

Quadrupole Coupling in Ammonium Metaperiodate at Low Temperature

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Z. Naturforsch. **57 a**, 661–662 (2002); received March 25, 2002

The temperature dependences of the ¹²⁷I nuclear quadrupole coupling in NH₄IO₄ and in ND₄IO₄ are reported. In each salt, the quadrupole coupling decreases to a very small value at low temperatures, and in the case of ND₄IO₄ passes through zero and changes sign at 87 K.

Key words: NQR; NMR; Temperature Dependence; Isotope Effect.

The ammonium salts of the meta-metallates NH₄MO₄ (M = Re, Tc and I) have attracted much interest because of their anisotropic properties. This interest was triggered by the observation that the nuclear quadrupole interaction for the M atom has a positive temperature dependence at constant pressure, contrary to simple theory, and is not compensated for by the pressure dependence at constant temperature [1 - 3]. In contrast, the temperature dependence of the quadrupole coupling in each of the alkali metal salts is normal. All three meta-metallates have the scheelite structure with no phase transitions in the relevant temperature range [4 - 6]. The anomalous temperature dependence of the Re quadrupole coupling in NH₄ReO₄ has been accounted for in terms of a pseudo-spin theory, based upon the two possible orientations of the ammonium ion [7 - 9].

We would like to report a feature that has been buried in the archives, namely that in ND₄IO₄, the ¹²⁷I quadrupole coupling passes smoothly through zero and changes sign, although not constrained by symmetry to do so. To our knowledge this is the only known case of such behaviour.

Figure 1 shows smoothed curves representing the temperature dependences of the ¹²⁷I quadrupole coupling in polycrystalline NH₄IO₄ and ND₄IO₄ based on 144 data points taken between 4 K and 380 K. The data are quoted as the nuclear quadrupole resonance frequency ν_Q , which is equal to $(3/20)e^2qQ/h$ for $I = 5/2$. The original data are as follows: 34 NH₄IO₄

data points and 26 ND₄IO₄ data points were measured from 4 K up to 130 K using first order splitting of the NMR line; 35 NH₄IO₄ data points and 10 ND₄IO₄ data points were measured from above 130 K to 250 K using the 2nd order splitting of the NMR central transition; 39 NH₄IO₄ data points were measured from above 250 K to 380 K using pure quadrupole resonance. The experimental apparatus included crossed coil spectrometers for the pure quadrupole data, and pulsed NMR spectrometers at magnetic fields of 2 T (Kingston), 6.7 T (Turku) and 9.4 T (Melbourne). The NMR lineshapes indicated zero asymmetry parameter, which is required by the site symmetry. The value of the quadrupole coupling at room temperature has been confirmed recently [10]. The ¹²⁷I quadrupole couplings in both NH₄IO₄ and ND₄IO₄ have essentially zero temperature dependence below about 80 K. The quadrupole couplings in the static lattice are so close to zero that the observed coupling is not affected by vibrational averaging. In contrast, ammonium perrhenate, NH₄ReO₄, shows a normal temperature dependence of the Re quadrupole coupling below about 100 K, and the abnormal positive-slope temperature dependence is observed above this temperature [3]. The entire temperature dependence of the coupling constants in NH₄IO₄ above 80 K is presumably due to the effect of the occupation of the higher energy ammonium ion orientation [4], as described by the pseudo-spin theory [7 - 9].

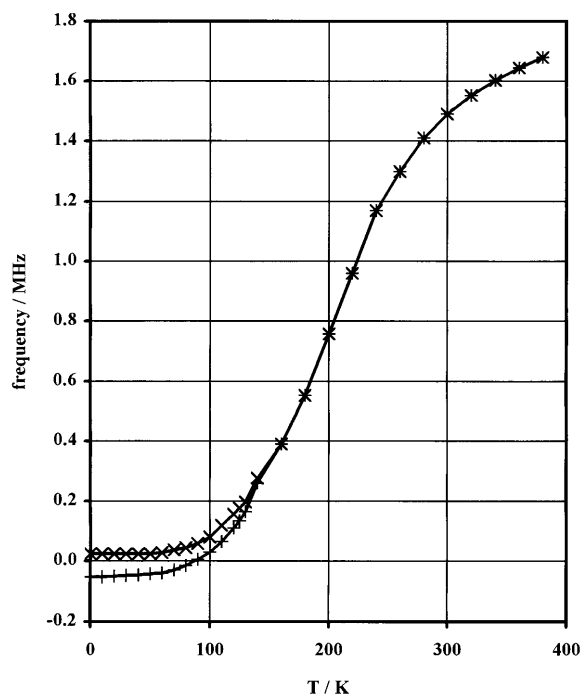


Fig. 1. The temperature dependence of ν_Q for $\text{NH}_4^{127}\text{IO}_4$ (\times) and $\text{ND}_4^{127}\text{IO}_4$ (+). The two curves coincide above about 140 K. The curves present smoothed data taken by first order splitting of the NMR line up to 130 K, by second order splitting of the central NMR transition from above 130 K to 250 K, and by pure NQR above 250 K. The small bend in the curves around 140 K corresponds to the change in measuring technique.

The ^{127}I quadrupole coupling in the deuterated salt ND_4IO_4 passes through zero at 87 K, though it is not constrained to do so by symmetry. The H/D isotope effect is observed only at low temperatures, and the quadrupole couplings for NH_4IO_4 and ND_4IO_4 converge at about 130 K. The slope $(\partial\nu_Q/\partial T)_P$ is a maximum at about 200 K, almost the same as the corresponding temperature in NH_4ReO_4 .

Thus the temperature dependences of the nuclear quadrupole couplings at the anion sites in NH_4ReO_4 and NH_4IO_4 are almost identical, except that in the latter salt the quadrupole coupling at zero Kelvin is close to zero. Both show the onset of pseudo-spin effects just below 100 K, with a maximum positive slope at about 200 K. Consistent with this, the peaks in the heat capacity [11, 12] and the thermal expansion coefficients [5, 13] are also found at about 200 K in both salts. Having observed these similarities, the quadrupole frequency in ammonium metaperiodate may be expected to be a linear function of the distortive strain ε_{20} [8].

Acknowledgement

Financial support from Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. SLS wishes to acknowledge hospitality and support at the Wihuri Physical Laboratory, Turku, and CSIRO, Melbourne.

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