

B. The Rotational Ordering in Solid H₂

The rotational motion of the H₂ molecules in the solid has been investigated both experimentally and theoretically.^{26,27} For the ortho molecules, the lowest rotational state is characterized by the quantum number $J=1$. The crystalline field removes the three-fold degeneracy of the m_J levels but the splitting is very small in comparison to the rotational energy $BJ(J+1)=2B \cong 120 \text{ cm}^{-1}$. Above T_λ the separation between the m_J levels is smaller than kT and these levels will then be almost equally populated. As a result the ortho molecules will be essentially spherically symmetric and the dipole-dipole interactions between the two nuclei will be very small. For a large enough ortho concentration, a cooperative process of alignment of the angular momenta takes place below T_λ . This is evidenced by a sharp anomaly in the specific heat.^{28,16} Tomita¹³ has presented a phenomenological theory of this transition. He treated it as a cooperative phenomenon from a Bethe-Peierls short-range point of view. As the exact form of interaction between the molecules is not known, he only made general assumptions concerning its nature. From his theory he derived the dependence of T_λ on concentration c and on the number of nearest-neighboring molecules. He concluded that at absolute zero all the molecules are in the $m_J=0$ state. This is in qualitative agreement with the analysis of NMR data by Reif and Purcell² who proposed such a type of ordering.

More recently the problem of the transition has been considered by Bell and Fairbairn¹⁴ who disagree with Tomita's treatment and results. These authors find that for cubic structures no cooperative transition should be observed. For a hexagonal close packed structure, a special ordering in alternating layers of molecules in the state ($m_J=\pm 1$ and $m_J=0$, respectively) is achieved below a temperature T_λ . Hence, the $m_J=\pm 1$ states will not be depopulated as the temperature falls, in apparent contradiction to Reif's results. Assuming electric quadrupole-quadrupole interaction to be responsible for the transition, a zero-order treatment gives $T_\lambda=5.8^\circ\text{K}$ for $c=1.0$. The dependence of T_λ on c has not yet been evaluated because of the mathematical complexities.

For solid H₂ there have been several experimental studies on the ortho-concentration dependence of T_λ at normal density. The results from NMR and specific-heat experiments are presented in Fig. 1. For c larger than about 0.65, the transition temperature as derived from the peak of the specific heat is systematically higher than that derived from the disappearance of the side peaks in the NMR spectrum. A convenient fit for NMR data at normal density ρ_0 below $c=0.77$ combined with specific-heat data below $c=0.65$ is given by a straight

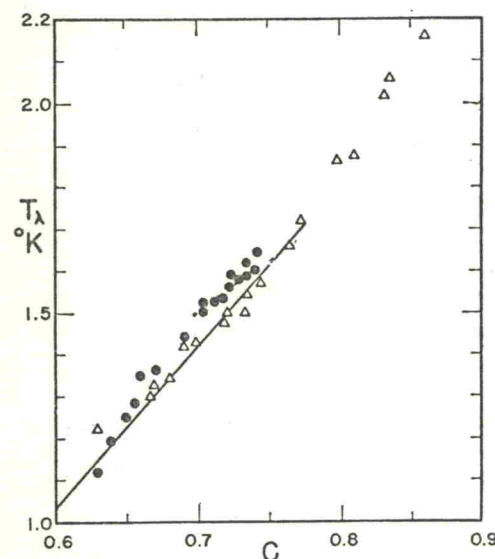


FIG. 1. The transition temperature versus concentration c . Δ nuclear-resonance data (Refs. 4, 7) $\bullet$ specific-heat data (Refs. 16, 28).

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$$T_\lambda(\rho_0, c) = -1.23 + 3.78c. \quad (1)$$

This expression will be of use later in connection with our own data.

So far only results at normal densities have been mentioned. At high densities London²⁹ has predicted that the decrease of molecular volume could result in the anisotropy of the Van der Waals repulsion between molecules becoming the major factor in determining their orientation. One would eventually obtain an oscillatory rather than a rotational type of motion.

From simple theoretical considerations for a cooperative transition³⁰ it is apparent that the transition temperature T_λ is proportional to the interaction energy between the molecules and also depends on the structure. This can be written as

$$T_\lambda(\rho, c) = V(\rho)\varphi(c), \quad (2)$$

where V is the interaction, which depends on density, and φ is a function of ortho concentration and the number of nearest neighbors and depends on the structure. At normal density, according to Nakamura,³¹ the electric quadrupole interaction is mainly responsible for the lifting of the degeneracy of the lowest rotational level. The Van der Waals interaction and the valence forces contribute in a minor way to this anisotropic potential. Hence this potential V and therefore T_λ would be expected to vary approximately as $\rho^{5/3}$. Smith and Squire⁶ reported no change in T_λ when the pressure was increased to 216 atm for H₂ with an ortho concen-

²⁶ L. Pauling, Phys. Rev. 36, 430 (1930).

²⁷ J. Van Kranendonk, Physica 25, 1080 (1959).

²⁸ R. W. Hill and B. W. A. Ricketson, Phil. Mag. 45, 277 (1954).
R. W. Hill, B. W. A. Ricketson, and F. Simon, *Conférence de Physique des Basses Températures, Paris, 1955* (Simon et Cie., Paris, 1955), No. 76, p. 317.

²⁹ F. London, Phys. Rev. 102, 168 (1956).

³⁰ See for instance J. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939).

³¹ T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955).