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

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The  $^{14}\text{N}$  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<sup>1</sup> (malononitrile) and by Coppens and Sabine<sup>2</sup> and Zussman<sup>3</sup> (*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  $^{14}\text{N}$  sites. At  $T_c$ , the transition temperature to the phase of lower symmetry (PLS), each line splits into two, indicating 4 inequivalent  $^{14}\text{N}$  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  $^{14}\text{N}$  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.<sup>4</sup>

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.<sup>5</sup> 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  $\Delta v$  could be described by the equation

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

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  $\Delta v$  along isotherms and along isobars was attempted by use of a "law of corresponding states" previously proposed for magnetic transitions.<sup>6</sup> This law expressed in the equation

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

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

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

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<sup>3</sup>/mole, comparable to some other molecular solids.<sup>5</sup>

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