

Letters to the Editor

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Second-Nearest-Neighbor Nuclear Magnetic Resonance Shifts in Iron Group Phosphates

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SHULMAN-JACCARINO shifts in the nuclear magnetic resonances of nonmagnetic atoms in paramagnetic substances have been reported¹ only for nuclei directly adjacent to magnetic atoms, e.g., F¹⁹ resonance in MnF₂. In the present letter there are reported shifts, similar in magnitude and direction, in the resonances of nuclei separated from the magnetic atom by another nonmagnetic atom, e.g., P³¹ resonance in LiMnPO₄. Further, the behavior of the shifts in a number of iron group phosphates as a function of temperature has suggested the probability that several of these phosphates undergo antiferromagnetic or ferrimagnetic transitions above helium temperatures. Measurements of magnetic susceptibility by R. M. Bozorth and Dorothy E. Walsh, to be reported in detail later, have established such transitions in several of these compounds, notably antiferromagnetism in LiMnPO₄ (Néel point ~42°K) and ferrimagnetism in Fe₃(PO₄)₂·4H₂O at a lower temperature. The size of the shifts in the P³¹ resonance indicates that the magnetization of the Mn⁺⁺ is being felt two atoms away by some mechanism (presumably electron transfer) other than direct dipolar field. The experiments thus demonstrate directly for the first time a long-distance interaction between nonadjacent ions.

We shall consider in detail the nuclear resonances of P³¹ and Li⁷ in LiMnPO₄. The mineral sample used was sufficiently single-crystalline so that the P³¹ resonance was resolved into eight orientation-sensitive components spread over a region 95 gauss wide at 77°K, the minimum shift from the P³¹ resonance in H₃PO₄ being ~65 gauss. All measurements were made with a 6520-gauss permanent magnet. The shifts of each component followed a Curie-Weiss law $\Delta H = C/(T+100^\circ)$; the widths were ~2.5 gauss at 298°K and followed a similar law. If we take $\omega_e = 3 \times 10^{12}$ sec⁻¹ we can calculate² a high-temperature width of ~2 gauss based on exchange-narrowed hyperfine interaction. The width due to

nuclear dipoles should be ~1 gauss. The width due to hyperfine interaction would not be expected to increase with decreasing temperature and the nuclear dipolar width should be independent of temperature. It is probable therefore that each component is made up of more than one line owing to slightly different magnetic environments of the four P in the unit cell³ and that the broadening at 77°K is due to the expected magnification of the slight differences in shift. The presence of eight components is being investigated further. A width from exchange-narrowed hyperfine interaction of 2 gauss corresponds to $T_1 \sim T_2 = 5 \times 10^{-5}$ sec. This value is consistent with our inability to saturate the components with a Varian Associates spectrometer. Approximate calculation of hyperfine interaction constants for 3s electrons in P shows that the amount of 3s electron deficiency at P in LiMnPO₄ is roughly 1%, or the same order as is calculated⁴ for F in MnF₂. The Li⁷ resonance was split by nuclear quadrupole interactions into a strong central component, shifted only a few gauss, and two weaker satellites almost symmetrically placed 5–10 gauss to the left and right. The components were roughly 3 gauss wide and showed evidence of further splitting presumably caused by different environments of the four Li nuclei in the unit cell. The small shifts, narrow lines, and relatively long T_1 of 2×10^{-3} sec measured by saturation agree roughly with predictions based on simple paramagnetic shift,⁵ nuclear dipolar broadening, and paramagnetic spin-lattice relaxation,⁶ with no recourse to electron transfer. That is what would be predicted since the Li—O bond would be expected, in contrast with the P—O bond, to be almost purely ionic and the hyperfine interaction of a 2s electron in Li is about one percent of that calculated for a 3s electron in P. The Li resonance was strong enough to be displayed on an oscilloscope and was observed to disappear and appear at 41.5°K. A sharp break in the cryostat cooling and warming rates at the transition temperature indicates that the antiferromagnetic transition is a sharp one with a considerable latent heat.

Powder samples measured are listed in Table I. The

TABLE I. Shifts in field for resonance of P³¹ in powdered phosphates relative to that in H₃PO₄. θ is described in the text.

| Compound | Shift (gauss) at 300°K | θ (°K) |
|--|---------------------------|---------------|
| Chromic phosphate ^{a, b} | 16 | |
| Mn ₃ (PO ₄) ₂ ·6H ₂ O ^{c, d} | 61 | 83 |
| Fe ₃ (PO ₄) ₂ ·4H ₂ O ^{e, f} | 58 | ~0 |
| Fe ₃ (PO ₄) ₂ ·8H ₂ O ^{c, d} | 69 | 52 |
| Ferric phosphate ^{a, b} | 66 | |
| Co ₃ (PO ₄) ₂ ·8H ₂ O ^{c, d} | 38 | 52 |
| Ni ₃ (PO ₄) ₂ ·8H ₂ O ^{c, d} | 26 | ~0 |
| Cu ₃ (PO ₄) ₂ ·3H ₂ O ^{c, d} | 12 | 36 |

^a Amend Drug and Chemical Company.

^b Gave no x-ray powder pattern.

^c Fisher Scientific Company.

^d Composition based on Brindley *et al.*, *X-ray Powder Data File* (American Society for Testing Materials, Philadelphia, 1957).

^e Mineral sample.

^f T. Ito and H. Mori, *Acta Cryst.* **4**, 412 (1951).

absorption derivatives observed were often quite asymmetrical and the tabulated shifts refer to the intersection of base line with the most strongly sloping segment of the recorder trace. θ is calculated by fitting $\Delta H = C/(T + \theta)$ to shifts in P^{31} resonance at 195°K and 77°K. These values of θ are usually not very different from those obtained using shifts at 298°K and 77°K.

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¹ R. G. Shulman and V. Jaccarino, *Phys. Rev.* **103**, 1126 (1956); Jaccarino, Shulman, and Stout, *Phys. Rev.* **106**, 602 (1957); J. M. Baker and W. Hayes, *Phys. Rev.* **106**, 603 (1957).

² T. Moriya, *Progr. Theoret. Phys. Japan* **16**, 641 (1956).

³ A. Byström, *Arkiv Kemi, Mineral. Geol.* **17**, No. 4, (1943).

⁴ R. G. Shulman and V. Jaccarino, *Phys. Rev.* (to be published).

⁵ N. Bloembergen, *Physica* **16**, 95 (1950).

⁶ T. Moriya, *Progr. Theoret. Phys. Japan* **16**, 23 (1956).

Detection of Optical Lattice Vibrations in Ge and ZrH by Scattering of Cold Neutrons*

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LATTICE vibrations in solids can be studied by measuring the energy distribution of scattered slow neutrons that have exchanged energy with the lattice vibrations. In experiments now under way at the Brookhaven reactor, an incident cold neutron beam is produced by filtering thermal neutrons in Be, and the velocity of the scattered neutrons is measured by the slow chopper, time-of-flight method. The filtered beam, which contains only the low-energy end of the Maxwellian distribution, has a sharp cutoff at 0.005 ev, and an effective energy of 0.004 ev. The cold neutron flux at the position of the scatterer is a factor of 25 greater than used previously;¹ this increase results from the use of a large beam port, with a full angular divergence of 9°, constructed in the top shield of the BNL reactor.² The resolution has been improved by using a chopper with much narrower slits, with a resolution of 3 μ sec/m. The present equipment is well adapted to detecting sharp neutron peaks in the spectrum of scattered neutrons in the 0.1-ev range, and it has now been successfully used to measure optical modes of vibration in Ge and ZrH.

The spectrum of neutrons inelastically scattered from crystalline materials is markedly different for coherent and incoherent nuclear scattering. In most elements, including germanium, the nuclear scattering is mainly co-

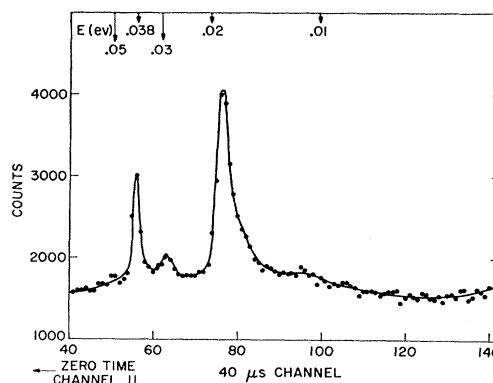


FIG. 1. Spectrum of neutrons inelastically scattered by a single crystal of Ge; the peak at 0.038 ev results from gain of energy from an optical lattice vibration.

herent, and the scattered neutrons must satisfy a coherence condition as well as energy conservation. In this case discrete energy peaks are observed in any given scattering direction. In hydrogen and vanadium, however, the nuclear scattering is incoherent and only energy conservation must be satisfied. The spectrum of neutrons inelastically scattered by acoustic vibrations is then continuous and is directly related to the lattice vibration spectrum of the scatterer.³

Among the peaks observed in the scattered neutron spectrum from a single crystal of germanium⁴ is one at the relatively high neutron energy of 0.038 ev. The neutron peak is shown at channel 56 in Fig. 1. Subtraction of the incident energy yields an energy of 0.034 ev for these vibrations. Whereas the energies of the other peaks, corresponding to acoustic vibrations, vary with different orientations of the crystal, the energy of this peak remains constant to within $\pm 5\%$. Since a difference in orientation causes interaction with lattice vibrations of different wave numbers, the small energy variation reveals the presence of lattice vibrations with energy relatively independent of wave number. This behavior, as well as the high energy

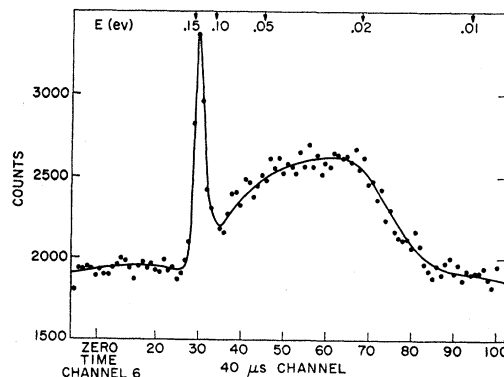


FIG. 2. Spectrum of neutrons inelastically scattered by polycrystalline ZrH; the peak at 0.134 ev corresponds to an optical lattice vibration.