RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 57, NUMBER 2 1 JANUARY 1998-II

Antiferroelectric phase transition in $Rb_3D(SO_4)_2$ single crystals studied by ^{87}Rb NMR

A. Titze, G. Hinze, and R. Böhmer
Institut für Physikalische Chemie, Johannes Gutenberg-Universität, 55099 Mainz, Germany

(Received 1 October 1997)

The quadrupole perturbed central transition of the magnetic ^{87}Rb resonance was used to study $Rb_3D(SO_4)_2$ single crystals. Three resonance lines were found at room temperature. This result is in accord with the monoclinic space group reported for these crystals and does not require the previously invoked self-trapped proton states. The number of resonance lines quadruples below the antiferroelectric phase transition near 82 K. From the line splitting the order-parameter exponent of the low-temperature phase was found to be $\beta=0.2$. Spin-lattice relaxation times have been determined in the fully protonated and deuterated disulfates and were used to deduce the temperature dependence of the order-parameter fluctuations. [S0163-1829(98)51902-9]

There is continued interest in the study of phase transitions of hydrogen bonded crystals, particularly of those which exhibit a large isotope effect. One of the best studied representatives of this class of crystals is the three-dimensional hydrogen network KD_2PO_4 for which complete proton vs deuteron substitution shifts the ferroelectric phase transition temperature almost by a factor of 2.[1] An even more dramatic effect is observed for some alkali disulfate crystals of the general composition $M_3H(XO_4)_2$ with $M=\mathrm{K,Rb}$ and $X=\mathrm{S,Se}$. While, e.g., $Rb_3H(SO_4)_2$ remains paraelectric down to the lowest temperatures, the deuterated isomorph orders antiferroelectrically near 80 K.[2] The particular interest that the disulfates have received derives from the fact that each hydrogen bond only connects two sulfate tetrahedra which form a dimeric ion.[3] Thus the through-space dipolar interaction between the hydrogen bridges is not rivaled by Pauling's ‘‘ice rules,’’ usually applied in three-dimensional hydrogen bonded systems such as KD_2PO_4.[1] With the absence of this complicating feature the disulfates are considered promising candidates for answering the question to what extent the isotope effect is quantum mechanical or rather purely geometrical in nature.[4] The latter viewpoint is usually linked to the observation of a strong correlation of the phase transition temperature with the length of the hydrogen bond.[5] However, from a recent calorimetric and dielectric study of the isotopic series $K_3D_{1-x}H_x(SO_4)_2$ the ‘‘determinative role of proton tunneling,’’ i.e., of quantum effects, has been emphasized.[6] It has been conjectured that the controversy may be resolved by the introduction of self-trapped (i.e., asymmetric) proton states which are thermally excited via a phonon-assisted tunneling mechanism that on the time-average restores an inversion symmetric hydrogen bond.[7] The relevant parameter thus appears to be the degree of spontaneous polaronic deformation. It is as yet unclear how such a quantity depends on the isotopic species and on the length of the hydrogen bond. Thus the unequivocal demonstration of the existence (or nonexistence) of self-trapped states would be useful. In this context it is interesting to mention that based on the observation of three resonance lines in a recent Rb-NMR study on powdered $Rb_3H(SO_4)_2$ it was claimed that the $[(SO_4)\cdot H\cdots(SO_4)]^{3-}$ bond is indeed asymmetric.[8]

We address this issue in the following, but in the present ^{87}Rb-NMR study of $Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$ single crystals we find no evidence for self-trapped asymmetric states in the paraelectric phase. However, the ^{87}Rb resonance was found to be suitable to investigate in detail the symmetry breaking associated with the antiferroelectric (AFE) transition in the deuterated compound.

Quasihexagonally shaped rubidium disulfate crystals of optical quality and with typical sizes of $2\times5\times10\ \mathrm{mm}^3$ were grown from aqueous solutions using the convection method. No signs for twinning were obtained under the polarization microscope. Using dielectric measurements a cusp in the permittivity, the signature of the AFE transition, was found for the deuterated compound at $T_N=82\pm1.5\ \mathrm{K}$.[9] The monoclinic $A2/a$ structure (with $Z=4$ formula units per unit cell) was confirmed at ambient temperature by x-ray diffraction and the lattice parameters were determined to be $a=10.2$ Å, $b=6.0$ Å, $c=15.0$ Å, and $\beta=103.1°$.[10] All ^{87}Rb-NMR experiments were carried out using the second-order quadrupole perturbed central transitions of the $I=3/2$ nucleus. Larmor frequencies of 55.1 and 85.8 MHz were employed. Spectra were taken with the standard solid echo sequence. Spin-lattice relaxation times were determined using the inversion recovery method or where spectral selection was required from a series of partly relaxed absorption spectra. Temperatures were measured from calibrated Ir sensors which are believed to be accurate to within ±0.5 K. Stability during one measurement typically was ±0.1 K.

The upper frame of Fig. 1 shows the NMR spectrum of $Rb_3D(SO_4)_2$ taken at room temperature which like that of the isostructural protonated compound[8,11] consists of three $\frac{1}{2}\rightarrow-\frac{1}{2}$ transitions. In order to understand this observation we note that out of the three cations of the formula unit one occupies the symmetric site Rb(1) in the nomenclature adapted from Noda *et al.*[3] There exist two other crystallographically equivalent sites which will be termed Rb(2) and Rb(2′) here since they are inequivalent magnetically. This is due to the fact that they can be transformed into one another only via a (glide) reflection operation. Thus three equally strong resonance lines are required by symmetry and from the ^{87}Rb spectra there is no reason to invoke the existence of self-trapped (asymmetric) states in the room temperature phase. From symmetry considerations[12] it also follows that

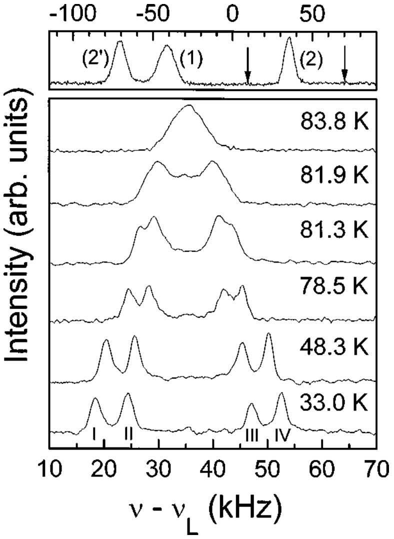

FIG. 1. Upper frame: Quadrupole perturbed ^{87}Rb central lines of $Rb_3D(SO_4)_2$ recorded at 83.8 K. The Larmor frequency was $\nu_L = 85.8$ MHz. The three lines correspond to the three magnetically inequivalent sites. Arrows mark the range which is magnified in the lower frame. Lower frame: Temperature dependence of line corresponding to the Rb(2) site. The roman numerals are used to identify the peaks. The measurements shown in this figure were taken with the crystalline *c* axis enclosing an angle of 65° with the external magnetic field and the crystalline (**a**+**b**) diagonal being perpendicular to it.

since the Rb(1) probe is located on the twofold *b* axis, one of the principal directions of its electrical field gradient (EFG) tensor should point along the monoclinic axis. From rotation patterns taken at room temperature this expectation is confirmed experimentally.[11] For brevity in the following we will mostly report on site Rb(2) which is characterized by a quadrupole coupling $\nu_Q = 3.84$ MHz and an asymmetry parameter $\eta = 0.45$.[11]

The lower frame of Fig. 1 reveals the temperature dependence of the Rb(2) resonance line. It is seen to split into four components below the phase transition temperature. From observations made on different samples we find that the splitting always results in four lines of *equal* intensity. Therefore we conclude that the formation of a multidomain structure is unlikely. In order to understand the quadruplication of lines we mention that while the low-temperature space group of $Rb_3H(SO_4)_2$ is not known,[13] for $K_3D(SO_4)_2$ the space groups $P2_1/a$ ($Z=4$) (Ref. 3) and later $A2$ ($Z=16$) (Ref. 14) have been reported. While the former suggestion only yields a line doubling and therefore can be ruled out, the latter suggestion, implying a quadruplication of the unit cell, is compatible with our observations.[15] A conclusive comparison of diffraction experiments and NMR requires that precise atomic positions in the AFE phase or low-temperature rotation patterns are available.

In any case the symmetry change associated with entering the low-temperature phase is reflected in the NMR spectrum. Therefore one should expect that variations in the EFG at the Rb site, and hence the magnitude of the line splitting $\Delta\nu$, are coupled to the order parameter of the AFE phase.[16] In Fig. 2 it is seen that $\Delta\nu$ strongly increases with decreasing temperature. It varies smoothly across T_N as expected for a second order phase transition. We have fitted the line splitting to a power-law behavior $\Delta\nu \propto (T_N - T)^\beta$ where β is the order-parameter exponent. We find $T_N = (82.3 \pm 0.1)$ K and $\beta = 0.2 \pm 0.03$.[17] Surprisingly this exponent is considerably lower than expected for the three-dimensional Ising model ($\beta_{3D} = 0.325$) but very close to the value reported from Raman scattering on $K_3D(SO_4)_2$.[18]

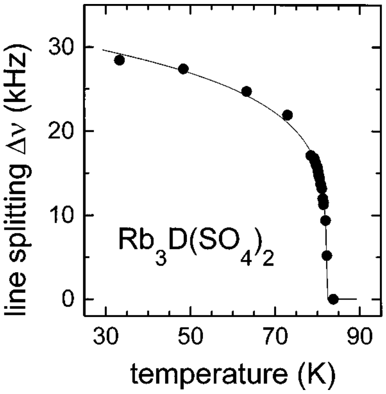

FIG. 2. Temperature dependence of the characteristic line splitting detected at the Rb(2) site (Ref. 17). The solid line is the result of a power-law fit, yielding an exponent of $\beta = 0.2$.

The fluctuations of the components of the EFG tensors at the Rb sites give rise to spin-lattice relaxation. In a first step we have measured the mean spin-lattice relaxation time $\langle T_1 \rangle$ by exciting all central transitions. We find that the magnetization recovery is very close to exponential except in the immediate vicinity of T_N. Spin-lattice relaxation times thus obtained for $Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$ are shown in Fig. 3. The shortest T_1 are found at high temperatures and are interpreted as precursor effects of the superionic phase transition taking place near 450 K. Using NMR techniques this transition has been studied in detail in the related compound $Rb_3H(SeO_4)_2$ by Abramic *et al.*[19] It is not in the focus of the present article.

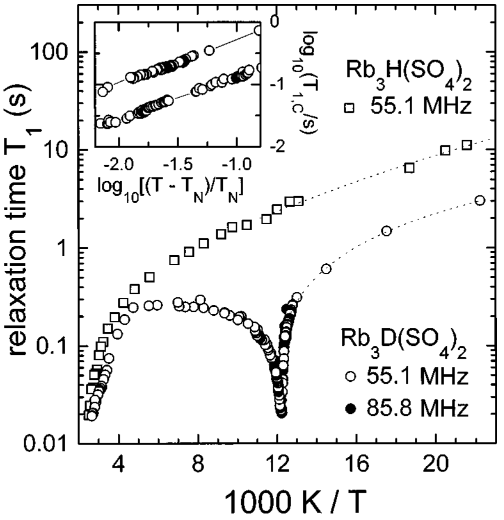

FIG. 3. Mean spin-lattice relaxation times of $Rb_3D(SO_4)_2$ and $Rb_3H(SO_4)_2$ measured at 85.8 or 55.1 MHz. The inset reflects the temperature dependence of $\langle T_1 \rangle$ in the vicinity of $T_N = 82.2$ K. The solid lines are indicative for a power law characterized by an exponent $\lambda = 0.65$. Dotted lines are to guide the eye only.

Upon cooling T_1 at first increases similarly for both protonated and deuterated samples. But while $Rb_3H(SO_4)_2$ exhibits a monotonic behavior down to low temperatures, T_1 of $Rb_3D(SO_4)_2$ shows a pronounced dip near T_N. The fluctuations in the elements of the EFG tensor are, however, always in the fast motion limit as evidenced by the fact that measurements at two different Larmor frequencies yield the same spin-lattice relaxation times; cf. Fig. 3. This frequency independence is a characteristic signature of a soft mode[1] which in our case condenses at the zone boundary.[14]

In order to extract the temperature dependence of the correlation time $\tau \propto 1/T_{1,C}$ of the order parameter fluctuations in $Rb_3D(SO_4)_2$ we have subtracted the noncritical contribution to $1/T_1$ (Ref. 20). The latter was approximated by the spin-lattice relaxation rate $1/T_{1,0}$ of the protonated, nonordering compound yielding $1/T_{1,C}=1/T_1-1/T_{1,0}$. In the inset of Fig. 3 we show a double logarithmic representation of $1/T_{1,C}$ vs $|T-T_N|$ with $T_N=82.2$ K which linearizes the data very well except close to T_N. Thus on either side of T_N we find that $1/T_{1,C}$ varies as a power law $|T-T_N|^{-\lambda}$. The exponent is given by the magnitude of the slope $\lambda=0.65$ (± 0.05) of the straight line shown in Fig. 3.

In order to investigate the failure of the power-law behavior near T_N we recorded a series of spectrally resolved T_1 measurements and in the following we focus again on the Rb(2) site. In Fig. 4 we present magnetization recovery curves $M(t)$ taken at several temperatures above T_N. In the case of quadrupolar relaxation $M(t)$ should be biexponential[21] and as seen from the solid lines in Fig. 4 $M(t) \propto e^{-W_1 t}+e^{-W_2 t}$ provides an excellent fit to the data. The rates W_1 and W_2 in our case both correspond to the same spectral densities, but to fluctuations in different elements of the EFG tensor.[21] In the inset of Fig. 4 we show the temperature dependence of the ratio of the rates which almost triples upon approaching T_N. We interpret this observation as being indicative for the occurrence of anisotropic order-parameter fluctuations.

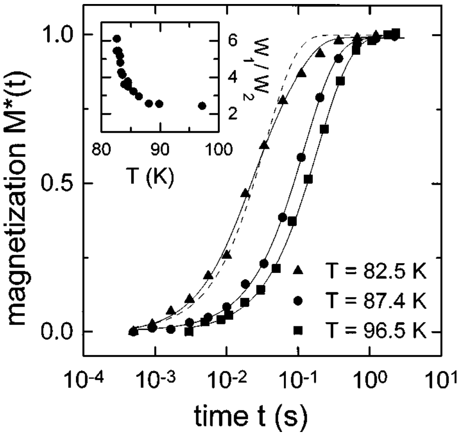

FIG. 4. Normalized magnetization recovery $M^*(t)=1-[M(t)-M_\infty]/[M_0-M_\infty]$ measured for the Rb(2) site of $Rb_3D(SO_4)_2$ at several temperatures. The dashed line represents a single exponential fit, the solid line biexponential ones, with rates W_1 and W_2. The temperature dependence of the ratio of these rates is shown in the inset. The orientation of the crystal is that specified in Fig. 1.

In summary, we have investigated the ^{87}Rb spectra of $Rb_3D(SO_4)_2$. At room temperature we find three resonance lines as expected from the monoclinic space group $A2/a$. Below the antiferroelectric transition temperature at $T_N=82$ K the quadruplication of resonance lines provides further support for the previously conjectured quadruplication of the unit cell in the disulfate compounds.[14] The temperature dependences of the line splitting (for $T<T_N$) as well as of the spin-lattice relaxation times were found to follow power laws.

Taken together our measurements show that the previously conjectured symmetry breaking associated with the existence of self-trapped proton states[8] is not borne out by the NMR spectra. Evidence for a time-averaged symmetry breaking is obtained for $Rb_3D(SO_4)_2$ below the antiferroelectric transition only. The transition itself is driven by a soft mode. This is deduced from the temperature dependence of the spin-lattice relaxation time which exhibits a sharp, frequency-independent drop in the vicinity of T_N. From spectrally resolved measurements of T_1 preliminary indications for a change in the anisotropy of order-parameter fluctuations were obtained slightly above T_N.

This research was supported by the Deutsche Forschungsgemeinschaft within project Bo1301/1-2. We thank A. Maiazza for growing the high-quality single crystals used for this work and D. Schollmeier for taking the x-ray measurements.

---

[1] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974); R. Blinc and B. Žekš, Ferroelectrics **72**, 193 (1987).

[2] K. Gesi, J. Phys. Soc. Jpn. **61**, 162 (1992).

[3] Y. Noda, Y. Watanabe, H. Kasatani, H. Terauchi, and K. Gesi, J. Phys. Soc. Jpn. **60**, 1972 (1991), and papers cited therein.

[4] R. J. Nelmes, J. Phys. C **21**, L881 (1988); H. Sugimoto and S. Ikeda, Phys. Rev. Lett. **67**, 1306 (1991).

[5] M. Ichikawa, T. Gustafsson, and I. Olovsson, Solid State Commun. **87**, 349 (1993).

[6] Y. Moritomo, Y. Tokura, N. Nagaosa, T. Suzuki, and K. Kumagai, Phys. Rev. Lett. **71**, 2833 (1993).

[7] S. Ikeda and Y. Yamada, Physica B **213&214**, 652 (1995).

[8] S. Takeda, F. Kondoh, N. Najamura, and K. Yamaguchi, Physica B **226**, 157 (1996).

[9] A somewhat lower transition temperature was reported in Ref. 2 suggesting that a lesser degree of deuteration was present there.

[10] In Ref. 3 slightly smaller lattice constants are reported for $K_3H_{1-x}D_x(SO_4)_2$.

[11] A. Titze, R. Böhmer, and A. Maiazza (unpublished).

[12] R. Kind, Z. Naturforsch. Teil A **41**, 122 (1986); O. Liechti, J. Magn. Reson. **80**, 71 (1988).

[13] Note that M. Ichikawa, T. Gustafsson, and I. Olovsson, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **48**, 603 (1992), report that for $Rb_3H(SeO_4)_2$ the low-temperature space group is also $A2/a$ ($Z=4$).

[14] Y. Noda, I. Tamura, H. Nakao, R. Matsuo, and Y. Kuroiwa, J. Phys. Soc. Jpn. **63**, 1803 (1994).

[15] Note that $A2/a$ $(Z=16)$ would give 12 lines as observed experimentally. However, also $A2$ $(Z=16)$, which in general yields 24 lines, is possible if there is only a very slight departure from the symmetry of $A2/a$ $(Z=16)$ as in fact suggested in Ref. 14.

[16] Below T_N the increase in the order parameter gives rise to changes in the elements of the EFG tensor in the percent range (i.e., $\Delta\nu \ll \nu_Q$). Therefore, the order-parameter variations are expected to couple *linearly* to $\Delta\nu$.

[17] The $\Delta\nu$ presented in Fig. 2 refer to $\Delta\nu = [(\nu_{\mathrm{I}}+\nu_{\mathrm{II}})-(\nu_{\mathrm{III}}+\nu_{\mathrm{IV}})]/2$ of site Rb(2). The same power law, within experimental error, was obtained for other linear combinations of splitting frequencies and even for other sites, see Ref. 11, as expected for a one-component order parameter.

[18] P. Kaung, M. Kasahara, and T. Yagi, J. Phys. Soc. Jpn. **65**, 1114 (1996).

[19] D. Abramic, J. Dolinsek, R. Blinc, and L. A. Shuvalov, Phys. Rev. B **42**, 442 (1990).

[20] The proportionality constant A in $\tau = A/T_{1,C}$ is hard to estimate on the basis of the present data. The lower limit of A is given by $A^{-1} = (2\pi\nu_Q)^2(1+\eta^2/3)/10$ [see A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), p. 314] as would be correct for isotropic motional processes. An upper limit can be derived from the fact that below 85 MHz T_1 is independent of the Larmor frequency. This yields as a very rough estimate $\log_{10} A = 13 \pm 2$.

[21] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. (London) **78**, 1 (1961).