the Space Telescope Science Institute reported on recent statistical studies that showed much tighter groupings among the brighter clusters than among the dimmer ones—almost, she said, as if the glowing matter in galaxies represented the peaks of a mountain range instead of the underlying continent.

It is not at all clear what the implications of such a 2σ effect would be for the dark matter problem. But the idea is still very new, and in any case the massive neutrino hardly marks the limits of the particle theorists' ingenuity. Popular dark mass particles discussed at Fermilab included the axion, predicted in certain unified field theories, and the gravitinos and photinos, predicted in theories of supersymmetry (*Science*, 29 April 1983, p. 491).

For cosmological purposes such particles are known as "cold" dark matter, as opposed to "hot" dark matter comprised of massive neutrinos; ultimately the term refers to the exceedingly weak interactions of the particles, and the fact that relic particles produced in the Big Bang would today be moving much more slowly than massive neutrinos.

The nice thing about primordial cold matter is that it would have naturally trapped the primordial baryons in clumps with the mass of galaxies, which is exactly what one needs if the galaxies are to be old. Arizona's Simon White showed computer simulations, similar to the ones that neutrinos failed so miserably, in which cold dark matter produced a large-scale structure very much like the structure we actually see. Of course, this picture does rely on unobserved particles—neutrinos, at least, are known to exist—but such is the state of particle theory that one has to take such possibilities seriously.

Several groups have proposed a varient of this model featuring cold, heavy neutrinos: the particles first catalyze galaxy formation, thus solving the small-scale dark matter problem, and then after a billion years or so decay into a uniform background of light neutrinos, thus solving the large-scale $\Omega = 1$ problem. Such particles have already been postulated in certain unified theories for mathematical reasons, so the model is not totally ad hoc.

Finally, for a completely different approach, the participants at Fermilab heard from Tufts University's Alex Vilenkin about cosmic string.

Strings, he explained, are something like quantum vortices in superfluid helium, and something like defects in a crystalline lattice. (More precisely, they are linear topological defects in field theories that have spontaneous breaking of CP symmetry.) But the upshot is that they would be infinitesimally thin, about 10^{-30} centimeter; enormously massive, about 10^{22} grams per centimeter; and exceedingly taut, about 10^{42} dynes tension. Thus, said Vilenkin, only infinite strings and closed loops of string are possible. A string with two ends would quickly collapse and dissipate.

Now, if such theories actually describe nature, said Vilenkin, then strings could have been produced abundantly in the early universe. While no one argues that they are candidates for the dark matter, they might have been excellent seeds for galaxies: calculations show that they would have gathered primordial gas around themselves at just about the right mass scale. Moreover, since big loops tend to shed little loops, large-scale and small-scale structure would be correlated in a certain way that does, in fact, resemble the way galaxies are correlated. Finally, the loops would have collected enough mass in their immediate vicinity to have collapsed into 10^6 solar mass black holes. Not only does our own galaxy seem to have such a black hole in its center (*Science,* 21 May 1982, p. 838), but quasars and other active galaxies are thought to be powered by central black holes.

However, what really got the Fermilab physicists excited about the string model is that it actually has observable consequences. An infinite string would deflect light and act as a gravitational lens, noted Vilenkin, so one could look for lines of double quasar images across the sky. Ripples in the string, especially in the loops, would also be a potent source of gravitational radiation. One could observe the very long wavelength waves by looking for gentle perturbations in the motion of Earth, using pulsars as clocks. In the case of the recently discovered millisecond pulsar, the observational limits on such radiation are already approaching the predicted value.

—M. MITCHELL WALDROP

NMR with No Magnetic Field

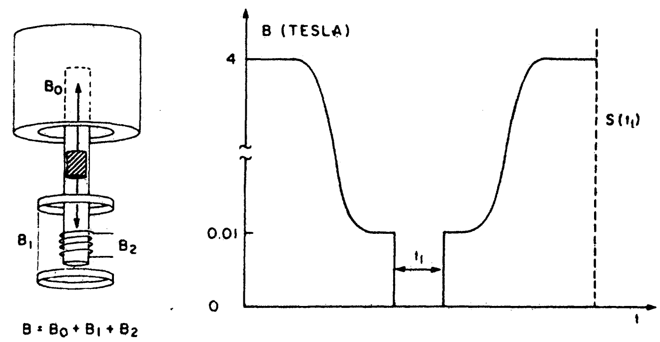
Zero-field NMR makes it possible to obtain high-quality spectra from powders and polycrystalline solids

A new technique to extend nuclear magnetic resonance (NMR) spectrometry to polycrystalline and amorphous solids has been developed by Alexander Pines, Daniel Weitekamp, and their colleagues at the University of California, Berkeley. The technique is called zero-field NMR because the spectrum is produced in the absence of an external magnetic field. The technique thus measures directly the effect of the magnetic field created by each atom's nuclear spin on the spin of nearby atoms and provides information about couplings and interatomic distances.

The new technique bucks the recent trend in conventional NMR spectrometry toward insertion of the sample in ever higher magnetic fields; higher fields are used to increase sensitivity and resolution. Except for single crystals, however, higher fields are of little value for the study of dipole couplings in solids. The problem is analogous to the problems associated with x-ray diffraction studies of amorphous or polycrystalline materials.

When a single crystal is placed in a beam of x-rays or in a magnetic field, each molecule in the crystal has the exact same orientation with respect to the beam or the field. The x-ray diffraction pattern or the chemical shifts of the NMR spectral lines change as the spatial orientation of the crystal is changed. By correlating these changes with that orientation, it is possible to extract structural information.

In a polycrystalline or amorphous solid, however, the orientation of each molecule with respect to the x-ray beam or magnetic field is random. For x-rays, this produces a diffraction pattern with limited information content. In NMR, individual spectral lines coalesce into a "powder pattern"—a broad, relatively featureless spectrum in which most structural information is lost.



Schematic diagram of the field cycling apparatus and the time-dependent effective field at the sample. The sample is moved slowly (about 100 milliseconds) from the bore of the superconducting magnet (magnetic field B_0) to a position about 75 centimeters below, where the fringe field due to B_0 is precisely canceled by B_1. Coil B_2 is then abruptly switched off; it remains off for time t_1, after which the whole process is reversed. [Source: Alexander Pines]

But in the absence of an external magnetic field, Pines says, "all orientations are equivalent and the spectrum of a powder should be 'crystal-like,' with all equivalent molecules yielding identical splittings." It is almost impossible to obtain zero-field NMR spectra directly, however, so Pines, Weitekamp, Kurt Zilm, David Zax, and Anthony Bielecki were forced to devise a roundabout way of obtaining the spectrum. Their method is a pulsed, Fourier-transform version of field cycling techniques introduced by Erwin Hahn, Alfred Redfield, and others for electron paramagnetic resonance spectrometry and certain types of nuclear quadrupole resonance (NQR) spectrometry; Pines and his colleagues have filed a patent application for it.

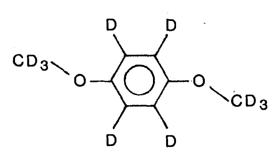
In the first step of the technique, the nuclear spins of the sample are strongly polarized in the high magnetic field of a 180-megahertz spectrometer. The sample is moved slowly into a much smaller magnetic field. This smaller field is then reduced to zero in a period of about 1 microsecond. In the absence of a field, the polarized nuclei undergo a process, called zero-field free precession, that is analogous to the free induction decay that follows a pulse in a conventional high-field experiment.

After a time t_1, the field is switched back on and the sample is moved back into the high field for detection of the signal. The entire procedure is repeated for regularly incremented values of t_1. Fourier transformation of the resultant signals produces the zero-field spectrum. "For technical reasons," says Pines, "both the preparation of the sample and the detection are done at high magnetic fields. But the NMR frequencies we're observing are those that were there while the field was switched off."

The technique was first disclosed last year [*Phys. Rev. Lett.* **50**, 1807 (1983)]. In that publication, the group reported that zero-field NMR produces spectra of powders of simple molecules with a sensitivity and resolution comparable to those of high-field spectra of single crystals or isotropic liquids. A proton NMR spectrum of powdered barium chlorate hydrate [$Ba(ClO_3)_2 \cdot H_2O$], for example, produces a triplet from which it is possible to calculate a proton-proton distance identical to that obtained in single-crystal NMR studies. Similarly, a spectrum of powdered dimethylterephthalate "yields resolved splittings which arise from couplings within the methyl group and between *ortho* aromatic protons."

In a more recent paper [*J. Chem. Phys.* **80**, 2232 (1984)], the group has extended pulsed field cycling to NQR spectrometry. NQR is a technique for studying highly polarizable nuclei in atomic or molecular electric field gradients rather than in magnetic fields. In the past, Pines says, NQR spectrometry has been used primarily for nuclei like that of bromine, which have large quadrupole couplings; these couplings produce a signal that is readily detectable. The use of field cycling makes it much easier to detect signals from nuclei with quadrupoles as small as that of deuterium.

A zero-field NQR spectrum of polycrystalline perdeuterated 1,4-dimethoxybenzene, for example, clearly shows coupling of the deuterons closest to the



methoxy groups and those farthest from the methoxy groups (because of the *trans* conformation of the molecule in the solid state), as well as splittings of the methyl resonance arising from interdeuteron dipolar couplings.

There are several significant advantages to this approach to NQR, Pines says. For one thing, the presence of protons on the sample does not introduce complications because proton-deuteron coupling is quenched in the absence of a field. No zero-field irradiation is required, furthermore, so that saturation broadening of signals is eliminated. Finally, the fact that this is a Fourier-transform method "makes possible [NQR] experiments with a wide range of initial conditions and allows zero-field pulsed experiments such as as spin-decoupling and two-dimensional spectroscopy." Of particular importance is the fact that "quadrupole couplings label particular molecular sites, while the dipolar couplings measure correlations and distances between those sites."

Other quadrupolar nuclei that are difficult to monitor by conventional techniques can also be observed readily by pulsed zero-field NQR. These include lithium-7, boron-11, nitrogen-14, sodium-23, and aluminum-27. A lithium-7 spectrum of powdered lithium sulfate, for example, clearly shows one resonance for each crystallographically inequivalent site. Pines predicts that the technique should be especially useful for studying aluminum in zeolites, which are of great interest in catalysis. The group has already resolved 27 different aluminum resonances in a model compound.

In a paper now in press in *Chemical Physics Letters*, the group also reports that the technique is useful for resolving heteronuclear coupling, such as that between protons and carbon-13, in both solids and liquids. By varying the initial polarization of the molecule in the high magnetic field, they find, it is possible "to disentangle spectral patterns arising from different functional groups." The zero-field period can also be used to transfer polarization from protons to the spins of other nuclei, a technique that is useful for strengthening weak signals from certain nuclei.

Pines and his colleagues are still exploring potential applications and limitations of the technique. "So far," he says, "we're restricted to small molecules. We have to improve our resolution and we also have to work out a way to handle the vast amount of data generated by the technique." In fact, Zax adds, the amount of data generated by zero-field NMR is comparable to that generated by two-dimensional NMR, but processing of the data is more complicated. The spectra are also "quite complicated: there are many more spectral lines than there are nuclei."

"The next step—applying zero-field NMR spectrometry to large, complex molecules—will require enormous computational facilities," notes Pines. This problem should be solved by the installation of a large new computer. Once that is installed, he concludes, "we hope to proceed quickly."—**Thomas H. Maugh II**