

Many Disciplines Unite to Study Solid Structure and Dynamics

At many topical conferences the emphasis has been on the study of a wide variety of materials with a particular experimental tool. The main purpose of the symposium on molecular dynamics and structure of solids, held at the National Bureau of Standards last October, on the other hand, was to emphasize the correlation of information from a number of experimental techniques applied to a single class of materials, namely, molecular solids. Any technique that could provide information on the structure and dynamical behavior of such materials was welcome. One result of this emphasis was that the 250 chemists and physicists who attended represented a broad spectrum of fields, and, for most of us, included many new faces.

Techniques and applications. Elliot Montroll discussed the theoretical basis that unifies the various experimental techniques and described the physical phenomena that can be probed by the different methods. Other introductory lectures on techniques and their applications were delivered by George Bacon (x-ray and neutron diffraction), George Wilkinson (infrared and Raman spectroscopy), Peter Egelstaff (neutron inelastic scattering) and Rex Richards (NMR).

The rest of the conference comprised invited and contributed papers summarizing recent work on molecular solids. The advantage of combining crystallographic, spectroscopic and theoretical studies to gain a deeper understanding of hydrogen bonding in crystals was clearly illustrated in lectures by Walter Hamilton (Brookhaven) and James Ibers (Northwestern). Ibers pointed out that spectroscopic data are easily interpretable only for simple hydrogen-bonded systems. By a combination of such data with crystallographic results it is sometimes possible to obtain quantitative information on hydrogen-bond potentials. He gave a detailed review of the dynamical and structural information on NaDF_2 and showed that the

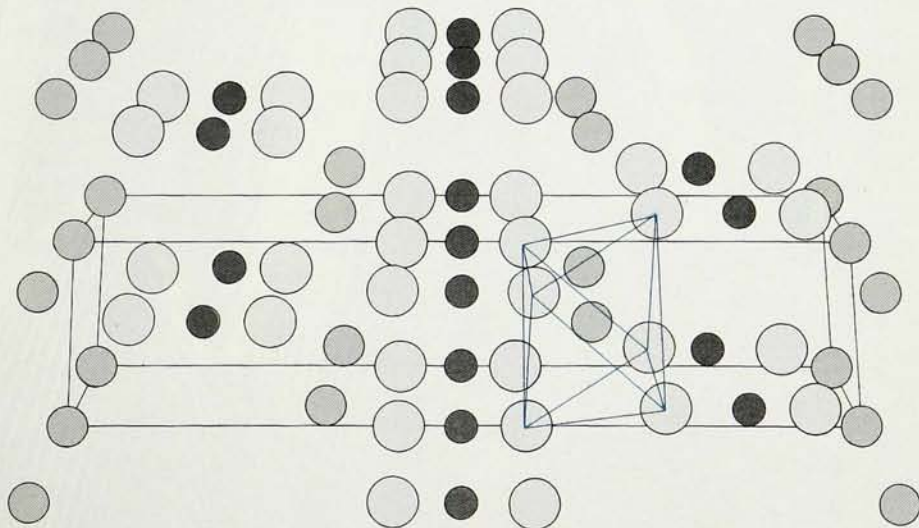
best agreement in fitting the experimental results to theoretical models occurs for a symmetric single-minimum potential. He also showed that substitution of deuterium in the hydrogen bonds of some simple solids yields some surprising, and potentially important, changes. For example studies of normal and deuterated chromous (HCrO_2) and cobaltous (HCoO_2) acid by neutron and x-ray diffraction, infrared spectroscopy and neutron inelastic scattering indicate differences of 0.005 nm in the length of the hydrogen bond and significantly different potentials. It appears that hydrogen atoms bound in these crystals "see" a symmetric environment but deuterium atoms are bound for a long time to one oxygen atom and thus see an unsymmetric environment.

Complex inorganic crystals. Hamilton discussed the study of structural and dynamical parameters and intermolecular forces in more complex inorganic crystals. He pointed out that it is often difficult to determine the shapes of potential surfaces in crystals with any great accuracy from the experimental data, and he suggested that the square-well potential might not be too unrealistic a model for potential

surfaces in some complex solids in which repulsive terms dominate the forces between neighboring atoms. He discussed recent experimental and theoretical studies on three complex-ion salts. In the first two, phosphonium iodide and ammonium fluorosilicate, there is good agreement between inelastic neutron scattering and diffraction data bearing on the motion of the XH_4^+ cation in its potential well. Further insight is gained by comparison with calculations of crystal energy as a function of group orientation, with combined electrostatic and Lennard-Jones terms. In a third compound, potassium hydrogen *bis*-acetylsalicylate, the combination of neutron and x-ray diffraction provides an extremely satisfactory analysis of hydrogen motion in a symmetric hydrogen bond.

Contributed papers also included interesting results on hydrogen-bonded crystals. Evidence was presented for the existence of the $[\text{H}_2\text{O}\cdots\text{H}\cdots\text{H}_2\text{O}]^+$ ion, in which two water molecules are hydrogen-bonded together to form a complex cation that can exist in a variety of crystals and configurations. In another paper the infrared investigation of crystal hydrates that contain dilute amounts of HOD molecules was

ARRANGEMENT OF THE ATOMS in HCrO_2 . The smallest spheres (dark) are hydrogen, the largest (light) are oxygen, and the others are chromium. Four hexagonal unit cells are seen in this perspective view; one of the CrO_6 octahedra is shown in color.





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shown to be a powerful tool for the study of bonding and environment of water molecules in solids. In an infrared study of the ammonium halides a measure of the orientational disorder of the NH_4^+ ions below the lambda transitions was derived from the intensity variation with temperature of an anomalous component of the ν_4 band. Detailed information was also presented on the tunneling and thermally activated jumping of H and D atoms in ferroelectric KH_2PO_4 and KD_2PO_4 .

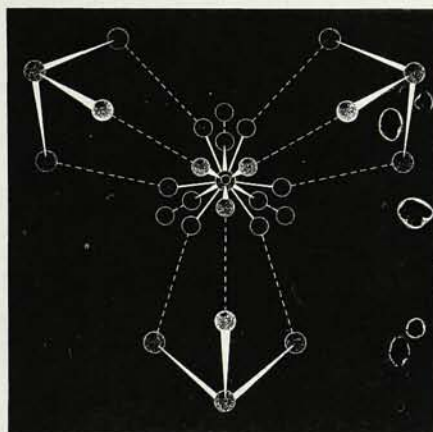
Lattice dynamics. A review on lattice dynamics in molecular crystals was given by Gerald Dolling (Oak Ridge National Laboratory and Chalk River). Coherent inelastic neutron scattering has in recent years provided a wealth of information on dispersion curves for lattice vibrations in metals and simple ionic crystals. Dolling demonstrated how the phenomenological framework developed by Max Born and K. Huang has been successfully utilized in the analysis of these dispersion curves in an attempt to learn more about interatomic forces. He pointed out that the extension of theory and neutron experiments to molecular crystals involves further complications although the potential reward, in terms of an increase in our knowledge of intermolecular forces, is great. Dolling stressed the essential problems in studying complex crystals: the development of dynamical models with reasonable arbitrary parameters representing intermolecular forces and the choice of crystals with symmetry properties that allow the reduction of independent parameters and enable the neutron-scattering measurements to sort out different vibration modes. It is also important to study solids in which the internal modes of vibration are well separated from the "lattice" modes.

Dolling also reviewed some of the first attempts to study the dynamics of complex crystals, including the work of the Chalk River group on sodium nitrite. He discussed the theoretical calculations of dispersion curves for organic crystals (such as hexamethylenetetramine and anthracene) by Stuart Pawley and William Cochran, using potentials that describe interac-

tions between individual atoms in molecules and all other atoms in neighboring molecules, assuming that the molecules are rigid. Attempts are now under way at ORNL and Chalk River to measure dispersion curves for such crystals.

Contributed papers on lattice dynamics ranged from the derivation of the frequency distribution of ice from neutron-scattering data to the observation of lattice modes in the far infrared as a function of pressure (which potentially offers a method for determination of Grüneisen constants and elucidation of anharmonic forces in solids) and a discussion of the derivation of the density of vibrational states from optical spectra of orientationally disordered crystals.

Organic crystals. Kenneth Trueblood (University of California at Los



Ammonium fluorosilicate

Angeles) presented a paper on precise diffraction studies of organic crystal structures. As the methods of measuring diffraction intensities and correcting for experimental errors have become more and more accurate the use of more sophisticated methods to refine crystal structures has become imperative. Least-squares refinement of structures by the use of anisotropic temperature factors has become routine. Physically meaningful analysis of these temperature factors to derive ellipsoids of thermal motion is made possible by the availability of high-speed computers. These results have, in many cases, shown impressive agreement with root-mean-square amplitudes determined from spectroscopic data. A number of structures have been analysed in terms of rigid-

body motions of molecules, motions that, in the most general case, require 20 independent parameters for their description.

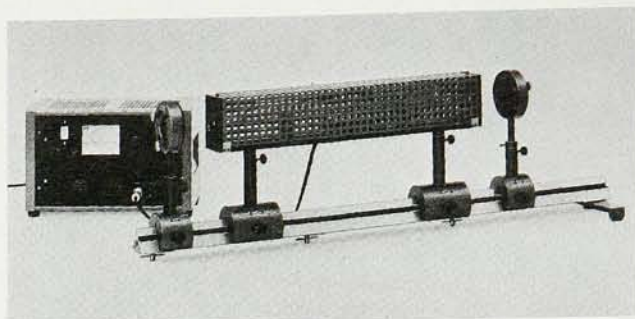
Several extensions of the concept of rigid-body motions were discussed by Trueblood and also in several contributed papers. Some molecules are not rigid, as when one part of the molecule is connected to another by a single bond. In this case the molecule can be treated as a set of segments, each of which librates with respect to the others. It was also pointed out that "temperature factors" in x-ray data include effects such as electron density distortions due to bonding, which are not thermal phenomena at all. In such cases, subtracting the thermal ellipsoids of motion determined from neutron diffraction from the apparent x-ray ellipsoids can reveal marked electronic anisotropies, especially in light atoms.

Molecular motions. Raymond Andrew (University of Nottingham) discussed the study of rotation in solids by nuclear magnetic resonance techniques. He concentrated on the analysis of spin-lattice relaxation-time measurements as providing the best quantitative information on molecular motion. By a review of work on substituted benzenes he demonstrated the improvements in technique and analysis that have occurred in recent years. These improvements include rotating-frame relaxation-time measurements to extend the measureable frequency range and the investigation of partially deuterated crystals to separate inter- and intramolecular contributions to the relaxation time and facilitate the identification of rotating groups. In a discussion of results on a series of methylbenzenes Andrew identified the reorientation of different methyl groups with different relaxation-time minima and showed the excellent correlation of the derived barriers to rotation with neutron-scattering results.

Recent studies of molecular rotation and diffusion in "globular" molecular crystals were discussed both by Andrew and in the contributed papers. From a detailed NMR study of rotational and self-diffusion in adamantane it was demonstrated that the self-diffusion coefficient in the plastic phase is at least five orders of magnitude greater than that for solid hexamethyl-

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enetetramine, a similar molecule with no plastic-crystal phase. A review of entropy data on plastic crystals was also presented, with a discussion of their implications concerning molecular disorder. Other papers included theoretical and Raman-spectral studies of rotation in solid and liquid methane with a correlation of infrared and neutron results. Clarification of spectral assignments in neutron scattering by hydrogenous molecules by selective substitution of atoms with lower cross sections was also discussed.

Polymers. David McCall (Bell Telephone Laboratories) gave a comprehensive survey of the investigation of molecular motion and relaxation in polymers by NMR, dielectric, and dynamic-mechanical methods. He discussed the various theoretical approaches to relaxation phenomena and provided a description of the various relaxation processes (main-chain reorientation, side-group motions, etc.). Correlation frequencies as functions of temperature, derived from the three types of relaxation measurements, were shown to be quite consistent with one another. In addition, molecular mechanisms and activation energies

were assigned for different relaxations. The contributed papers were primarily concerned with the study of vibrational spectra of polymers such as polyethylene and polyoxymethylene by inelastic neutron scattering. Stretched polymers were studied as a function of orientation to aid in the assignment of particular transverse and longitudinal modes, and detailed comparisons were made with infrared results and theoretically calculated vibration spectra to gain insights into the forces that link polymer chains. Of particular interest was an attempt to study dispersion relations by coherent neutron scattering from deuterated polyethylene.

As evidenced by both the lectures and related discussions, the conference succeeded admirably in demonstrating the important advantages of combining results from a number of techniques.

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The symposium was sponsored by the Institute for Materials Research of the National Bureau of Standards. The proceedings will be published as an NBS monograph available from the Government Printing Office.

EDWARD PRINCE
US Naval Research Laboratory
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The Electret: from Freak to Familiarity in Fifty Years

The emergence of the electret as a potentially very useful device whose behavior is quite comprehensible was evident at the symposium on electrets, held in Chicago last October as part of the 132nd meeting of the Electrochemical Society. Electrets, discovered nearly 50 years ago by Mototarô Eguchi, are solid dielectrics that have acquired a real surface charge (homocharge) and also manifest a charge of opposite sign (heterocharge) because of a volume effect. Fascinating phenomena of spontaneous net surface-charge reversal and growth followed by eventual decay result from different decay rates of homocharge and heterocharge. Decay times are typically months or years.

The symposium opened with theoretical papers that showed that the electret can be understood on the basis of very general principles applicable to a wide class of solid dielectrics. Martin Perlman and Donald Tilley

(Collège militaire royal, Saint Jean, Québec) reviewed and developed isothermal phenomenological theories. Bernhard Gross (Comissão Nacional de Energia Nuclear) presented the first of a series of major contributions to the meeting made by physicists from Brazil. His powerful general theory treats nonisothermal transients in solid dielectrics with the assumption of linearity and a new principle of "charge reversibility." Succeeding papers given by Sergio Mascarenhas and others (Universidade de São Paulo) showed that "ionic thermal current" measurements are a key to the understanding of the microscopic mechanisms responsible for electret heterocharge and to the study of fundamental solid-state phenomena. This work illuminates the vexed question of the importance of space-charge contributions to electret heterocharge; volume polarization in potassium chloride is due to impurity-vacancy dipoles rather than to

space charge, but in ice electrets space-charge effects dominate. Space charge is also significant in naphthalene.

New techniques and applications. Reports from industrial laboratories in the United States and Canada described new techniques and results for surface-charge measurement and interfacial phenomena. Clifford Lilly and others (Philip Morris Research Center) measured thin-film conduction and showed that a Schottky treatment is compatible with the results.¹

Substantial progress was reported in two quite different applications. The electret microphone, pioneered and developed by Gerhard Sessler and James West at the Bell Telephone Laboratories² has been advanced to the stage of field tests in telephones after the discovery by Perlman and Cornelis Reedyk (Northern Electric Research and Development Laboratories) of film electrets with charge lifetimes estimated to be hundreds of years. Preston Murphy and Frank Holly of the Thermo Electron Engineering Corp., who are interested in the eventual construction of an artificial heart, described a series of experiments on the effect of electrified polymers on the clotting of blood and demonstrated that negative electrets placed in the cardiovascular system of dogs remain reasonably free of thrombus while positive electrets thrombosed severely.

As the participants in this symposium dispersed, they left with the conviction that further investigation of the electret effect will add to our knowledge of fundamental physical processes and lead to many practical applications.

References

1. A. C. Lilly Jr, J. R. McDowell, J. Appl. Phys. **39**, 141 (1968).
2. G. M. Sessler, J. E. West, J. Acoust. Soc. **40**, 1433 (1966).

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The proceedings of the symposium are available from the national headquarters of the Electrochemical Society, 30 E. 42nd St., New York, for \$11.00. Selected papers will be published in the Journal of the Electrochemical Society and in Electrochemical Technology.

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