Pseudospin Dynamics of the One-Dimensional $S = \frac{1}{2}$ XY System PrCl₃ Studied by Electronic Raman Scattering

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Direct confirmation of the one-dimensional $S = \frac{1}{2}$ XY character of the interactions between the pseudospins of the Pr^{3+} ions in PrCl₃ is obtained through a study of the pseudospin dynamics by means of electronic Raman scattering, with and without a magnetic field. This is concluded from an analytic calculation of the spectral moments and from a numerical finite-chain calculation of the line shapes, both of which are in excellent agreement with the experimental data.

We present an experimental and theoretical study of the electronic Raman transition from the non-Kramers ground-state doublet to the lowest excited singlet of the Pr^{3+} $(4f^2;\ ^3H_4)$ ion in PrCl₃ (Hougen and Singh[1]), at 32 cm⁻¹. There is a keen and continued interest in this crystal because it is one of the very few physical realizations of the one-dimensional (1D) $S = \frac{1}{2}$ spin system with XY interactions between nearest-neighbor (nn) spins.[2] Many of the properties of this model system can be calculated exactly[3] and as a result comparison with experiment is often possible. We demonstrate that the dynamical properties of the pseudospins in PrCl₃ are reflected in the linewidth and line shape of the electronic Raman spectra, observed with and without an applied magnetic field.

The 1D properties of PrCl₃ above the structural phase transition temperature $(T_c = 0.428$ K$)$ were suggested by measurements of low-temperature heat capacity, magnetic susceptibility, and chlorine nuclear quadrupole resonance.[4] The gyroscopic ratio[5] of Pr^{3+} impurities as well as the "exchange" constants[6] of axial Pr^{3+}-Pr^{3+} pairs in the isomorphic crystal LaCl₃ were found to be extremely anisotropic as a result of the non-Kramers nature of the Pr^{3+} ground-state doublet. Through a careful analysis of chlorine nuclear magnetic resonance data and of electric susceptibility measurements, Harrison, Hessler, and Taylor[2] have shown that the dominant spin-spin interactions are nonmagnetic. Transverse components of the $S = \frac{1}{2}$ pseudospins carry an electric dipole moment related to local distortions of the lattice, and the coupling between pseudospins can be regarded as antiferroelectric interactions between Jahn-Teller systems. The experimental data concerning the statics and dynamics of PrCl₃ previously available have been interpreted in terms of the spin Hamiltonian

$$\mathcal{H}_S = J\sum_p (S_p^x S_{p+1}^x + S_p^y S_{p+1}^y) + h\sum_p S_p^x, \quad (1)$$

in which $h = g_{\parallel}\mu_B H_z$, H_z is the static magnetic field component along the hexagonal axis, the z axis, and μ_B is the Bohr magneton. The parameters for isolated Pr^{3+} in LaCl₃ were employed, i.e., the transverse exchange constant $J/k_B = J_\perp/k_B = 2.85 \pm 0.14$ K between axial Pr^{3+} pairs,[6] and the gyroscopic ratio $g_{\parallel} = 1.035 \pm 0.005$.[5] A far-infrared absorption feature in PrCl₃ has been attributed to zero–wave-vector $(k \approx 0)$ excitations of the 1D spin system.[7] Recently, the low-frequency response of the pseudospins in PrCl₃ has been investigated by means of Cl nuclear spin relaxation[8] and was shown to be consistent with the picture of the 1D spin-spin interactions given above.

The ground multiplet $4f^2\ ^3H_4$ of the Pr^{3+} ion is split by a crystal field of C_{3h} symmetry.[9] The resulting ground doublet belongs to the E' representation of C_{3h} and carries the $S = \frac{1}{2}$ pseudospin. Accordingly, the states will be labeled $|\pm\frac{1}{2}\rangle$, corresponding to phase factors $e^{\pm i2\pi/3}$ under a threefold rotation around the z axis. An A'' singlet state, labeled $|0\rangle$, is split from the ground doublet by an energy ϵ, $\epsilon/k_B = 46$ K. In Fig. 1 the electronic Raman spectrum of PrCl₃ is shown in the absence of a magnetic field (curve a), and in an applied field of 6.31 T (curves b,c). The laser beam is incident along the z axis with right (curve b) and left (curve c) circular polarization, while the scattered light is collected at a right angle and is polarized linearly along the z axis. Reversal of the circular polarization is equivalent to a reversal of the magnetic field H_z to $-H_z$. The shift of the Raman line corresponds essentially to the Zeeman splitting of the levels of the ground doublet, and the circular
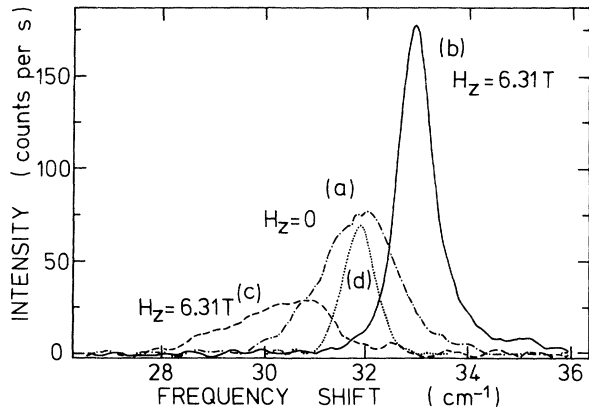
FIG. 1. Electronic Raman spectra of Pr^{3+} in $PrCl_3$ measured at $T = 5.4$ K with the laser beam incident along the hexagonal axis z, (curve a) in the absence of a magnetic field, and (curves b and c) in a field of $H_z = 6.31$ T along this axis, using right and left circular polarized light, respectively. Curve d shows the Raman line of Pr^{3+} diluted in $LaCl_3$, in zero magnetic field, shifted down in frequency by 2.0 cm^{-1} for the purpose of comparison with curves $a-c$. The spectra have been smoothed and a constant background has been subtracted. The experimental resolution is ≈ 0.5 cm^{-1} for curves $a-c$, and ≈ 0.7 cm^{-1} for spectrum d.

polarization of the light singles out only one of these states as the initial state for the scattering process. We also give the spectrum of Pr^{3+} diluted in $LaCl_3$:1 mol% $PrCl_3$ in the absence of a magnetic field (Fig. 1, curve d). For the purpose of comparison with the spectra in $PrCl_3$ this curve was shifted down in frequency by 2.0 cm^{-1}. The observed width of this narrow line (≈ 0.7 cm^{-1}) is determined by the experimental resolution.

The Raman spectra in the undiluted system $PrCl_3$

are much broader (≈ 1.8 cm^{-1}) than that for the isolated Pr^{3+} ions in $LaCl_3$. Moreover, with increasing magnetic field the signal in $PrCl_3$ becomes narrower for the right circular polarization, and broader for the left circular polarization. Finally, at high magnetic fields the two lines split and a clear asymmetry develops in the low-intensity peak (c) with the steep edge at the high-energy side. For the other peak (b) the asymmetry, with the steep edge now at the low-energy side, is much smaller but its presence has been established through repeated careful measurements. When the temperature is increased the asymmetry of the Raman lines gradually disappears. At about $T = 20$ K the spectra for right and left circular polarization possess nearly the same intensities and linewidths, and no asymmetry is observable any more. The larger linewidth of the electronic Raman spectrum in $PrCl_3$ as compared to that of isolated Pr^{3+} in $LaCl_3$ as well as the field dependence of the line shape result, as we show below, from the dynamics of the chains of $S = \frac{1}{2}$ pseudospins.

In calculating the electronic Raman spectra of a chain of Pr^{3+} ions in $PrCl_3$, we will only consider the one-ion operators acting between the three lowest states of these ions: first the components of the pseudospin S^x, S^y, and S^z, which possess the usual matrix elements between the states $| \pm \frac{1}{2} \rangle$. Furthermore, we define operators $a(\mu)$, with $\mu = \pm \frac{1}{2}$, converting the doublet states into the singlet state, $a(\mu)|\nu\rangle = \delta_{\mu,\nu}|0\rangle$, in which $\nu = 0$, $\pm \frac{1}{2}$, and correspondingly the conjugate operators $a^\dagger(\mu)$. For the polarization geometry employed in the experiments the electronic Raman spectrum is proportional to the Fourier transform of the time-dependent correlation function:

$$I_\pm(\tau) = \sum_p \langle [\mathscr{P}_{zx}(\tau,p) \mp i\mathscr{P}_{zy}(\tau,p)][\mathscr{P}_{zx}(p) \mp i\mathscr{P}_{zy}(p)]^\dagger \rangle, \qquad (2)$$

in which $\mathscr{P}_{\alpha\beta}(p)$ is the part of the polarizability of a single ion at site p which depends on the operators defined above. In (2) we implicitly assumed that the polarizability of the crystal is the sum of single-ion polarizabilities. The time dependence is governed by the Hamiltonian $\mathscr{H} = \mathscr{H}_S + \mathscr{H}_E$, where $\mathscr{H}_S$ is the $S = \frac{1}{2}$ XY Hamiltonian given in Eq. (1), and $\mathscr{H}_E = \epsilon\sum_p n_p$ is the singlet excitation energy. At low temperature, $T \ll \epsilon/k_B \approx 46$ K, singlet excitations possess a very low probability, and we can replace the thermal average $\langle\rangle$ by an average $\langle\rangle_{spin}$, in which we sum only over the states having all of the ions in the ground doublet. Making use of the symmetry properteis of the polarizability $\mathscr{P}_{\alpha\beta}(p)$, and of its Hermiticity, one finds $\mathscr{P}_{zx}(p) \mp i\mathscr{P}_{zy}(p) = c[a_p(\mp\frac{1}{2}) + a_p^\dagger(\mp\frac{1}{2})]$, where c is a numerical factor. It is now straightforward though somewhat tedious to show that

$$I_\pm(\tau) = |c|^2 e^{-i\epsilon\tau}\sum_p \langle \exp(i\mathscr{H}_S\tau)\exp[-i(\mathscr{H}_S - h_S^{(p)})\tau](\frac{1}{2} \mp S_p^z)\rangle_{spin}, \qquad (3)$$

where

$$h_S^{(i)} = S_i^x(S_{i-1}^x + S_{i+1}^x) + S_i^y(S_{i-1}^y + S_{i+1}^y) + hS_i^z.$$

Obviously, the expectation value in (3) is not a spin-correlation function of the usual kind. This is related to the usual kind. This is related to the electronic Raman process which excites one ion out of its ground doub-

let state, i.e., out of the space described by the pseudospins. Although a vast amount of exact results are available on spin correlation functions of the $S = \frac{1}{2}$ XY model,[3] it is very hard to calculate (3) analytically.

However, it is straightforward to calculate the zeroth, first, and second frequency moments of the Fourier transform (3) by use of the techniques of Ref. 3. Fitting the theoretical results for the moments to the experimentally determined spectral moments, obtained at several values of the magnetic field H_z between zero and 6.31 T, we obtain $\epsilon/k_B = 45.6 \pm 0.2$ K, $g_\parallel = 0.827 \pm 0.007$, and $J/k_B = 2.4 \pm 0.2$ K. To our knowledge, this is the

first accurate determination of the g value of Pr^{3+} in the undiluted system $PrCl_3$. This g value is quite different from that in $LaCl_3$. Moreover, the value determined for the exchange constant is somewhat lower than the value 2.85 K quoted for Pr^{3+}-Pr^{3+} pairs in $LaCl_3$ which was employed in previous work.[2,7-9]

More information about the line shapes of the Raman spectra is obtained from finite chain calculations. For a chain of $2N - 1$ sites with free ends we have diagonalized the Hamiltonian $\mathcal{H}_S$ and the operator $\mathcal{H}_S - h_S^{(N)}$ in order to obtain their eigenstates, Ψ and Φ, and eigenvalues, E_Ψ and E_Φ, respectively. The Raman spectra were then calculated using the expression

$$I_\pm(\omega) = [(2N-1)|c|^2/2\pi]\sum_{\Psi,\Phi}\delta(\omega - \epsilon + E_\Psi - E_\Phi)\exp(-\beta E_\Psi)\langle\Psi|\Phi\rangle\langle\Phi|\tfrac{1}{2} \mp S_z^N|\Psi\rangle, \tag{4}$$

in which $\beta = 1/k_B T$. We can prove that for the $S = \frac{1}{2}$ XY chain with free boundary conditions the calculation of (4) for a chain of $2N - 1$ sites can be reduced to a similar calculation for a chain of N spins, again with free ends, by making a suitable adaption of spin Hamiltonian (1).

In Fig. 2 we present the calculated Raman spectra for a chain of seventeen sites, using the $g_\parallel$ and J parameters determined from the moment fitting. The line shapes are in very good agreement with those of the experimental spectra (Fig. 1), reproducing the changes in width and asymmetry introduced by the applied magnetic field. The ratio of the integrated intensities of the I_+ and the I_- spectra is somewhat larger in the calculation (Fig. 2) than in the experimental results (Fig. 1). In fact, a
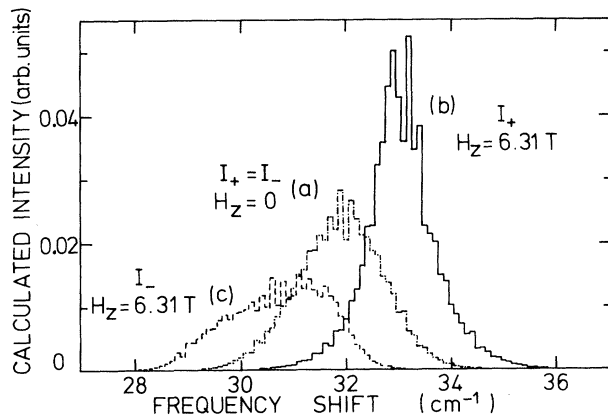

FIG. 2. Calculated electronic Raman spectra for a linear chain of seventeen Pr^{3+} ions ($N = 9$) at $T = 5.4$ K using the parameters $\epsilon/k_B = 45.6$ K, $g_\parallel = 0.827$, $J/k_B T = J_\perp = 2.4$ K, and $J_\parallel = 0$, in the same conditions of polarization geometry and magnetic field as quoted for the experimental spectra in Fig. 1.

more accurate fit is obtained if a lower temperature (≈ 4.2 K) is employed in the calculation, but a careful temperature calibration has shown that the experimental accuracy is better than a tenth of a degree. We have repeated the calculation for higher temperatures up to 20 K and found a good agreement with the changes in line shape of the experimental spectra: The intensities and linewidths of the Raman lines for opposite circular polarization tend to become equal, and the asymmetry of each of the Raman lines disappears.

The question arises whether the calculated line shapes are characteristic for model Hamiltonian (1). Therefore we have studied the influence of the introduction of exchange interactions between the z components of nn spins. In Fig. 3 we present calculated spectra for similar values of the parameters, except for the introduction of either a ferromagnetic or an antiferromagnetic Z-Z exchange term, with $J_\parallel = \pm J_\perp/2 = \pm J/2$. In either case the two Raman peaks for opposite circular polarization both exhibit asymmetries in the same sense, i.e., for both peaks the steepest side is at high energy for $J_\parallel = -J_\perp/2$, and at low energy for $J_\parallel = J_\perp/2$, in contradiction with the experimental results. Such an effect would have been detected in the experimental spectra, and therefore $J_\parallel$ must indeed be much smaller than $J_\perp$.

We conclude that the features of the electronic Raman spectra of $PrCl_3$ with and without an applied magnetic field are caused by the dynamics of the $S = \frac{1}{2}$ pseudospin system of almost pure one-dimensional character with almost pure XY interactions between nn spins. Through the analysis of the Raman spectra we have directly determined the spin-Hamiltonian parameters of $PrCl_3$, which are different from the previous values derived from the
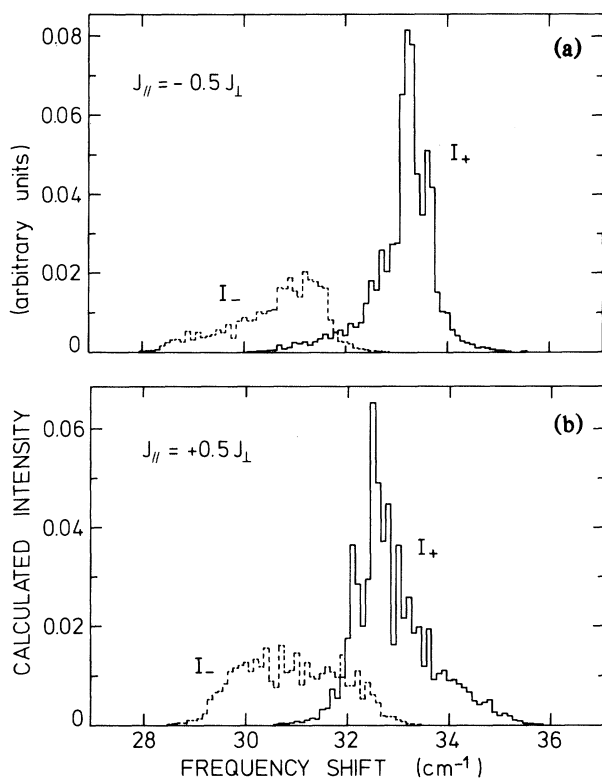
FIG. 3. Calculated electronic Raman spectra ($T = 5.4$ K, $H_z = 6.31$ T) of a chain of nine Pr^{3+} ions including either a ferromagnetic or an antiferromagnetic exchange interaction between z components of the pseudospins, $J_\parallel = \pm J_\perp/2$, and again as in Fig. 2 for the parameter values $\epsilon/k_B = 45.6$ K, $g_\parallel = 0.827$, and $J_\perp/k_B = J/k_B = 2.4$ K.

dilute system Pr^{3+} in $LaCl_3$.

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