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TEMPERATURE DEPENDENCE OF THE ORIENTATIONAL ORDER PARAMETER IN SOLID HYDROGEN AT REDUCED ORTHO CONCENTRATIONS

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Résumé. — Dans l'hydrogène solide pour les concentrations des espèces ortho-inférieures à 50 %, on a mesuré la dépendance en température de la structure fine des raies RMN. La disparition de la dégénérescence des niveaux de rotation vue à basse température n'est pas compatible avec un modèle utilisant seulement un champ cristallin anisotrope.

Abstract. — Measurements of the temperature dependence of the fine structure splitting of the NMR spectra of solid hydrogen having ortho concentrations less than 50 % indicate that the lifting of the rotational degeneracy observed at low temperatures cannot be attributed to a dominant temperature independent anisotropic crystalline field interaction.

As a result of the anisotropic intermolecular interactions, principally the electrostatic quadrupole-quadrupole interactions, pure solid ortho hydrogen (nuclear spin $I = 1$, orbital angular momentum J odd) undergoes a phase transition [1] at 3 K from a rotationally disordered phase to an orientationally ordered phase in which the molecules become aligned parallel to one of the four body diagonals of the f.c.c. structure. The ordered configuration of the molecules is described by the space group Pa_3 which consists of four interpenetrating simple cubic sublattices such that in each sublattice one of the body diagonals forms a local quantisation axis $\hat{\xi}$ for the molecules.

The axial symmetry of the electric field at a given site due to the neighbouring quadrupoles of the ordered structure lifts the rotational degeneracy and the states $J_{\xi} = \pm 1$ are separated from the ground state $J_{\xi} = 0$ by an energy gap Δ . (At low temperatures we need only consider $J = 1$).

The relevant orientational order parameter for the symmetry described above is $S(T) = \langle 3 J_{\xi}^2 - 2 \rangle$ and as a result of the collective nature of the interactions both S and Δ are temperature dependent. $S(T)$ vanishes discontinuously at the critical temperature T_c ; i.e. the transition is first order.

The temperature dependence of the order parameter can be followed directly by observation of the NMR spectrum which, for a powdered specimen consists

of a Pake doublet [2] whose principal peaks are separated in frequency by

$$\nu_D = \frac{3}{2} \xi d S(T) \quad (1)$$

where $\xi = 0.98$ is a renormalisation factor [3] and $d = 57.68$ kHz.

Thermodynamic measurements at elevated ortho concentrations [1] showed that the critical temperatures $T_c(X)$ decreased smoothly as the fractional ortho concentration X was reduced towards a critical concentration $X_c \approx 0.55$ below which no orientationally ordered states were detected for temperatures greater than approximately 0.4 K. Subsequent measurements with the use of a dilution refrigerator [4] demonstrated the existence of ordered structures for X well below X_c . The concentration dependence of the critical temperatures is very different for the two regimes $X > 0.55$ and $X < 0.55$ (see figure 2 of reference [4]), and the ordering mechanism for the dilute alloys is not understood.

Although measurements of the microwave absorption spectra observed for extremely dilute ortho concentrations (0.2 %) [5] indicate that the anisotropic crystalline fields are less than 20 mK, such fields have been invoked to explain the low temperature results for $0.25 < X < 0.55$. (The reader is

referred to the review article of Silvera [6] and the discussion that follows the review for further details.) While it is true that the values of the crystalline fields inferred from the observations at very dilute ortho concentrations in the hexagonal structure may not be relevant for elevated concentrations in what are probably metastable cubic structures, it is difficult to justify the magnitude of the crystalline fields that would be needed to explain the values of the critical temperatures observed ($T_c \simeq 0.3$ K at $X = 0.5$). The purpose of this letter is to report experimental studies of the temperature dependence of the separation of the Pake doublet for reduced ortho concentrations ($X \lesssim 0.55$) which seem to exclude any interpretation in terms of a dominant anisotropic crystalline field for that concentration regime.

The NMR studies were carried out at 100 MHz using a straightforward Q-meter circuit operating at low R.F. levels. The hydrogen, derived from a purified 75% ortho gas mixture, was condensed onto a bundle of very fine copper wires (10^{-2} m.m. o.d.) soldered to a copper cold finger extending from the mixing chamber of a dilution refrigerator. The addition of the wires is believed to be important since the ortho-para conversion heats the sample and as a result of the Kapitza resistance, a significant temperature discontinuity can occur at the hydrogen-copper interface if the surface area is inadequate. The hydrogen was contained in a teflon cell and the temperatures were monitored by a calibrated carbon resistor affixed to the cold finger. In order to study samples having reduced ortho concentrations the hydrogen was allowed to age at (or below) 4.2 K and the ortho contents were deduced from the ages [4]. Following cooling well below the critical temperature, the temperature dependence of the separation $\nu_{DD}(T)$

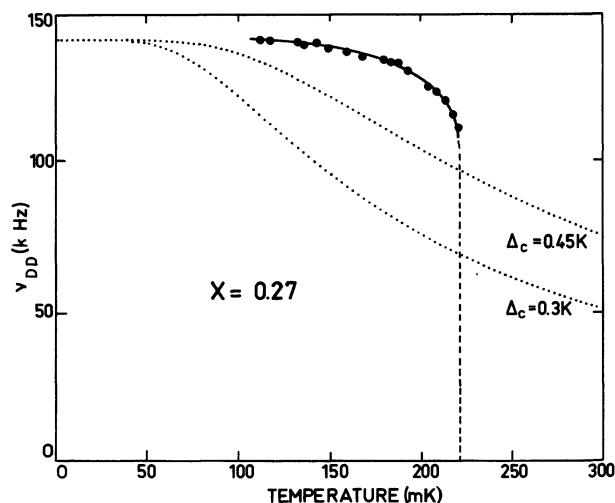


FIG. 1. — Observed temperature dependence of the separation ν_{DD} of the derivative NMR absorption lineshape of solid hydrogen having an ortho concentration of 27%. The dotted curves refer to the temperature variations that would be expected if the temperature dependence of the order parameter were attributed to a constant crystalline field interaction Δ_c . The broken line marks the phase transition at $T \simeq 0.22$ K.

of the principal peaks of the derivative of the NMR absorption spectra was recorded as the temperature was allowed to warm very slowly towards T_c . Figure 1 displays the results obtained for a sample having an ortho concentration of 27% (as inferred from its age). One observes that following a rapid but smooth decrease of $\nu_{DD}(T)$ by approximately 25%, there is a discontinuous transition to the disordered state. Similar variations have been observed for several independently prepared specimens having concentrations in the range $0.18 < X < 0.52$ and they can be compared to the temperature dependences reported by Amstutz *et al.* [7] for very high ortho concentrations. (Zero point librational deviations of the order parameter as well as a perturbation resulting from the intermolecular nuclear dipole-dipole interactions account for the difference between the low temperature limit of 141 kHz indicated in figure 1 and that predicted by equation (1). The reader is referred to references [4] and [8] for further details.)

The rapid variation of the order parameter near the transition (apparently first order) allows one to identify the transition temperatures without ambiguity and with a considerably improved precision in comparison with earlier studies [4].

This allows us to test the reproductibility of the data and preliminary results for several samples are shown in the phase diagram represented by figure 2.

The variation predicted by a temperature independent axial crystalline field

$$V_c = \frac{1}{3} \Delta_c (3 J_c^2 - 2),$$

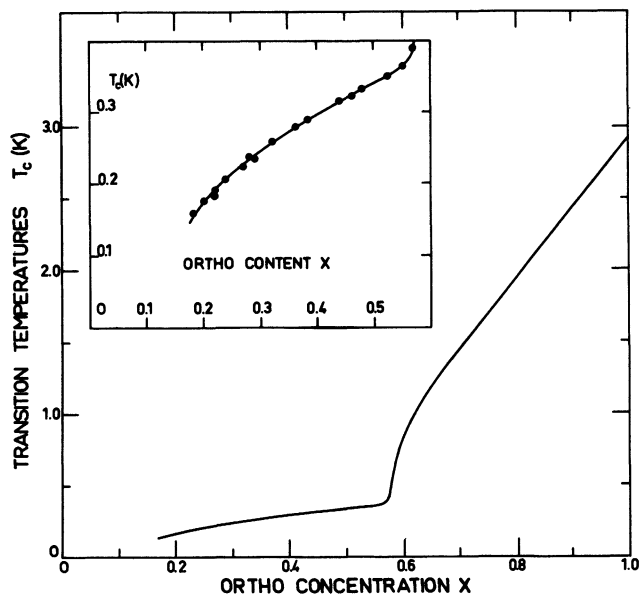


FIG. 2. — Transition temperatures $T_c(K)$ as a function of the ortho mole fraction X . The variation for $X > 0.59$ represents the data reported in reference [1], while that for $X < 0.59$ (replotted on an expanded scale in the insert) was obtained from the temperature dependence of the order parameter as illustrated in figure 1 for the case $X = 0.27$.

which would imply a temperature dependence

$$S(T) = 2(e^{-\Delta_c/k_B T} - 1)/(2e^{-\Delta_c/k_B T} + 1)$$

for the order parameter, is illustrated by the dotted curves in figure 1. Comparison with the experimental results leads to the conclusion that the ordering cannot be attributed to crystalline field interactions alone. The abrupt nature of the transition supports the view [4] that the transition at low ortho concentrations results from the cooperative ordering of the rotational degrees of freedom of the ortho molecules. While treatments of the orientational ordering based on nearest neighbour quadrupolar interactions indicate that there is a critical concentration of approximately 50% below which no well defined long range orientational order is predicted [9], the origin of the second distinct branch of the phase diagram for $X < 0.5$ remains unexplained.

It is possible that at reduced ortho concentrations there is a *local* orientational ordering analogous to the

spin glass ordering seen in dilute ferromagnetic alloys [10].

In the analogous *quadrupolar phases* the orientation of the ortho molecules could become frozen into a glass like configuration in which there is no long range correlation between the equilibrium orientations of the molecules. The present NMR results obtained for powder specimens does not enable one to distinguish between a local ordering and a long range orientational ordering.

Systematic studies of the critical temperatures for several aged samples have been carried out and the results together with the interpretation of the fine structure splittings will be reported elsewhere. This work has benefited from several discussions with H. Meyer, A. Landesman and M. Goldman. The collaboration of J. Vaissière in the construction and operation of the low temperature apparatus is also gratefully acknowledged. C. Urbina is especially thanked for his help in the recording of some of the more recent data.

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