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## Bromine nuclear quadrupole resonance study of PrBr<sub>3</sub>

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**Abstract.** Measurements of the bromine nuclear quadrupole resonance frequency and spin-spin relaxation time ( $T_2$ ) are reported for praseodymium tribromide (PrBr<sub>3</sub>) from 4.2 K to 0.125 K. The frequency data indicate that at  $T=0.130$  K a phase transition to a three-dimensional antiferroelectric ordered state occurs. This distortion is believed to be a Peierls dimerization; a dimerization parameter is deduced. The  $T_2$  results, which are not understood in detail, are shown to be due to a magnetic dipole interaction mechanism.

### 1. Introduction

The praseodymium trihalides, PrBr<sub>3</sub>, are of particular interest because the nearest-neighbour Pr-Pr interaction along the hexagonal crystal axes in these crystals provide a good physical realization of the ideal one-dimensional XY model. Early nuclear spin relaxation measurements (Mangum and Thornton 1969) for the <sup>35</sup>Cl nuclei in PrCl<sub>3</sub> yielded both spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times. The temperature dependence of these relaxation times was described as 'unusual'. In 1969 it was thought that PrBr<sub>3</sub> was an antiferromagnet; it is now known that this is incorrect (Hessler and Carlson 1971). Recent more accurate measurements of the <sup>35</sup>Cl spin-lattice relaxation time in PrCl<sub>3</sub> and of <sup>79</sup>Br and <sup>81</sup>Br relaxation times in PrBr<sub>3</sub> have been reported (Su *et al* 1991) from a nuclear quadrupole resonance (NQR) experiment carried out in the pseudo-one-dimensional regime. These data were shown to be in excellent agreement with the predictions of a relaxation theory based on a rigorous treatment (Katsura *et al* 1970) of the longitudinal dynamical correlation function  $\langle S_z^m(t)S_z^n(0) \rangle$  of the electronic pseudo-spins  $S^m$  associated with the crystalline electric-field ground states.

The CW NQR spectrum of the <sup>35</sup>Cl nuclei in PrCl<sub>3</sub> (Colwell *et al* 1969) indicated that a phase transition occurs at  $T_c=0.428$  K. The single <sup>35</sup>Cl NQR line above  $T_c$  symmetrically splits into two lines of equal intensity below  $T_c$ . On the basis of a group theoretical analysis (Morra *et al* 1983) it was deduced that the phase transition was a co-operative Jahn-Teller distortion to a three-dimensional antiferroelectric ordered state, predicted to be a Peierls dimerization. To date this identification has not been verified directly by a neutron diffraction measurement.

In the present paper an NQR investigation of the two bromine isotopes in PrBr<sub>3</sub> is reported. Measurements of the NQR frequency spectrum and  $T_2$  were carried out

from 4.2 K to 0.125 K using a dilution refrigerator and a Fourier-transform NQR spectrometer. The data are presented in section 2 and discussed in sections 3 and 4.

## 2. Data

The samples, the dilution refrigerator, the NQR spectrometer and the basic experimental method have been described in an earlier publication (Su *et al* 1991). The bromine NQR frequency data were obtained from a one-pulse experiment. A typical  $\pi/2$  pulse length was  $5.5 \mu\text{s}$ . The  $^{81}\text{Br}$  data are shown in figure 1. The  $T_2$  magnetization-decay curves were obtained using two different pulse sequences: (a) the  $(\pi/2)_0 - \tau - (\pi)_0$  Hahn-echo sequence (Hahn 1950), and (b) the  $(\pi/2)_0 - \tau - (\pi/2)_{90}$  solid-echo sequence (Powles and Strange 1963). Typical echo decays are shown on the semi-logarithmic plots in figure 2. These magnetization-decay plots,  $M(\tau)$  versus  $\tau$ , are linear and their slopes give the corresponding  $T_2$  values. The temperature dependences of  $T_2$  for both the  $^{79}\text{Br}$  and  $^{81}\text{Br}$  resonances and for both pulse sequences are plotted in figure 3. The curve drawn through  $^{81}\text{Br}$  data is a 'guide to the eye'. Each point on the curve drawn through  $^{79}\text{Br}$  data corresponds to a  $T_2$  value 1.16 times larger than the corresponding  $^{81}\text{Br}$  point.

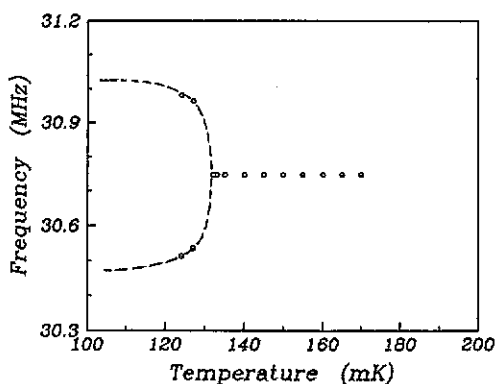


Figure 1. Temperature dependence of the  $^{81}\text{Br}$  NQR frequency in  $\text{PrBr}_3$ . The dashed line represents reasonable extrapolation to low temperature as explained in the text.

## 3. Temperature dependence of the resonance frequency

From figure 1 we see that  $\text{PrBr}_3$  undergoes a phase transition at  $0.130 \pm 0.010$  K. This transition temperature is much lower than that observed for  $\text{PrCl}_3$  (Colwell *et al* 1969). Since this was not expected, we also measured the  $^{35}\text{Cl}$  NQR spectrum in  $\text{PrCl}_3$  as a check on our sample temperature determination. The data yielded a transition temperature of  $0.410 \pm 0.010$  K, which is in reasonable agreement with the earlier result of 0.428 K.

The only previous report of the transition temperature in  $\text{PrBr}_3$  was based on electric susceptibility measurements (Taylor *et al* 1977) above 0.27 K. The data are plotted in figure 4 as a function of  $J/k_B T$ . Curie law behaviour is shown for

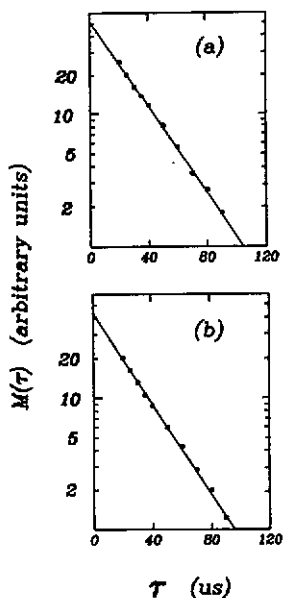


Figure 2. Typical decay as measured in  $\text{PrBr}_3$ : (a) Hahn-echo decay for the  $^{79}\text{Br}$  resonance at 1.8 K; (b) solid-echo decay for the  $^{79}\text{Br}$  resonance at 1.8 K.

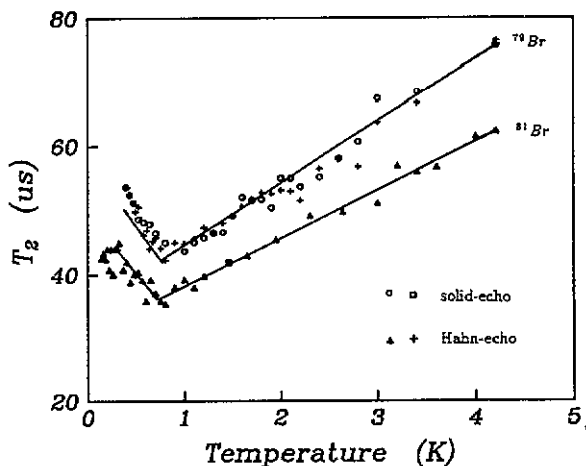


Figure 3. Temperature dependence of  $T_2$  for both bromine isotopes in  $\text{PrBr}_3$  as measured by the Hahn-echo and solid-echo sequences.

reference. The data follow the 1D XY model, at least for temperatures above 2.5 K ( $J/k_B T < 1.2$ ). The authors argue that an 'abrupt change of slope' occurs at  $T = 0.37$  K ( $J/k_B T = 8.1$ ), as indicated by the arrow, signalling the onset of long-range order. We do not find this interpretation convincing and it is certainly not supported by the NQR data.

The dashed line in figure 1 represents a 'reasonable' extrapolation of the frequency data to low temperatures. It assumes that the data for the two temperatures below  $T_c$  are sufficient to conclude that the phase transition in  $\text{PrBr}_3$  is of the same nature as that in  $\text{PrCl}_3$ . Also, the dashed line satisfies the assumption that the limiting value

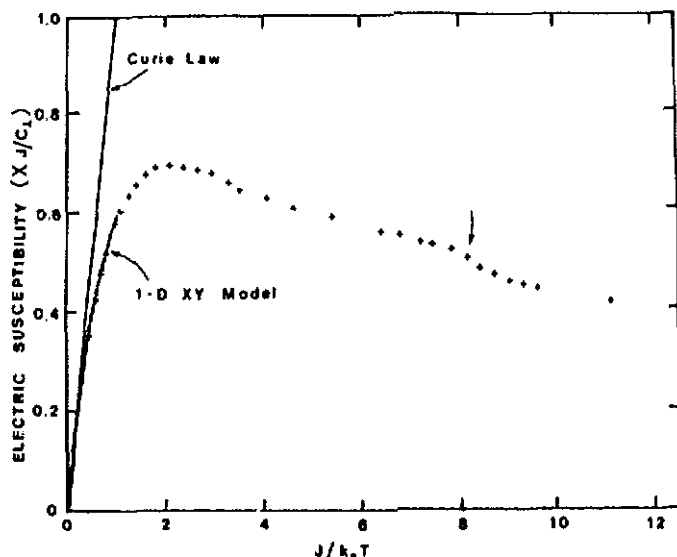


Figure 4. Temperature dependence of the electric susceptibility of  $\text{PrBr}_3$  (from Taylor *et al* 1977).  $J/k_B = 3.0$  K is the interaction parameter. The arrow indicates the data point corresponding to  $J/k_B T = 8.1$  ( $T = 0.37$  K) and indicates 'an abrupt change of slope'.

of the frequency splitting,  $\Delta\nu_L$  in  $\text{PrBr}_3$  is such that

$$(\Delta\nu_L/\nu_0)_{\text{PrBr}_3} = (\Delta\nu_L/\nu_0)_{\text{PrCl}_3} \simeq 0.018$$

This result would be expected if the magnitude of the dimerization in the two compounds is nearly the same.

A previous estimate of the magnitude of the Peierls dimerization (Taylor *et al* 1983) in  $\text{PrCl}_3$  yielded  $\Delta c/c \simeq 0.2\%$ . The estimate was deduced from a consideration of the dependence of the NQR frequency on the unit cell dimension  $c$  in the series of isostructural compounds  $\text{CeCl}_3$ ,  $\text{PrCl}_3$  and  $\text{NdCl}_3$ . It is certainly not obvious that this procedure is a reliable one.

There is, however, a better way to estimate the magnitude of the dimerization which makes use of only the limiting frequency splitting,  $\Delta\nu_L$ , below  $T_c$  and the frequency,  $\nu_0$ , just above  $T_c$ . Dimerization can be characterized by a parameter

$$D_{\pm} = r_0(\text{Pr}) - r_{\pm}(\text{Pr})$$

where  $r_0$  and  $r_{\pm}$  are defined in figure 5. For  $T > T_c$  the Pr ions are equally spaced along 1D chains with separation  $r_0$ . For  $T < T_c$  dimerization occurs and alternate Pr ion separations are greater than ( $r^+$ ) and less than ( $r_-$ ) the spacing  $r_0$ .

Denoting the NQR parameters above  $T_c$  as  $(eq)_0$  and  $\eta_0$  and below  $T_c$  as  $eq$  and  $\eta$ , it follows that

$$\nu(D_{\pm}) = \frac{(eq)_{D_{\pm}} [1 - \eta^2(D_{\pm})/3]^{1/2}}{(eq)_0 [1 - \eta_0^2/3]^{1/2}} \nu_0$$

The point-charge model can be used to calculate the components of the electric field gradient tensor, and hence to obtain values of the field gradient parameter and

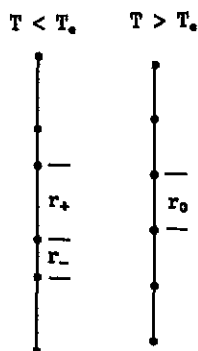


Figure 5. Definition of the quantities  $r_0$ ,  $r_+$  and  $r_-$  for the normal and dimerized chains of Pr ions (dots) in  $\text{PrBr}_3$ . Neglecting thermal expansion,  $r_+ + r_- = 2r_0$ .

asymmetry parameter, both above and below  $T_c$ , for a series of values of  $D_{\pm}$ . The above relation remains correct for the values of  $\nu_0$  and  $\nu(D_{\pm})$  so obtained, provided only that the antishielding factor is not altered by the dimerization.

The point-charge calculation performed included contributions from 900 unit cells. The magnitude of the dimerization deduced is  $D/c = 0.007$  for the limiting value of the frequency splitting observed for  $\text{PrCl}_3$ . This result is of comparable magnitude to that estimated for the spin-Peierls transition in TTF-CuBDT (Bray *et al* 1975). A similar result is expected near the phase transition in  $\text{PrBr}_3$ .

#### 4. Temperature dependence of the spin-spin relaxation time

$T_2$  data were previously reported (Mangum and Thornton 1969) for the  $^{35}\text{Cl}$  nuclei in  $\text{PrCl}_3$ . We repeated these measurements for several temperatures and obtained results in substantial agreement. Our new  $T_2$  data for  $\text{PrBr}_3$  measured above  $T_c$  are shown in figure 3 for both the  $^{79}\text{Br}$  and  $^{81}\text{Br}$  resonances and as measured by both the Hahn-echo and solid-echo pulse sequences. Several conclusions may be drawn. Firstly, the two sequences yield the same results. This is to be expected in the rigid-lattice regime. Secondly, the isotope ratio is  $T_2(^{79}\text{Br})/T_2(^{81}\text{Br}) = 1.2 \pm 0.1$ . This is in agreement with the theoretical ratio  $T_2(^{79}\text{Br})/T_2(^{81}\text{Br}) = [\mu(^{81}\text{Br})/\mu(^{79}\text{Br})]^2 = 1.16$  for a magnetic relaxation mechanism.

The temperature dependence of  $T_2$  is remarkable. As with the previous data for  $\text{PrCl}_3$ ,  $T_2$  decreases with temperature in an approximately linear fashion from 4.2 K to just below 1 K, but then undergoes an abrupt reversal, and increases as the temperature decreases further.

A previous study (D'Iorio *et al* 1983) of spin-spin relaxation in  $\text{PrCl}_3$  at 4.2 K using a Hahn-echo sequence reported a non-exponential decay of the magnetization. The data were fitted to a function of the form  $\exp(-bt^{3/2})$ . The  $\hat{T}_2$  values deduced from these fits indicated that  $\hat{T}_2$  was dominated by an electric quadrupolar mechanism, rather than a magnetic dipolar mechanism. We attempted to reproduce the behaviour reported for  $\text{PrCl}_3$  but were unable to do so and have concluded that the result by D'Iorio was a spurious result.

It is possible to calculate the temperature dependence of  $T_2$  for a magnetic relaxation mechanism. By using the spin correlation function  $\langle S_z^m(t)S_z^n(0) \rangle$  given by Katsura *et al* (1970), we were able to compute the temperature dependence of  $T_2$  for

a resonant nucleus experiencing magnetic interaction with the electronic pseudo-spin  $S^m$  associated with the crystalline electric-field ground states. The result predicts that  $T_2$  should increase with decreasing temperature, in agreement with the calculation for  $\text{PrCl}_3$  (D'Iorio *et al* 1983), but contrary to the experimental temperature dependence of the  $T_2$  data.

At present we are unable to provide a theoretical explanation of the temperature dependence of  $T_2$ . We present the results as a stimulus to theorists interested in the dynamical properties of the one-dimensional XY model.

## References

- Bray J W, Hart H R, Interrante L V, Jacobs I R, Kasper J S, Watkins G D and Wee S H 1975 *Phys. Rev. Lett.* **35** 744
- Colwell J H, Mangum B W and Utton D B 1969 *Phys. Rev.* **181** 842
- D'Iorio M, Armstrong R L and Taylor D R 1983 *Phys. Rev. B* **27** 1964
- Hahn E L 1950 *Phys. Rev.* **80** 580
- Hessler J P and Carlson E H 1971 *J. Appl. Phys.* **42** 1316
- Katsura S, Horiguchi T and Suzuki M 1970 *Physics(Utrecht)* **46** 67
- Mangun B W and Thornton D D 1969 *Phys. Rev. Lett.* **22** 1105
- Morra R M, Armstrong R L and Taylor D R 1983 *Phys. Rev. Lett.* **51** 809
- Powles J G and Strange J H 1963 *Proc. Phys. Soc.* **82** 6
- Su S, Armstrong R L, Wei W and Donabarger R 1991 *Phys. Rev. B* **43** 7365
- Taylor D R, Harrison J P and McColl D B 1977 *Physica* **86-88** B 1164
- Taylor D R, Morra R M and Armstrong R L 1983 *J. Mol. Struct.* **111** 239