^{17}O Quadrupole Dips in Ammonium Persulphate *

N. F. Peirson, J. A. S. Smith *
Chemistry Department, King's College London, Strand, London, WC2R 2LS, U.K.

D. Stephenson
Chemistry Department, University of the West Indies, St. Augustine, Trinidad, W.I.

Z. Naturforsch. **49a,** 345–350 (1994); received August 16, 1993

The magnetic field dependence of the ^1H spin-lattice relaxation time in ammonium persulphate shows pronounced minima near the ^1H magnetic resonance frequencies of 1,200 and 2,200 kHz. These are interpreted in terms of a model involving cross-relaxation between ^1H in the NH_4^+ ion and ^{17}O in natural abundance in the $S_2O_8^{2-}$ ions, the latter having a much shorter spin-lattice relaxation time. A theoretical analysis of the shape of the minima is used to derive values for the ^{17}O quadrupole parameters. This analysis results in best estimate values for the quadrupole coupling constant of 6.75 (± 0.05) MHz and an asymmetry of 0.30 (± 0.02). Such values are indicative of O–H hydrogen bonding and suggest the $S_2O_8^{2-}$ ion is not undergoing rapid reorientation at temperatures below 320 K.

Key words: NMR; NQR; Field cycling, Oxygen-17.

Introduction

Magnetic field cycling spectroscopy provides a convenient method for obtaining quadrupolar parameters in solids containing an abundant spin $I = 1/2$ nucleus such as ^1H as well as a quadrupolar spin ($I \geqq 1$) present in reasonable abundance [1–3]. The method consists in observing the ^1H n.m.r. signal in a constant high magnetic field, which is modulated by cycling down to low fields for variable times. By choosing the low field such that the ^1H n.m.r. frequency in that field corresponds to a quadrupolar frequency, energy may be transferred between the spin systems. If, as is normally the case, the spin-lattice relaxation time, T_1, for the quadrupolar nucleus is shorter in that field, than that for the ^1H nucleus, then the ^1H is relaxed at a faster rate than in the absence of the quadrupolar nucleus. By magnetising the ^1H spins in high field and then cycling to low field, 'quadrupole dips' [4] are observed corresponding to the enhanced relaxation of the ^1H spins at frequencies corresponding to quadrupole transitions. Such dips have also been observed for ^{14}N [1], ^{35}Cl [2], and other abundant nuclei [3]. In this paper, we report for the first time the observation of quadrupole dips for a quadrupolar nucleus in low abundance, namely ^{17}O in natural abundance (0.037%). The effect of ^{17}O in natural abundance on $T_{1\varrho}$ has already been shown in a number of compounds [5–8].

The T_1 (^1H) measurements reported here were performed on a sample of ammonium persulphate, $(NH_4)_2S_2O_8$. A plot of T_1 (^1H) as a function of ^1H n.m.r. frequency in low field showed dips in the region of 1 to 3 MHz. High field measurements of T_1 (^1H) at 16, 20, and 60 MHz for $(NH_4)_2S_2O_8$ have shown this is independent of frequency in the range from about 100 to 350 K [5, 9]. No minimum in T_1 is exhibited in this range, but a maximum is observed at 318 K of about 20 s [9]. The activation energy for reorientational motion of the ammonium ion has been calculated as 7.5 kJ mol^{-1} [9]. Morimoto [5] has also studied the proton $T_{1\varrho}$, and obtained minima in the temperature dependence which are attributed to the motionally modulated dipolar interaction between ^1H and ^{17}O and cross relaxation between ^1H and ^{17}O. The $T_{1\varrho}$ data have been used to determine an ^{17}O quadrupole coupling constant (e^2Qq/h) of 9.6 MHz in $(NH_4)_2S_2O_8$ [5] and 9.1 MHz in $(ND_4)_2S_2O_8$ [6], leading to the conclusion that the sulphate ion undergoes a rotation about the near 3-fold axis.

The crystal structure [10] indicates that the S_2O_8 group consists of two SO_4 groups linked via an

---

* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

Reprint requests to Prof. Dr. J. A. S. Smith, Chemistry Department, King's College London, Strand, London, WC2R 2LS, U.K.

0932-0784 / 94 / 0100-0345 $ 01.30/0. – Please order a reprint rather than making your own copy.

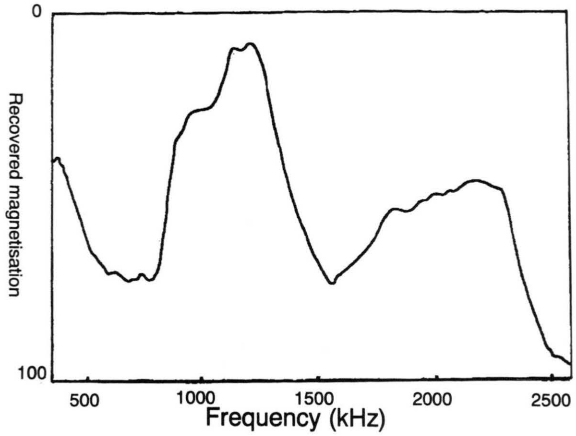

Fig. 1. The experimental cross relaxation spectrum of ammonium persulphate measured by mechanical field cycling. The residence time in a high field, of approximately 1 T, was 22 s, the residence time at the variable low field was 8 s. The spectrum was recorded at an ambient temperature of around 295 K.

oxygen-oxygen bond. The point symmetry of the $S_2O_8^{2-}$ is $\bar{1}$ (C_i), so all the oxygen atoms of a given $-SO_3$ group are crystallographically distinct and should have different quadrupole parameters.

Experimental Technique

A sample of $(NH_4)_2S_2O_8$, supplied as a 98+% A.C.S. reagent by the Aldrich Chemical Company Ltd. was used as received. Two types of field cycling measurements were carried out. A cross relaxation spectrum, Fig. 1, was obtained using a mechanical field cycling instrument [11] with fixed residence times of 22 s in high field and 8 s in low field. This measurement was carried out at room temperature, approximately 295 K. The measurement of T_1 (^{1}H) dispersion was carried out using a fast field cycling spectrometer [12], in which the sample remains static whilst the field is switched electronically from about 1 T to low or zero field in 0.7 ms [12]. The dispersion was measured in low fields from the Earth's field (ca. 1.8 kHz for ^{1}H) to ca. 4000 kHz for ^{1}H at three temperatures (270, 297, 323 K). The temperature stability was of the order of 0.1 K with a gradient of ca. 0.5 K or less across the sample. Figure 2 shows the measured T_1 (^{1}H) dispersion spectra.

Calculation of the theoretical spectra, discussed below, were carried out using a Digital 333 SXLP computer, based on a 386 processor and equipped with a maths coprocessor.

Results and Discussion

The results of the cross relaxation and dispersion experiments are in broad agreement. Both experiments show a similar pattern of features within the range 800–2600 kHz, which are in the region expected for ^{17}O [13]. Above this frequency no significant dispersion in T_1 is observed (below the maximum accessible frequency of 40 MHz). T_1 (^{1}H) is about 16 s in a 40 MHz field at room temperature, falling to about 10 ms in the Earth's field. Below 600 kHz, the dispersion appears to be due to the rapid reorientation of the ammonium ion and ^{14}N relaxation effects, the nature of which is currently being investigated. The interpretation of the effects of ^{17}O will concentrate on the T_1 dispersion data, although the cross relaxation data are essentially the same. Figure 2 indicates that the lineshapes and frequencies have a small temperature dependence with more fine structure apparent at 270 K. For this reason a more satisfactory fit of theory to experiment can be obtained at lower temperatures. The lower temperature spectrum appears to be sharper, suggesting that the broadening may be attributable to the thermal motion of the nuclei. Accordingly the theoretical spectra have been broadened by a Lorentzian function (although a Gaussian gives similar results) to give a better estimate of the experimental lineshape. There appears to be no obvious correlation of line frequency with temperature. The theoretical spectra were derived for Zeeman-broadened ^{17}O lineshapes for various values of the quadrupole parameters. The Hamiltonian was calculated for complete Zeeman plus quadrupolar interactions with no assumption of the relative contributions. The orientation of the ^{17}O electric field gradient (e.f.g.) is defined with respect to the magnetic field, B_0, by polar angles θ, ϕ, which are varied over a sphere. Iteration of the magnetic field strength to produce an energy match between each pair of Zeeman perturbed quadrupole energy levels and the proton energy levels was performed. When a match was obtained, typically after two or three iterations, the transition probabilities W_1 ($\Delta m = \pm 1$) and W_2 ($\Delta m = \pm 2$) were then calculated. In practice, the ratio $\gamma = \frac{W_2}{W_1}$ was taken as one of the fitting parameters [14].

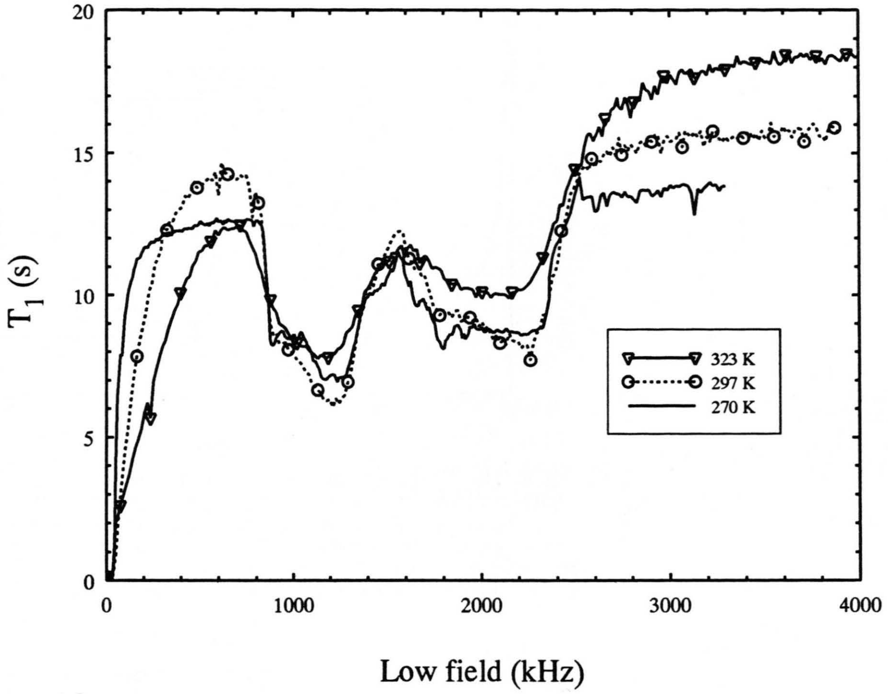

Fig. 2. The experimental T_1 dispersion spectra of ammonium persulphate at three temperatures. Each spectrum was obtained by magnetising the ^{1}H spins in a high field of approximately 1 T for 30 s and then cycling to a variable low field. The residence time in low field was varied to permit T_1 to be determined from the decrease in recovered signal with increasing time spent in the low field. The recovered magnetisation was fitted to an exponential decay at each field to obtain a T_1 value. The signals showed apparently single exponential behaviour over a wide range of relaxation times giving typical errors of the order of 5 to 10%. Non-exponential behaviour is apparent below 100 kHz and to some extent in the region of the minima. The effect of non-exponential decays are most apparent at the lower temperature. The spectra were recorded at 270, 297 and 323 K with a temperature stability of approximately 0.1 K and a gradient of about 0.5 K across the sample. The step in the low field between each measurement was 8 kHz.

A flow chart for the program used in these calculations is given in Figure 3. The calculation produced 1200 data points from 12 transitions for each crystal orientation and one hundred different crystallites. The raw output data were filled 16 fold in θ and 4 fold in ϕ, by linear interpolation, and then assembled into the final spectrum; points every 5 kHz were used in the range 0–4000 kHz. The program requires about 90 minutes to produce a complete spectrum, so that iterative computer fitting of the experimental spectrum was not a viable option.

Accordingly, a number of plots were produced with parameters around the values of

$$\left(\frac{e^2 Q q}{h}\right) = 6750\ \text{kHz and}\ \eta = 0.3,$$

which might be expected for ^{17}O, given the experimental lineshape. Only $\Delta m = \pm 1$ transitions appear to contribute to this spectral fit. One other set of parameters; viz.

$$\left(\frac{e^2 Q q}{h}\right) = 4750\,(\pm 50)\ \text{kHz and}\ \eta = 0.92\,(\pm 0.02),$$

and dominated by $\Delta m = \pm 2$ transitions, has been found to fit the general form of the experimental lineshape. However, the fit is not so good for the ca. 2200 kHz band and in poorer agreement with the $T_{1\varrho}$ studies [5], which would favour the higher quadrupole coupling constant. The $\eta = 0.9$ value is also much higher than would be expected for the S–O bond, which would be expected to have near axial symmetry. Results for sulphones [15, 16] would also indicate a relatively low value for the asymmetry parameter.

The 270 K T_1 data have been compared to spectra calculated with and without broadening functions. The resulting best matches are

$$\left(\frac{e^2 Q q}{h}\right) = 6750\,(\pm 50)\ \text{kHz},\ \eta = 0.30\ (\pm 0.02)$$

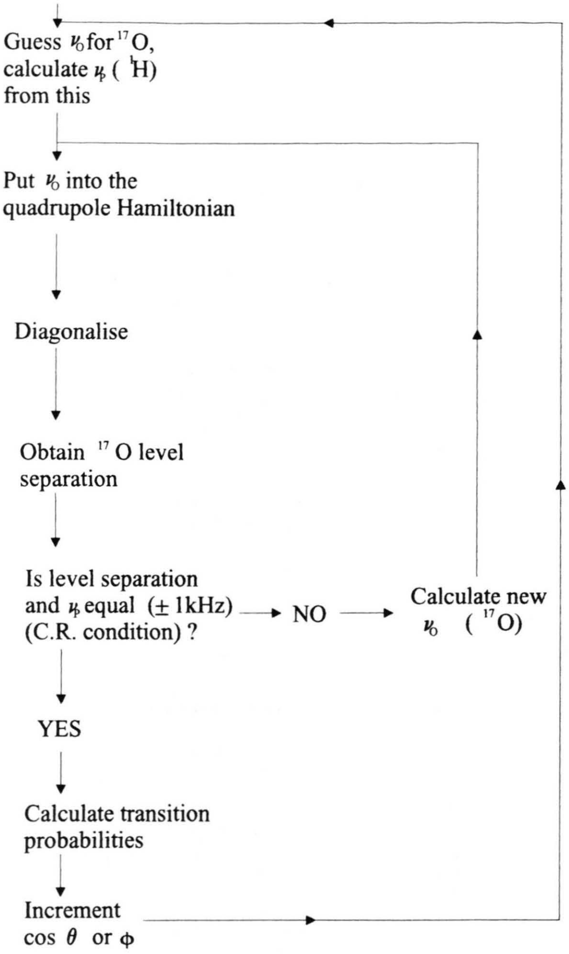

Fig. 3. A flow diagram showing the major steps in the calculation of the cross-relaxation spectrum of ^{17}O with ^{1}H.

with broadening, and

$$\left(\frac{e^2 Q q}{h}\right) = 6750\,(\pm 50)\ \text{kHz},\ \eta = 0.38\ (\pm 0.02)$$

without.

These fits are shown in Figs. 4 and 5, respectively, the experimental results being represented by the continuous line. The good fit of theory with experiment suggests that the assignment of the dips to ^{17}O cross-relaxation is correct, and that the dips are observable because of the very much shorter ^{17}O T_1 relative to that of ^{1}H. The results of the theoretical calculation indicate that the best values of the $S_2O_8^{2-}$ ion in $(NH_4)_2S_2O_8$ are

$$\left(\frac{e^2 Q q}{h}\right) = 6.75 \pm 0.05\ \text{MHz},\ \eta = 0.30 \pm 0.02.$$

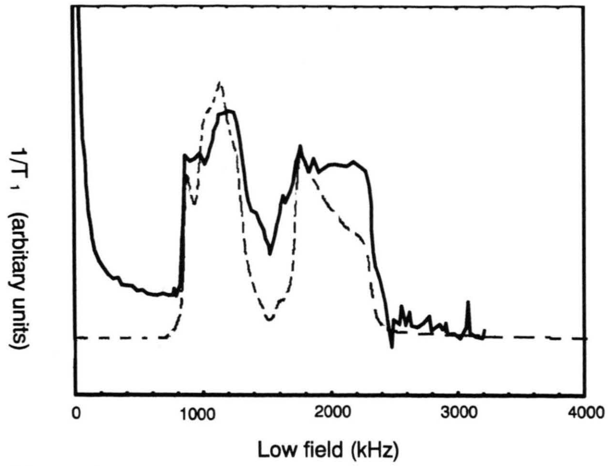

Fig. 4. The T_1 dispersion spectrum of ammonium persulphate at 270 K (solid line), shown together with the calculated broadened spectrum (dashed line). The quadrupole coupling constant for the calculated spectrum is 6.75 MHz, the asymmetry parameter $\eta = 0.3$, and the broadening is achieved by a Lorentzian function of 50 kHz half width.

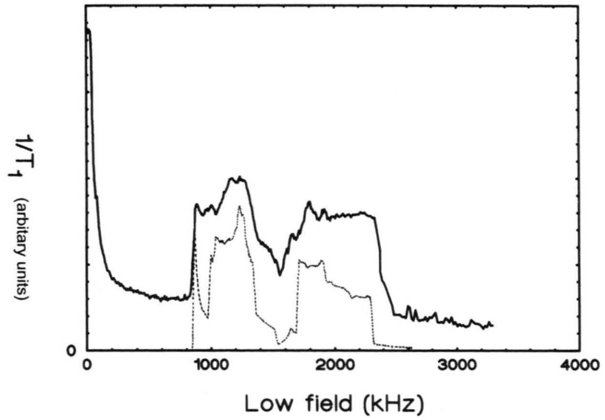

Fig. 5. The T_1 dispersion spectrum of ammonium persulphate at 270 K (solid line), shown together with the calculated unbroadened spectrum (dotted line). The quadrupole coupling constant for the calculated spectrum is 6.75 MHz and the asymmetry parameter $\eta = 0.38$.

Note that the resolution is inadequate to separate the differences expected between the $-SO_3$ oxygen nuclei. The results are in reasonable agreement with the values for related compounds given in the Table 1.

Comparison of (9) in [17] and (7) in [5] indicates that the value of $(e^2 Q q/h)$ obtained in [5] for $(NH_4)_2S_2O_8$ is not significantly dependent on an assumption of axial symmetry for the S–O bond. In general, η would be expected to be small or zero for the S–^{17}O bond,

Table 1. A table of results for the quadrupole coupling constants measured in MHz and the asymmetry parameter η, for a number of compounds relevant to this study.

	$\frac{e^2Qq}{h}$ (MHz)	η	References
$(NH_4)_2S_2O_8$	6.75	0.3	This work
$(NH_4)_2S_2O_8$	9.6	(0)*	Morimoto 1987 [5]
$(ND_4)_2S_2O_8$	9.1	(0)*	Morimoto and Hihara 1989 [6]
$(ND_4)_2Cr_2O_7$	9.8	(0)*	Morimoto and Hihara 1989 [6]
$NH_3CH_3ClO_4$	9.7	(0)*	Morimoto 1987 [5]
KH_2PO_4	4.85	0.18	Blinc *et al.* 1974 [18]
$(C_6H_4Cl)_2SO$	9.494	0.221	Cheng and Brown 1980 [15]
$(C_6H_4Cl)_2SO_2$	6.642	0.252	Cheng and Brown 1980 [15]
$(C_6H_5)_2SO$	9.494	0.221	Brown and Cheng 1979 [16]
$(C_6H_5)_2SO_2$	6.734	0	Brown and Cheng 1979 [16]
$(C_6H_5)_3PO$	4.684	0.085	Cheng and Brown 1980 [16]
Zeolites	3.0–6.5	0.0–0.3	Timken *et al.* 1986 [19]
Silicates	2.4–5.1	0.0–0.3	Mueller *et al.* 1991 [20]

* The calculation of the quadrupole coupling constant assumes an η value of zero. The use of a non-zero η value should not substantially effect the result (see text).

however a significant degree of hydrogen bonding, such as in $H_2PO_4^-$, appears to result [18] in a somewhat higher value (see Table). The contribution to the signal from the S–O–^{17}O–S oxygen is likely to be smaller than that from the terminal oxygens as at least one of the latter is much closer to a proton in the NH_4^+ group.

The value obtained by Morimoto [5] is based on the assumption that the oxygen sites are symmetrically equivalent and also relies on the proper estimation and subtraction of other contributions to $T_{1\varrho}(^1H)$ from relaxation mechanisms not associated with the oxygen. It appears from studies of $(NH_4)_2S_2O_8$, $(ND_4)S_2O_8$, $(ND_4)_2Cr_2O_7$ and $NH_3CH_3ClO_4$ by the same method that similar values of (e^2Qq/h) are obtained (see Table), which is surprising in view of the different chemical nature of the atoms to which the oxygen is attached.

Morimoto suggests that the motion responsible for relaxation in $(NH_4)_2S_2O_8$ is a 3-fold hindered rotation of the $-SO_3$ group about its near symmetry axis; however, if fast on the n.q.r. time scale, this motion would be expected to produce a reduction by a factor of about three in the ^{17}O quadrupole coupling constant to a value of about 3 MHz. It is however possible that the effects of $-SO_3$ rotation are being observed at 323 K, notably in the broadening of the ^{17}O quadrupole dips observed at this temperature. It seems most likely that the major contribution to the ^{17}O quadrupole dips observed originate from the two terminal oxygens, sited 0.291 and 0.298 nm from the nitrogen [10], which are hydrogen bonded to the NH_4^+ ion, and that the rather large asymmetry parameter of 0.3 arises from this hydrogen bonding. The ^{1}H n.m.r. spectrum of the NH_4^+ ion is motionally narrowed, and the relatively flat T_1 dispersion above 800 kHz apart from the ^{17}O dips suggest that this motion is fast on the n.m.r. timescale.

Conclusion

The $T_1(^1H)$ dispersion with magnetic field has been measured for $(NH_4)_2S_2O_8$ between 1.8 kHz and 40 MHz and temperatures of 270, 305, and 323 K, and shows quadrupole dips between 800 and 2600 kHz which have been assigned to cross-relaxation to ^{17}O in natural abundance. ^{17}O quadrupole parameters of

$$\left(\frac{e^2Qq}{h}\right) = 6.75 \pm 0.05 \text{ MHz}, \ \eta = 0.30 \pm 0.02$$

have been determined from a fit to a theoretical calculation.

Quadrupole dips should also be observable in other oxygen containing compounds where an abundant spin is available as a monitor. For an observable signal the ^{17}O spin must be in close physical proximity to the abundant spin and have a much shorter spin lattice relaxation time. In practice the effect is only likely to be observed in compounds containing ^{1}H or possibly ^{19}F as the detecting species.

Acknowledgements

We thank the S.E.R.C. and the Defence Research Agency for their support of this work.

[1] R. Kimmich, F. Winter, W. Nusser, and K.-H. Spohn, J. Magn. Resonance **68,** 263 (1986).

[2] H. T. Stokes, T. A. Case, D. C. Ailion, and C. H. Wang, J. Chem. Phys. **70,** 3569 (1979).

[3] J. W. McGrath, and A. A. Silvidi, J. Chem. Phys. **36,** 1496 (1962).

[4] P.-O. Westlund and H. Wennerström, J. Magn. Resonance **63,** 280 (1985).

[5] K. Morimoto, J. Phys. Soc. Japan **56,** 3294 (1987).

[6] K. Morimoto, and T. Hihara, Phys. Lett. A **142,** 49 (1989).

[7] K. Morimoto, and T. Hihara, J. Phys. Soc. Japan **58,** 2272 (1989).

[8] K. Morimoto and K. Shimomura, J. Phys. Soc. Japan **53,** 2752 (1984).

[9] F. Köksal, and S. Bahçeli, J. Chem. Soc. Faraday II **74A,** 1844 (1987).

[10] B. K. Sivertsen, and H. Sørum, Zeitschrift für Kristallographie, **130,** 449 (1969).

[11] D. Stephenson, and J. A. S. Smith, Proc. Roy. Soc. London **A416,** 149 (1988).

[12] M. Blanz, T. J. Rayner, and J. A. S. Smith, Meas. Sci. Technol **4,** 48 (1993).

[13] Nuclear Quadrupole Resonance Spectra Database, JAICI, Tokyo, 1993.

[14] N. E. Ainbinder, and I. G. Shaposhnikov, Adv. Nucl. Quad. Resonance **3,** 67 (1978).

[15] C. P. Cheng, and T. L. Brown, J. Amer. Chem. Soc. **102,** 6418 (1980).

[16] T. L. Brown, and C. P. Cheng, Faraday Symp. Chem. Soc. **13,** 75 (1979).

[17] F. Li, J. R. Brookeman, A. Rigamonti, and T. A. Scott, J. Chem. Phys **74,** 3120 (1981).

[18] R. Blinc, J. Seliger, R. Osredkar, and M. Mali, Phys. Lett. A **47,** 131 (1974).

[19] H. K. C. Timken, G. L. Turner, J. P. Gilson, L. B. Welsh, and E. Oldfield, J. Amer. Chem. Soc. **108,** 7231 (1986).

[20] K. T. Mueller, Y. Wu, B. F. Chmelka, J. Stebbins, and A. Pines, J. Amer. Chem. Soc. **113,** 32 (1991).