfrac{5}{2},\tag{3}$$

are mixed in the axial basis set ψ_m, where $m_i=-\frac{5}{2}$, $-\frac{1}{2}$, and $\frac{3}{2}$, since the quadrupole Hamiltonian connects only the states differing by $\Delta m=2$. The rf magnetic dipole transition $1\leftrightarrow 2$ imposes for $H_{\text{rf}}\perp Z$ the I_z selection rule $\Delta m=\pm 1$ which is satisfied by the eigenvectors

$$|m_1\rangle=\sum_m a_m\psi_m,\quad m=\tfrac{5}{2},\ \tfrac{1}{2},\ -\tfrac{3}{2},\tag{4a}$$

$$|m_2\rangle=\sum_m b_m\psi_m,\quad m=-\tfrac{5}{2},\ -\tfrac{1}{2},\ \tfrac{3}{2},\tag{4b}$$

or their conjugates ($m\rightarrow -m$) and can now be applied to (2a).

The excited-state nuclear wave function $|m_3\rangle$ requires special care, however, since its $Z'_{1,2}$ axes are rotated by the angles $\pm\beta$ relative to the $Z_{1,2}$ ground-state orientation as in Fig. 2. For $|m_3\rangle$ to be represented in the same basis set as the ground-state wave functions (3), we perform an Eulerian rotation transformation[5] $P(\alpha,\beta,\gamma)$ on (3),

$$|m_3\rangle=P(\alpha,\beta,\gamma)\sum_m c_m\psi_m,\quad m=\tfrac{5}{2},\ \tfrac{1}{2},\ -\tfrac{3}{2},\tag{5a}$$

$$=\sum_{m,m'} c_m\psi_{m'}D^{(j)}(\alpha,\beta,\gamma)_{m'm},\quad m'=\pm\tfrac{5}{2},\ \pm\tfrac{3}{2},\ \pm\tfrac{1}{2}.\tag{5b}$$

The general angular momentum transformation matrix element[5] is

$$D^{(j)}(\alpha,\beta,\gamma)_{m'm} = e^{-im'\alpha}e^{-im\gamma}\sum_k \frac{(-1)^k[(j+m)!(j-m)!(j+m')!(j-m')!]^{1/2}}{k!(j+m-k)!(j-m'-k)!(k+m'-m)!} \times (\cos\beta/2)^{2j-2k-m'+m}(-\sin\beta/2)^{2k+m'-m}, \tag{6}$$

and for Pr^{3+}:YAlO_3, $j=\frac{5}{2}$ with $\alpha=\pi/2, \gamma=-\pi/2$, under the assumption of rotations about a space-fixed right-hand coordinate system (X,Y,Z), the principal quadrupole axes of the ground state. Thus, the nuclear overlap integrals of (2a) become

$$\langle \tilde{m}_1 | \tilde{m}_3(\beta)\rangle = \sum_{m',m} a_{m'} c_m D(\beta)_{m'm}, \quad m',m = \tfrac{5}{2},\ \tfrac{1}{2},\ -\tfrac{3}{2}, \tag{7}$$

$$\langle \tilde{m}_2 | \tilde{m}_3(\beta)\rangle = \sum_{m',m} b_{m'} c_m D(\beta)_{m'm}, \quad -m',m = \tfrac{5}{2},\ \tfrac{1}{2},\ -\tfrac{3}{2}. \tag{8}$$

Equation (7) contains matrix elements $D(\beta)_{m'm}$ where $m-m'=0, \pm 2, \pm 4$ and thus have the property as (6) shows of being even functions of the angle β. The elements of (8), on the other hand, satisfy $m-m'=\pm 1, \pm 3, +5$ which are odd functions of β. Since μ_{12} is independent of β, we conclude that the Raman heterodyne signal

$$S(\beta) \sim \mu_{12} |\langle \phi_1|\mu|\phi_3\rangle|^2 \langle m_2 | m_3(\beta)\rangle \langle m_3(\beta) | m_1\rangle \tag{9}$$

is an odd function of β. It follows that the two signals $S_{1,2}$ associated with sites 1 and 2 will be of opposite sign since the transformation angles for sites 1 and 2 are $+\beta$ and $-\beta$, respectively. The resulting signal S_1+S_2 will then vanish since the rf transition frequencies of the two sites are equal in a zero external field.

Furthermore, should the quadrupole axes of upper and lower electronic states be congruent so that $Z_{1,2}=Z'_{1,2}$ making $\beta=0$, we then find from (6) that $D(\pi/2,0,-\pi/2)_{m'm}=\delta_{m'm}$. This has the consequence that $|m_3\rangle = \sum_m c_m \psi_m$ with $m=\frac{5}{2},\ \frac{1}{2},\ -\frac{3}{2}$, and hence $\mu_{23}=0$ causing the Raman heterodyne signal to vanish. We conclude that for $H_0=0$ the Raman heterodyne signal of a hyperfine transition vanishes when either (1) $\beta=0$, because for $H_{\mathrm{rf}} \perp Z$ one of the three required matrix elements is zero, or when (2) $\beta \neq 0$, as then the two sites generate signals of opposite sign which just cancel.

Upon application of a static magnetic field H_0, the twofold degeneracy of $|\pm m\rangle$ in (3) is lifted. In this 2×2 problem, the eigenvalues are

$$W_{\pm m_i}(H_0) = W_{\pm m_i}(0) \pm (\hbar H_0/2)(\gamma_z^2 A_i^2 \cos^2\theta + \gamma_y^2 B_i^2 \sin^2\theta)^{1/2}, \tag{10}$$

and the eigenvectors display mixing of the basis states $|\pm m_i\rangle$ of the form

$$|\pm m_i\rangle = \cos\alpha_i(\theta)|\pm m_i\rangle - i\sin\alpha_i(\theta)|\mp m_i\rangle. \tag{11}$$

Here, $\theta=\angle(H_0,Z)$ for the ${}^3H_4$ state (Fig. 2), $\tan 2\alpha_i = (B_i\gamma_y/A_i\gamma_z)\tan\theta$, $\gamma_{z,y}$ are components of the Pr gyromagnetic ratio, and B and A are functions[4] of the mixing coefficients $a_m^{(i)}$ in (3). Taking the upper signs of (11) and using (4) and (5), we obtain for the nuclear overlap integrals

$$\langle \tilde{m}_1 | \tilde{m}_3\rangle = a_m c_{m'} \{D_{mm'}(\beta)\cos(\alpha_1-\alpha_3) + iD_{m-m'}\sin(\alpha_1-\alpha_3)\}, \tag{12a}$$

$$\langle \tilde{m}_i | \tilde{m}_3\rangle = b_m c_{m'} \{D_{-mm'}(\beta)\cos(\alpha_2-\alpha_3) + iD_{mm'}\sin(\alpha_2-\alpha_3)\}, \tag{12b}$$

where $m,m'=\frac{5}{2},\frac{1}{2},-\frac{3}{2}$. Consider now the symmetrical case where H_0 points along the crystal b axis $(\theta_1=-\theta_2)$ or a axis $(\theta_1=\pi-\theta_2)$ of Fig. 2 and produces a sign reversal in α_1 for the two sites. Since $D_{mm'}$ is even and $D_{-mm'}$ is odd in β, it follows that the sign of (12a) is preserved and the sign of (12b) is reversed in the two sites. Similarly, we find that μ_{12} is independent of β and invariant to a sign change in α. Consequently, for this symmetrical case the overall signal S_1+S_2 vanishes. However, for arbitrary angles θ_1, θ_2, and β, analytic and numerical calculations show that for certain choices of $|\tilde{m}_1\rangle$, $|\tilde{m}_2\rangle$, and $|\tilde{m}_3\rangle$, S_1 and S_2 are again of opposite sign, but in general sign reversal is not a universal property when the symmetry is broken.

The origin of the interference phenomenon is illustrated in Fig. 3, where absorption Raman heterodyne spectra are given for a 0.1-at.% Pr^{3+}:$YAlO_3$ platelet with dimensions $5 \times 5 \times 1.1$ mm^3 parallel to the crystal axes a:b:c, the temperature being 1.51 K. With the experimental arrangement of Refs. 1 and 2, the $^3H_4 \rightarrow {}^1D_2$ transition is excited by a Coherent 500 dye-laser beam, 25 mW in a 100-μm diameter at a wavlength of 610.5 nm, propagating with linear polarization along the crystal c axis. The $^3H_4$ $|\pm\frac{1}{2}\rangle \rightarrow |\pm\frac{3}{2}\rangle$ transitions, two strong and two weak ones for each site, are excited by sweeping a 0.3-G rf magnetic field, oriented along the crystal c axis, over the range 6 to 8 MHz. The static field H_0 lies in the a-b plane at an angle of 33.6° to the b axis, and as it increases from 0 to 69 G, the signal evolves into the four-line spectrum predicted by (10). For $H_0 \sim 0$, the interference effect predicted by (9) is observed as the signal amplitude approximates zero because of the cancellation of S_1 and S_2. For $H_0 = 4$ G, the anomalous second-derivative-like line shape observed previously[1,2] appears, and above 32 G all four strong lines are fully resolved and display sign reversal in the two sites. In addition, the signal is found to vanish because of interference when $H_0 \neq 0$ is oriented symmetrically so that $\theta_1 = -\theta_2$ or $\theta_1 = \pi - \theta_2$. Furthermore, interference is independent of the polarization direction of the light beam.

Since the Raman interference effect hinges on $\beta = |\angle(Z_{1,2}, Z'_{1,2})|$ being nonzero, it is important to determine the magnitude of this angle. By rotating the field H_0 about the c axis to different angles $\theta_{1,2}$ relative to $Z_{1,2}$ in the a-b plane, the angular dependence of the Zeeman spectrum is found and hence the Z orientation $\beta_0 = \angle(b,Z)$. Figure 4 shows a least-squares fit, using Eq. (10), to the observed points for the excited state $^1D_2$ transition $|\pm\frac{3}{2}\rangle \rightarrow |\pm\frac{5}{2}\rangle$ which is an eight-line spectrum, four lines for each site, where the zero-field splitting is 1.569 MHz. These data and similar measurements for the ground state $^3H_4$ transitions $|\pm\frac{1}{2}\rangle \rightarrow |\pm\frac{3}{2}\rangle$ (zero-field splitting, 7.062 MHz) yield

$$^1D_2,\ \beta_0 = 69.2° \pm 1°; \quad {}^3H_4,\ \beta_0 = 56.4° \pm 1°.$$

The result for $^3H_4$ is in good agreement with a previous value.[6] The $^1D_2$ measurement of β_0 represents the first solid-state determination of the nuclear quadrupole orientation in an excited electronic state. For this specific angle of $\beta = 69.2° - 56.4° = 12.8°$, sign reversal is obeyed for arbitrary H_0 orientation.

It is possible to generalize these ideas further. Clearly, the Raman heterodyne interference effect is a general phenomenon that will occur in any impurity-ion crystal possessing two or more inequivalent nuclear quadrupole sites when $\beta \neq 0$. For the interference signal to vanish, site symmetry is required, and must be preserved upon application of a static field H_0. The crucial requirement is that ground and excited electronic state quadrupole axes be incongruent, a property that can now be examined quantitatively by Raman heterodyne detection. Finally, Raman interference is expected for other kinds of transitions, besides hyperfine, and even for a single site as in the recently observed Zeeman transitions.[3]

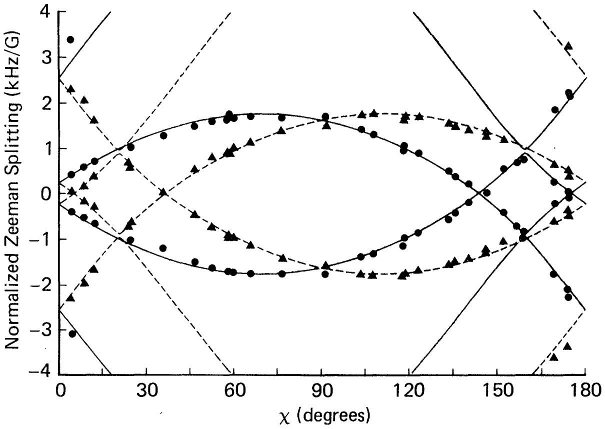

FIG. 4. Zeeman absorption spectrum of the excited state $^1D_2$ $|\frac{5}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ transition of 0.1-at.% Pr^{3+}:$YAlO_3$ as a function of the angle χ that $H_0 \sim 50$ G makes with the crystal b axis. Experimental points for sites 1 (circles) and 2 (triangles). Theoretical curves for sites 1 (solid) and 2 (dashed). The angle $\chi = 20.8°$ locates the Z'_2 axis angle $\beta_0 = \pi/2\chi = 69.2°$.

We are indebted to K. L. Foster for technical aid. One of us (E.S.K.) acknowledges an IBM Graduate Fellowship. This work was supported in part by the U.S. Office of Naval Research.

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