IV. OPTICAL AND INFRARED SPECTROSCOPY*

Academic and Research Staff

Prof. C. H. Perry

Graduate Students

Jeanne H. Fertel
E. F. Young

RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

The research of this group continues to be the study of the vibrations of crystal lattices by infrared and Raman spectroscopy. The frequencies of many of the normal modes of lattice vibration can be determined in this way, which give results of significance for many of the properties of solids and assist in the deduction of interatomic-force laws for the crystal.

C. H. Perry

1. Interferometric Spectroscopy[1]

The far infrared interferometer has had a vacuum sample chamber added which has two transmission foci and a reflection focus; thus measurements can be made at an angle of only 10° from normal incidence. Provision has been made so that samples can be studied from 4-700°K with suitable cryostats and heated sample holders. A polarizer mount and gas cells can also be located at either transmission focus. Reflection gratings and ionic crystal powder filters can be conveniently inserted as short-wave cutoff filters. A Texas Instrument Company low-temperature bolometer has recently been incorporated and considerable improvement in signal-to-noise ratio has been observed. This detector allows more accurate intensity measurements to be made, but a new lock-in amplifier and an analog-to-digital converter with greater dynamic range are needed.

C. H. Perry, E. F. Young

References

1. C. H. Perry, R. Geick, and E. F. Young, "Solid-State Studies by Means of Fourier Transform Spectroscopy," Boulder Millimeter Wave and Far Infrared Conference, Estes Park, Colorado, August 30-September 1, 1965.

2. Lattice Vibrations

a. Infrared Spectra of Solids

Instrumentation described above, and in previous reports,[1] has been used for observing these data. The normal modes in pyrolitic boron nitride[2] have been analyzed and the structure interpreted. The lattice vibrational properties of hexagonal CdSe[3] have been observed and a number of multiphonon phonon peaks have been interpreted in terms

*This work is supported by the Joint Services Electronics Programs (U. S. Army, U. S. Navy, and U. S. Air Force) under Contract DA 36-039-AMC-03200(E).

of representative phonon energies for the edge of the Brillouin zone. The temperature dependence of the far infrared reflectivity of magnesium stanide has been measured and analyzed by means of a classical dispersion formula that includes Drude terms for the free-carrier effects.[4] The room-temperature far infrared spectra of some cubic (ABF_3) perovskite fluorides have been obtained and the results are in agreement with group theoretical considerations.[5] This work will continue to obtain the modes, oscillator strengths, and damping constants as a function of temperature.

Reflectance measurements of some alkali halides, silver salts, and ammonium halides will be studied and the results will be treated with a Kramers-Kronig and classical dispersion analysis to give the lattice vibration parameters as a function of temperature to test deviations from ideal behavior caused by the overlap of neighboring ions.

Investigations of materials exhibiting a Curie-Weiss law dependence of their dielectric constants continues,[5] and a new series consists of mixed crystals of potassium-sodium tantalates. Reflectance and transmittance spectra of mixed crystals of some II-VI compounds have also been started. The long-wave vibrations of several inorganic complexes have been completed[6] and this work may be continued with related compounds.

References

1. C. H. Perry, Quarterly Progress Report No. 70, Research Laboratory of Electronics, M. I. T., July 15, 1963, pp. 19-31.
2. R. Geick, C. H. Perry, and G. Rupprecht, Quarterly Progress Report No. 78, Research Laboratory of Electronics, M. I. T., July 15, 1965, pp. 37-45.
3. R. Geick, C. H. Perry, and S. S. Mitra, Bull. Am. Phys. Soc., March 1965, p. 332 (Abstract) (to be published in J. Appl. Phys.).
4. R. Geick, Quarterly Progress Report No. 79, Research Laboratory of Electronics, M. I. T., October 15, 1965, pp. 37-41.
5. C. H. Perry, R. Geick, E. F. Young, and H. J. Guggenheim, Proc. VIII European Congress on Molecular Spectroscopy, Copenhagen, Denmark, August 1965, p. 286 (Abstract); Quarterly Progress Report No. 78, Research Laboratory of Electronics, M. I. T., July 15, 1965, pp. 45-51.
6. C. H. Perry, Japanese J. Appl. Phys., Vol. 4, Supplement I, p. 564, 1965.
7. J. H. Fertel and C. H. Perry, J. Phys. Chem. Solids 26, 1 (1965).

b. Raman Spectra of Solids

The Raman spectrum of $BaTiO_3$ has been observed on a Cary Model 81 spectrophotometer in the range 4°-400°K, and an unusual temperature dependence of one of the normal modes has been related to its ferroelectric properties.[1,2] This work continues on other ferroelectric materials, including $SrTiO_3$ and $KTaO_3$. Observation of the temperature-dependent Raman spectrum of the ammonium halides has begun, and will be extended to a number of other crystals.

A laser-Raman spectrometer is being constructed and both photographic and photoelectric recording will be incorporated. The He-Ne laser source should allow accurate polarization measurements to be made, and also permit study of the angular dependence of the scattering for anisotropic materials.

Raman spectroscopy is complementary to the infrared measurements, and it gives accurate values for the frequencies of one-phonon transitions that are not infrared active. Also, "second-order" Raman spectra provide information on anharmonicity in a crystal lattice.

C. H. Perry

References

1. C. H. Perry and D. B. Hall, Phys. Rev. Letters 15, 700 (1965).
2. D. B. Hall and C. H. Perry, Quarterly Progress Report No. 78, Research Laboratory of Electronics, M. I. T., July 15, 1965, pp. 51-61.

A. LATTICE VIBRATIONAL PROPERTIES OF HEXAGONAL CdSe

[This report is an abstract of a paper that was presented at the Spring Meeting of the American Physical Society, Kansas City, Missouri, March 1965, and is to be published in the Journal of Applied Physics.]

The reflectivity of single-crystalline CdSe has been studied with linearly polarized light at room temperature and at liquid-nitrogen temperature. The characteristic data of the fundamental lattice vibration were determined by means of a classical oscillator fit. A shift of 6 cm^{-1} or 3.5 per cent in the infrared eigenfrequency was found, resulting from anisotropy splitting. Transmission measurements yielded several multiphonon peaks and an impurity band. The multiphonon peaks are interpreted in terms of a set of four representative phonon energies for the edge of the Brillouin zone.

Dr. S. S. Mitra, of the Physics Research Division, I. T. T. Research Institute, Chicago, Illinois, cooperated in this work.

R. Geick, C. H. Perry

[Dr. R. Geick is now at the Physikalisches Institut der Universität, Freiburg.]