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^{14}N PNQR Investigation of the Effect of Pressure on Phase Transitions in Malononitrile and s-Triazine

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^{14}N PNQR Investigation of the Effect of Pressure on Phase Transitions in Malononitrile and *s*-Triazine

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The ^{14}N pure nuclear quadrupole resonance (PNQR) frequencies in the molecular crystals malononitrile and *s*-triazine were measured as a function of hydrostatic pressure to 6 kbar along several isotherms. Both these solids undergo second-order phase transitions classed in the category of displacive transitions. The evolution of the transitions with temperature had been previously studied by Zussman and Alexander[1] (malononitrile) and by Coppens and Sabine[2] and Zussman[3] (*s*-triazine).

In both solids the phase of higher symmetry (PHS) is the high temperature, low pressure phase. In the PHS of malononitrile the PNQR spectrum consists of 4 lines corresponding to 2 inequivalent ^{14}N sites. At T_c, the transition temperature to the phase of lower symmetry (PLS), each line splits into two, indicating 4 inequivalent ^{14}N sites. Similarly in *s*-triazine the PNQR spectrum in the PHS (hexagonal) consists of 2 lines, and below T_c each line splits into two, corresponding to 2 equivalent and 1 nonequivalent ^{14}N sites in the PLS (monoclinic).

The splitting $\Delta\nu$ was shown to be proportional to the order parameter and was found to obey the relationship $\Delta\nu \propto (T_c - T)^{\beta}$ in the vicinity of T_c, with the critical exponent $\beta = 0.5$, in good accord with the theory of Landau.[4]

The hydrostatic pressure experiments in the present study were performed in a simple piston-cylinder apparatus. The system with the PNQR spectrometer had been previously described.[5] Temperature was stabilized within 0.02°C. Pressure increments or decrements of 4 bar could be detected. The overall accuracy in pressure measurements was better than $\pm$20–40 bar at 6 kbar.

Along isotherms p_c is defined as the transition pressure at which the splitting appears.

The pressure dependence of $\Delta\nu$ could be described by the equation

$$\Delta\nu = a(p - p_c)^{0.5}$$

again in good agreement with Landau's theory.

The variation of T_c with pressure was measured to 2 kbar in malononitrile and to 6 kbar in *s*-triazine. T_c was found to be a linear function of pressure of the form

$$T_c(p) = T_c(0) + \gamma p$$

where $\gamma = dT_c(p)/dp$.

Correlation of the variation of $\Delta\nu$ along isotherms and along isobars was attempted by use of a "law of corresponding states" previously proposed for magnetic transitions.[6] This law expressed in the equation

$$\begin{aligned}\Delta\nu &= F(T/T_c(p)) \\ &= F(\varepsilon)\end{aligned}$$

where $\varepsilon = (T_c(p) - T)/T_c(p)$, states that the variation of $\Delta\nu(p)$ with p is due only to the variation of $T_c(p)$ with p. In the present study the law of corresponding states

$$(\Delta\nu)^2 = a(T_c(p) - T)/T_c(p)$$

was found to be only approximate and it was found that $a = a(T, p)$ is a weak function of temperature and pressure.

Spin lattice relaxation and linewidth measurements indicate that the predominant relaxation mechanism in *s*-triazine is via molecular reorientation around the 3-fold axis. The activation enthalpy for this motion was found to be $\Delta H^* = 14$ kcal/mole. The activation volume, computed from the pressure variation of the lifetime of the free decay signal (T_2), was found to be $\Delta V^* = 28$ cm^3/mole, comparable to some other molecular solids.[5]

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