PHYSICAL REVIEW B VOLUME 56, NUMBER 5 1 AUGUST 1997-I

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "^{1}H NMR observation of the critical slowing down in ammonium chloride"

Roman Goc and J. Wąsicki
Institute of Physics, A. Mickiewicz University, Umultowska 85, 61-615 Poznan, Poland

(Received 9 December 1996)

K. W. Lee *et al.* have reported the NMR measurements on ammonium chloride near the λ transition temperature [Phys. Rev. B **52**, 16 028 (1995)]. Unfortunately, the second moment values given in their paper differ completely from the same values published by many authors during the last 40 years. We give here the correct values of the second moment, measured and calculated from the crystal structure. We also discuss the possible reason for errors in the commented paper. [S0163-1829(97)03029-4]

Lee *et al.*[1] presented Van Vleck's second moment measured on ^{1}H in a powder sample of ammonium chloride in the vicinity of the λ transition temperature (243 K). The results depicted in Fig. 2 of their paper[1] differ from the second moment values for the ammonium chloride known and repeatedly published during the last forty years.[2] An extensive review of ammonium ion studies in solids was published by Smith.[3]

The values of the second moment published by Lee *et al.*[1] increases from about 7 G^2 at 230 K to 15.5 G^2 near the λ transition (T_c=243 K) temperature and then decreases to initial value (7 G^2) at 260 K. All values of the second moment in powdered ammonium chloride known to us, measured in the same temperature interval, lie between 3.2 G^2 and 3.3 G^2.

We ourselves have also measured the proton second moment for ammonium chloride in the same temperature range. Our sample was ammonium chloride from Aldrich, carefully purified by means of recrystallizing, and sealed after being kept for 12 h under vacuum. The homemade cw NMR spectrometer operating at 20 MHz was used for recording the derivative of the absorption curve. Each spectrum was accumulated from 8 to 16 times to improve the signal to noise ratio. The second moment value obtained from these measurements is 3.3±0.1 G^2. We were not able to notice any change in the second moment when passing the λ transition temperature, which for our sample was 243±0.5 K. To the best of our knowledge, no author has observed any detectable change in the second moment of powdered ammonium chloride (or any other powdered ammonium salt) when passing the T_c temperature.

We are familiar with only two published evidences of second moment changes in ammonium salt when passing the T_c temperature.[4,5] Both cases concern NMR measurement for the single-crystal samples at a specially chosen orientation of the magnetic-field direction with respect to the crystallographic axis. The observed increase in the second moment value reported in these papers is about 10%.

Summarizing the experimental results concerning NMR second moment in ammonium chloride, one can conclude that the second moment values given in Fig. 2 of the paper by Lee *et al.*[1] are highly unrealistic.

We have also performed a calculation of the second moment based on the Van Vleck formula averaged for rotation of ammonium ions about four C_3 axes, as described by Watton *et al.*[6] Calculations were performed for the block of 1331 (11×11×11) unit cells. Assuming the nitrogen hydrogen distance to be 0.103 nm and the lattice constance $a = 0.387$ nm, we obtained the second moment value of 3.23 ±0.05 G^2 for the ordered phase (below T_c) and 3.4±0.1 G^2 for the disordered phase, immediately above the transition temperature.

Lee *et al.*[1] did not give the details of the second moment measurements, but most probably the reason for their erroneous results lies in determining the second moment from the shape of the solid echo near its maximum, as this method is very sensitive to the time value chosen as the origin.

---

[1] K. W. Lee, C. H. Lee, and C. E. Lee, Phys. Rev. B **52**, 16 028 (1995).

[2] H. S. Gutowsky, G. E. Pake, and R. Bersohn, J. Phys. Chem. **22**, 643 (1954).

[3] D. Smith, Chem. Rev. **94**, 1567 (1994).

[4] R. Bersohn and H. S. Gutowsky, J. Chem. Phys. **22**, 651 (1954).

[5] J. Itoh, R. Kusaka, and Y. Saito J. Phys. Soc. Jpn. **17**, 463 (1962).

[6] A. Watton, E. C. Reynhardt, and H. E. Petch, J. Chem. Phys. **65**, 4370 (1976).