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Pake G E. Nuclear resonance absorption in hydrated crystals: fine structure of the proton line. *J. Chem. Phys.* **16**:32736, 1948.
[Lyman Lab. of Physics, Harvard Univ., Cambridge, MA]

Magnetic interactions between the nuclei of atoms held relatively rigidly in a crystalline solid can produce resolvable splitting of the nuclear magnetic resonance (NMR) line. This experiment provided the first observation of such fine structure and a quantitative analysis based on the atomic positions in the lattice. [The *SCI®* indicates that this paper has been cited over 435 times since 1961.]

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"Many NMR experiments require either correction for, or experimental elimination of, the nuclear magnetic dipoledipole interaction, which would otherwise mask the chemical shifts and indirect nuclear spinspin couplings more useful in most chemical and biological applications. Frequent citation of this paper is probably because it established the quantitative aspects of the basic coupling between nuclear magnets.

"This research was begun just as pioneering experiments of Bloembergen et a/.[1] had demonstrated that molecular motions in typical liquids 'average away' most of the local magnetic dipole field. I investigated whether these fields are demonstrable in the rigid la'ttices of solids.

"Crystalline hydrates were attractive because of the robust magnetic moment of the proton. (Ice was not suitable because motion of the hydrogen nuclei narrows the resonance.[2]) Gypsum, $CaSO_4.2H_2O$, stood out because its other nuclei ($_{20}Ca^{40}$, $_{16}S^{32}$, and $_8O^{16}$) are 'eveneven' and thus have zero nuclear moment. If the H_2O molecules were 'pinned down,' then gypsum was magnetically a kind of dilute rigid 'ice' possessing isolated pairs of protons in each water molecule.

"Inquiring at the mineralogy department whether there are sizable gypsum single crystals in nature, I found I was standing by one about three feet long!

"Using a single crystal about the size of my little finger, I measured the resonance line as a function of crystal orientation in the magnetic field and discovered a splitting into pairs. The angular dependence was appropriate to the component of the neighboring proton's local magnetic field along the direction of the laboratory field.

"But comparing the measured splitting with what I calculated from the known proton magnetic moment indicated a protonproton distance about 15 percent smaller than for H_2O molecules in the gas phase. Bonding H_2O into $CaSO_4.2H_2O$ could not possibly involve energies that would shorten the OH bond by 15 percent. Could the HOH angle be bent smaller? That too seemed unreasonable.

"The key to the mystery —and a thrill to a student applying newly learned quantum mechanics to his own experiment —was to treat the proton magnetic moments as two identical nuclear spins coupled into either a triplet, spin 1, or a singlet, spin 0. The perturbing effect of the protonproton magnetic interaction on the large interaction with the laboratory magnetic field produces 1.5 times the splitting calculated classically. The HOH angle in gypsum could thus be opened up to the tetrahedral 108°, very nearly the 104°31' value for gaseous H_2O. The relationship of line splittings to crystal orientation was fully consistent with each OH bond pointing toward a vertex oxygen atom of a sulfate tetrahedron.

"The experiment demonstrated (a) the role in a solid of neighboring nuclear magnets in determining the NMR line width and (b) the potential value of the gyroscopic nuclear magnet as a noninvasive probe of the structure of condensed matter. Subsequent discovery of the chemical shift and indirect spinspin coupling in liquids qualified NMR for structural analysis and the study of atomic motions in molecules as well as crystals. The stage was set for the many applications that NMR now has in physics, chemistry, biology, and medicine."[3]

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1. **Bloembergen N, Purcell E M & Pound R V.** Relaxation effects in nuclear magnetic resonance absorption. *Phys. Rev.* **73**:679712, 1948. [Citation Classic. *Current Contents* (18):7, 2 May 1977.)
2. ...., Nuclear magnetic relaxation. *Nature* **160**:4756, 1947.
3. **Slichter C P.** *Principles of magnetic resonance.* New York: Springer-Verlag, 1978. 397 p.