degeneracy temperature proportional to the width of the peak. The susceptibility χ above T_c could only be calculated if the precise structure of the peak and the exchange energy were known. However, as exemplified in Fig. 7 of Elcock et al.,[8] and as frequently discussed for normal ferromagnetic metals and alloys,[9] the $1/\chi, T$ curves calculable on this basis frequently appear to be very closely linear over relatively wide ranges of temperature above T_c. The slopes of such linear curves then bear no relation whatever to the saturation magnetizations obtained from low-temperature measurements. For the Sc-In alloys there was indeed no such relation: The saturation magnetic moments per atom are given as 0.035 to 0.039 Bohr magneton while the values derived from the apparent Curie-Weiss constants ranged from 0.65 to 0.70 over the ferromagnetic composition range. This divergence shows that a localized model is not applicable here, while the discussion just given shows that the observations can be explained in terms of a band model including a peaky structure. Further evidence bearing on this interpretation would come from low-temperature specific heat measurements.

We wish to thank B. T. Matthias and A. M. Clogston for helpful discussions of their results.

*Present address: Department of Mathematics, Leeds University, Leeds, England.

[1]L. Van Hove, Phys. Rev. 89, 1189 (1953).

[2]J. C. Phillips, Phys. Rev. 104, 1263 (1956).

[3]J. F. Cornwell and E. P. Wohlfarth, Conference on Magnetism and Crystallography, Kyoto, September, 1961 [J. Phys. Soc. Japan (to be published)].

[4]J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[5]J. H. Wood, Quarterly Progress Report, Massachusetts Institute of Technology Solid State and Molecular Theory Group, January 15, 1961 (unpublished), p. 79.

[6]J. F. Cornwell, Proc. Roy. Soc. (London) A261, 551 (1961).

[7]B. T. Matthias, A. M. Clogston, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters 7, 7 (1961).

[8]E. W. Elcock, P. Rhodes, and A. Teviotdale, Proc. Roy. Soc. (London) A221, 53 (1953).

[9]E. P. Wohlfarth, Proc. Roy. Soc. (London) A195, 434 (1949).

NUCLEAR SPIN STATES IN MOLECULAR CRYSTALS*

L. B. Borst, S. L. Borst, L. Koysooko,† H. Patel, and E. Stusnick
Department of Physics, New York University, University Heights, New York, New York
(Received August 21, 1961; revised manuscript received October 9, 1961)

Nuclear spin states are commonly identified in gases, but are not generally expected to exist in condensed phases. Whereas ortho and para forms are acknowledged for hydrogen both in liquid and solid,[1] restrictions in other cases imposed by neighboring molecules presumably prevent quantized rotation with a clear distinction between odd and even rotational quantum numbers with associated parallel and antiparallel nuclear spin alignment.

In the case of molecular hydrogen, the elastic neutron scattering cross section for the ortho state is large compared to the para state for both liquid and gas (30:1 in the case of the gas).[2] Neutron scattering measurements therefore permit the identification of ortho and para states.

The experiment consisted of measuring the attenuation of a neutron beam by the sample under investigation which was immersed in liquid helium. Temperatures below 4°K were achieved by evacuating the liquid helium and reducing the boiling point. The beam intensity as measured by a thin BF_3 counter was observed as a function of time with sudden changes in sample temperature, holding other experimental parameters constant. The neutron beam was derived from a reentrant hole in an aqueous moderator immersed in liquid helium. A velocity spectrum of the emergent beam was best fitted by a Maxwell distribution having a temperature of 40°K.

Solid acetylene (HCCH), a linear molecule, was cooled, first to 4°K and then to 2°K, and the total cross section was followed as a function of time (Fig. 1). The cross section changed from an initial value of 140 barns to 10 barns per molecule. The temperature was rapidly raised to 77°K, after which the cross section returned to its original value. The time for 50% conversion from the low-temperature form (mostly para) to high-temperature form (3 ortho-1 para) was about 10 minutes.

Heat capacity data for water were once interpreted in terms of ortho and para states.[3] The Pauling model[4] so completely explained the residual entropy that the alternate interpretation was

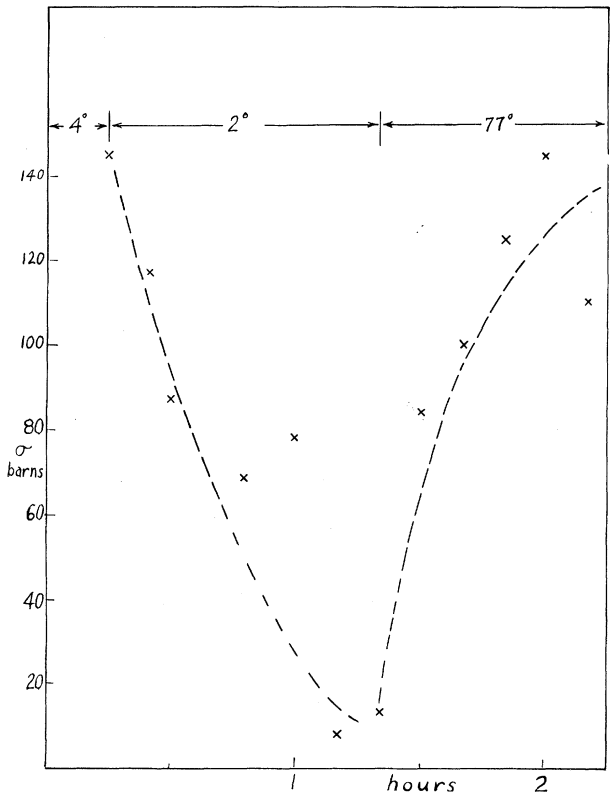

FIG. 1. Time-dependent cross section of acetylene.

forgotten. Comparison of the scattering cross section of molecular hydrogen with water for the high-temperature mixture (3 ortho-1 para) shows comparable cross sections and energy dependence. Even though hydrogen-bonded, water would seem to have ortho and para modifications.[5,6] Transmission experiments similar to those on acetylene confirm this prediction.

Water has been studied as a neutron moderator at cryogenic temperatures.[6,7] Allowed transitions between ortho and para states are possible by means of spin exchange scattering. This inelastic process constitutes an additional moderation mechanism.[5] A kilogram sample was cooled to 4°K. The neutron spectrum within the moderator, as measured by a foil activation technique, indicated the existence of a substantial fraction of the neutrons in a Maxwell distribution near the thermodynamic temperature.[6] A beam of neutrons was removed under geometric conditions which assured minimum perturbation of the velocity distribution function.

An absorption curve, using $1/v$ absorber and a thin $1/v$ detector, showed that 20% of the neutrons in the beam from a 4° moderator had an effective cross section in indium of 1500 barns. This soft component was not present at moderator temperatures of 77 or 300°K. These data are considered evidence that 20% of the neutrons reaching 300°K enter a thermal distribution near 4°K. All the foregoing experiments were conducted immediately after cooling the moderator and were conducted within a period of less than an hour.

A velocity spectrum did not, however, clearly delineate this low-temperature thermal distribution. Plotting the intensity per channel as a function of time disclosed an exponential decay with a half-life of about 100 minutes (Fig. 2). Under the experimental conditions of constant moderator temperature and careful monitoring, the intensity change could only be identified with a change in the scattering power of the moderator. A reduction in scattering power would increase the leakage of neutrons from the refrigerated moderator, thereby reducing the thermal source intensity. At the end of the refrigeration period the thermal neutron distribution returned to its original intensity. A change in intensity by a factor of ten was observed in the course of eight hours for neutrons between 500 and 1500 μsec/m reciprocal velocity. The channel covering 0-500 μsec/m shows a less pronounced time dependence because it includes fast and epithermal neutrons.

These changes in spectral intensity are considered evidence of substantial ortho to para transformation with associated loss of scattering power. After para transformation, the neutron flux is so low that it is not possible to distinguish a Maxwell distribution near the thermodynamic temperature from background effects. During the first part of the experiment, when ortho molecules are present, and earlier measurements showed evidence of a Maxwell distribution near the thermodynamic temperature, velocity selector statistics are inadequate again to demonstrate its existence.

Water is therefore an ineffective neutron moderator at 4°K. In the para state no levels exist near the ground state so that there is no effective mechanism for inelastic scattering and neutron moderation. While the ortho state has an appropriate transition for neutron energy loss, the lifetime of the ortho molecule for spontaneous transformation to para is short. If the temperature is such that a significant fraction of the molecules exist in the ortho state, then its neutron moderating properties should be good.

Nuclear spin states found in water and acetylene are expected in many molecular crystals, the rotational energy levels being shifted to higher tem-

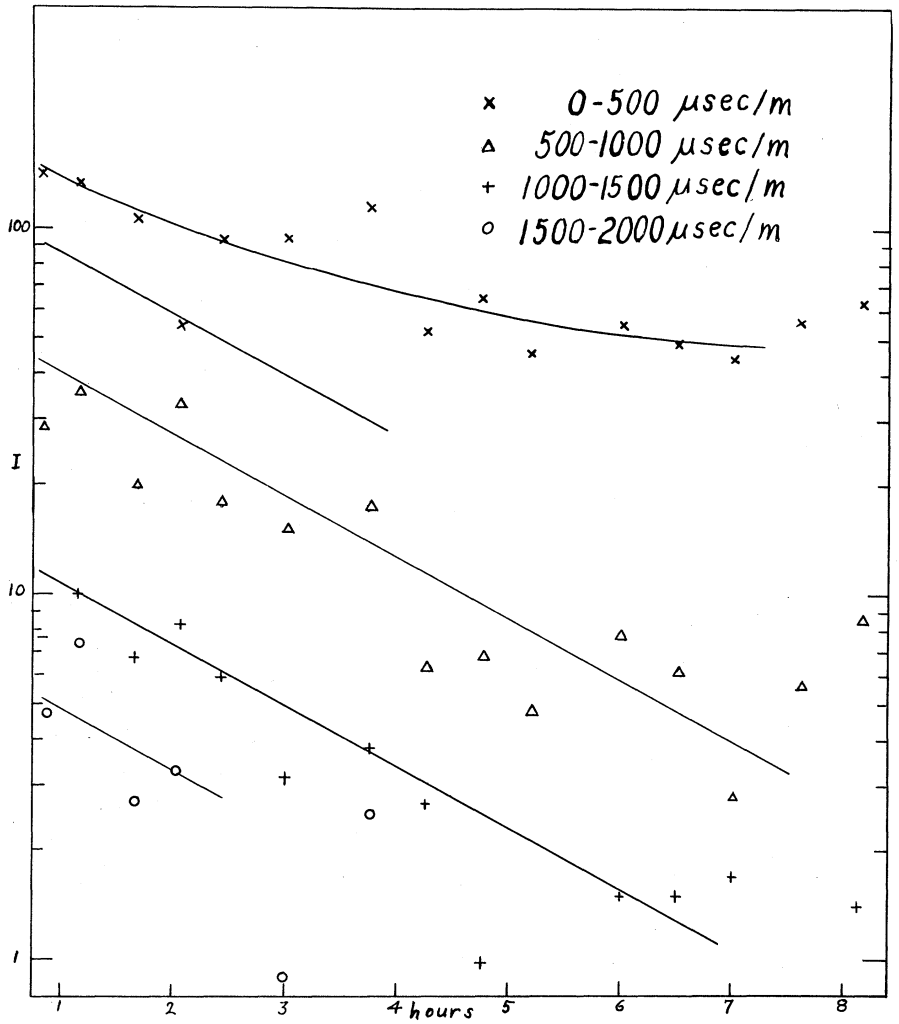

FIG. 2. Time-dependent spectral distribution from aqueous moderator at 4°K.

peratures by the crystal potential. Neutron scattering is an incisive tool at least in the case of dihydrogen molecules because of the large change in scattering power between ortho and para states. Crystal structure determinations using neutrons must now be reviewed in the light of these observations, particularly in the case of water.

---

*Research supported by John S. Barnes Corporation and the National Science Foundation.

†International Atomic Energy Authority Fellow from Thailand.

[1]A. Farkas, Orthohydrogen, Parahydrogen, and Heavy Hydrogen (Cambridge University Press, New York, 1935).

[2]R. B. Sutton et al., Phys. Rev. 72, 1147 (1947).

[3]W. F. Giauque and J. W. Stout, J. Am. Chem. Soc. 58, 1144 (1936); E. A. Long and J. D. Kemp, J. Am. Chem. Soc. 58, 1829 (1936).

[4]L. Pauling, J. Am. Chem. Soc. 57, 2680 (1935).

[5]L. B. Borst, Phys. Rev. Letters 4, 131 (1960).

[6]L. B. Borst, International Atomic Energy Agency Symposium, Vienna, October, 1960 (to be published), Paper No. IS/30.

[7]A. W. McReynolds and W. L. Whittemore, International Atomic Energy Agency Symposium, Vienna, October, 1960 (to be published), Paper No. IS/33.