formation during irradiation, only mechanisms giving Frenkel defects are relevant.

The work was supported by the Deutsche Forschungsgemeinschaft and the Bundesministerium für Wissenschaftliche Forschung.

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HEXAGONAL-TO-CUBIC TRANSITION IN HYDROGEN*

R. L. Mills, A. F. Schuch, and D. A. Depatie
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

(Received 28 October 1966)

Solid hydrogen can exist in the form of either hexagonal or cubic closest packing of molecules.[1-3] The transition between these two forms is dependent upon the concentration of orthohydrogen and occurs[1,2] at temperatures very near to those of the anomaly in nuclear magnetic resonance[4,5] and of the λ anomaly in specific heat.[6-8] The present study was undertaken to determine accurately the phase-transition line and possibly gain a clearer understanding of the anomalous behavior of solid hydrogen. The structure change was observed in detail by the method of x-ray diffraction at 1.5 atm between 1.3 and 2.7°K for orthohydrogen mole fractions of from 0.67 to 0.95. The pressure dependence was estimated from additional runs at 29 and 60 atm made on normal hydrogen.

Transitions from the hexagonal to cubic structure and from cubic to hexagonal were followed by observing the disappearance and reappearance, respectively, of the 101 reflection from hexagonal hydrogen. Occasionally the 200 reflection from cubic hydrogen was used.

Hydrogen gas, enriched in ortho content,[9] was solidified at 1.5 atm in a beryllium cell[10] cooled to liquid-helium temperature. The temperature of the sample was deduced from a He^3 vapor-pressure bulb on the cell and a He^4 vapor-pressure bulb in the bath. Filtered copper x-radiation was focused on the H_2 sample through a Be window in the cryostat large enough to permit the reflected beam to exit and be detected with a scintillation counter, ratemeter, and recorder. A single crystallite of H_2, oriented at the proper Bragg angle, could usually be selected from the conglomeration of crystallites in the cell by adjusting the height and angular position of the cryostat which was mounted on a diffractometer table. The H_2 crystallites were a few mils in diameter as estimated from the positional adjustments; they gave reflected intensities up to 800 counts/sec above a background of about 5. The crystal phase line was crossed at heating and cooling rates of 5 to 30 mdeg/min. The temperature at which the reflected x-ray beam reached half-intensity was taken as the transition temperature T_{tr}.

Since ortho-para conversion takes place fairly rapidly in solid H_2, a series of measurements of T_{tr} with decreasing ortho fraction $[o\text{-}H_2]$ could be made from a single filling of the cell. Indeed one observation of the transition was made at constant T by allowing the natural decrease in ortho content to cause a crossing of the phase boundary. The ortho-para conversion in the solid sample proceeded according to the rate equation

$$-d[o\text{-}H_2]/dt = k[o\text{-}H_2]^2, \qquad (1)$$

where $k = 0.019 \pm 0.001\ h^{-1}$, as determined from 11 separate experiments. Similar rate constants have been observed[11] and derived theoretically[12] by others. The value of k was the same in both crystal phases and was unchanged during repeated cycling between phases.

In all, 51 determinations were made of the temperature of the transition from hexagonal to cubic with decreasing temperature. The results are shown in Fig. 1 and the points can

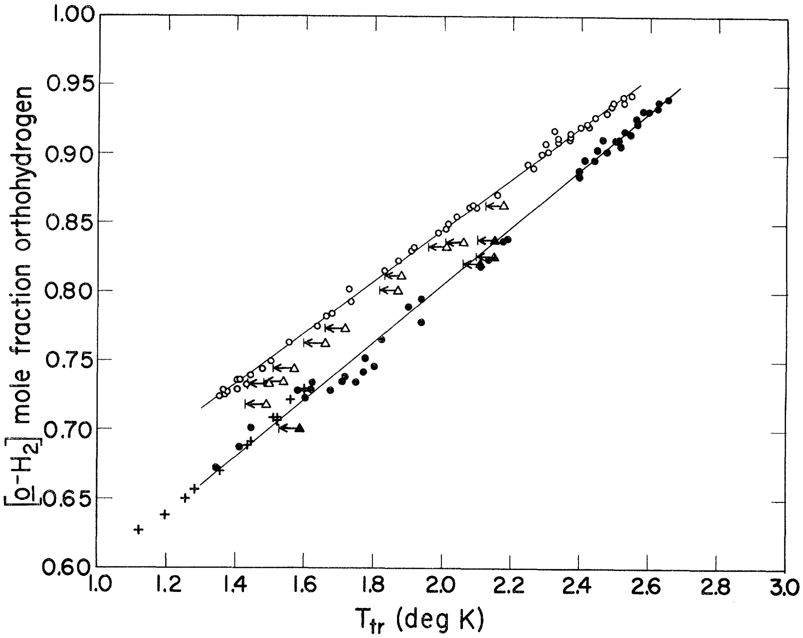

FIG. 1. The transition temperature as a function of orthohydrogen concentration. Open circle, transition hexagonal→ cubic, temperature falling; closed circle, transition cubic→ hexagonal, temperature rising; plus, λ spike in heat capacity, temperature rising, Ref. 7; open triangle, anomaly in nmr, temperature falling, Ref. 5; closed triangle, anomaly in nmr, temperature rising, Ref. 5. Arrows shift points to center of transition.

be represented, within an average deviation of ±12 mdeg, by the linear equation

$$T_{\text{hex}\rightarrow\text{cube}} = 5.388[o\text{-H}_2] - 2.553°\text{K}$$

$$(p = 1.5 \text{ atm}, \quad 0.72 < [o\text{-H}_2] < 0.95). \quad (2)$$

The reverse transition from cubic to hexagonal took place on warming to temperatures significantly higher than those on cooling for a given $[o\text{-H}_2]$. The results of 43 observations made with increasing temperature are shown in Fig. 1 and can be represented by

$$T_{\text{cube}\rightarrow\text{hex}} = 4.792[o\text{-H}_2] - 1.860°\text{K}$$

$$(p = 1.5 \text{ atm}, \quad 0.67 < [o\text{-H}_2] < 0.95). \quad (3)$$

These transition temperatures were not always sharp and well defined. At the smallest orthohydrogen mole fractions the structure change spread over a ΔT of ~100 mdeg. The curves of intensity versus temperature looked much like those observed in the infrared work of Clouter and Gush.[1] For ortho-rich fractions the transition was completed over the much narrower range of 20 mdeg. The hysteresis between the cooling and warming curves of Fig. 1 was less for the richer orthohydrogen samples.

The earlier heat-capacity measurements[6-8] showing a λ anomaly were necessarily made with increasing temperature. In Fig. 1 it is seen that values[7] of T_λ coincide with the curve representing T_{tr} for the transition cubic → hexagonal. It is evident that a change in crystal structure must by included in the events contributing to the λ spike. Nakamura[13] and Orttung[14] have shown that a prominent maximum in specific heat arising from the removal of the degeneracy of the ortho molecules is to be expected. Upon cooling, it may be that both events, the change in structure and the cooperative ordering of rotation, occur together or nearly together. The appearance of multiple peaks in the λ anomaly[8] is not inconsistent with such an idea.

The entropy change accompanying the crystal transition can be estimated from the Clapeyron relation using available p-V-T data for normal hydrogen at low pressure. The present measurements give a value of 4×10^2 atm/deg for the slope of the transition curve. From this and the recent determination[15] that the cubic phase is 0.3% more dense than the hexagonal phase, ΔS_{tr} is computed to be 0.6 cal/

deg mole. This value is of the order of that observed by Ahlers and Orttung[8] for the entropy under the λ spike.

Temperatures[5] at which side peaks in the nuclear-magnetic-resonance lines of solid H_2 appear and disappear upon cooling and warming, respectively, are plotted also in Fig. 1. These temperatures appear to be those at which the H_2 crystal first starts to change from hexagonal to cubic on cooling or finally complete the transition from cubic to hexagonal on warming. When the points are shifted down in temperature by half the ΔT over which the structure change takes place, then the agreement with $T_{\rm tr}$ and T_λ is quite satisfactory as shown by the arrows in Fig. 1. It is a reasonable conjecture that the nmr anomaly results because the cubic symmetry of the crystal favors a splitting of the energy levels.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

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ABSENCE OF FERROMAGNETISM OR ANTIFERROMAGNETISM IN ONE- OR TWO-DIMENSIONAL ISOTROPIC HEISENBERG MODELS*

N. D. Mermin† and H. Wagner‡
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York
(Received 17 October 1966)

It is rigorously proved that at any nonzero temperature, a one- or two-dimensional isotropic spin-S Heisenberg model with finite-range exchange interaction can be neither ferromagnetic nor antiferromagnetic. The method of proof is capable of excluding a variety of types of ordering in one and two dimensions.

The number of exact results on the presence or absence of phase transitions in systems with realistically short-range interactions is small: Van Hove has proved that there are no phase transitions in a one-dimensional classical gas with hard-core and finite-range interactions, and Griffiths has proved that the Ising model is ferromagnetic in more than one dimension.[1] More recently Hohenberg[2] has shown that an inequality due to Bogoliubov[3] can be used to exclude conventional superfluid or superconducting ordering in one or two dimensions. We have found that a similar application of the Bogoliubov inequality leads to a surprisingly elementary but rigorous argument that the one- and two-dimensional isotropic Heisenberg models with interactions of finite range can be neither ferromagnetic nor antiferromagnetic at nonzero temperature. These conclusions have long been suspected, being suggested by calculations of the elementary excitations from the ordered state,[4] as well as by considerations of the energetics of domain walls.[5] In view of the present degree of activity in critical-point studies, it nevertheless seems worth recording that these very plausible results can be proved rigorously.[6]

We prove that there can be no spontaneous magnetization or sublattice magnetization in an isotropic Heisenberg model with finite-range