

than magnetoresistance by a factor equal to the mobility ratio.⁵ It should thus be a valuable tool for isolating out the scattering properties and possible anisotropy of the lighter band. Further it will be interesting to compare M_{xy} with the imaginary part of rf magnetoconductivity⁷ and the frequency dependence of Faraday rotation in the range $\omega\tau \ll 1$. The latter effects both involve the same scattering terms S in the isotropic τ approximation, but differ in their anisotropy dependence, and (in case of degenerate bands) are less sensitive to the light minority carrier⁸ than M_{xy} .

The author is greatly indebted to Mr. Paul Coluccio for his valuable help in constructing

the apparatus and in taking the measurements.

*Supported by the U. S. Air Force Office of Scientific Research.

¹B. Donovan and J. Webster, Proc. Phys. Soc. (London) **A79**, 46, 1081 (1962).

²B. Lax and L. M. Roth, Phys. Rev. **98**, 549 (1955).

³See, e.g., B. Lax, H. J. Zeiger, and R. N. Dexter, Physica **20**, 818 (1954).

⁴J. K. Furdyna and S. Broersma, Phys. Rev. **120**, 1995 (1960).

⁵E. M. Conwell, Proc. IRE **46**, 1281 (1958).

⁶For example, in *p*-type germanium the light hole (approximately 4% of the population) contributes over 99% of the total value of M_{xy} at low fields.

⁷K. S. Champlin, Phys. Rev. **130**, 1374 (1963).

⁸J. K. Furdyna, unpublished.

LATTICE VIBRATIONS IN IONIC CRYSTALS OF FINITE SIZE

Marvin Hass

U. S. Naval Research Laboratory, Washington, D. C.

(Received 20 August 1964)

The existence of size and shape effects in lattice-vibration spectra of crystals of finite size has been predicted by a number of investigators.¹⁻⁴ These effects will be important for phonons whose wavelength approaches the dimensions of the specimen. This Letter offers evidence for the existence of such effects based on a study of the infrared lattice-absorption spectrum using specially prepared samples. Such effects are not readily identified employing the usual techniques for studying lattice absorption. A specific effect capable of being observed in the infrared absorption spectrum of ionic crystals was predicted by Fröhlich,¹ who pointed out that the nature of the polarization due to the optical-branch lattice vibrations depends upon the size and shape of the crystal. In the case of small spherical crystals of a cubic diatomic compound having a radius R , Fröhlich showed that there will be one (triply degenerate) mode of frequency ω_s expected to interact strongly with electromagnetic radiation. The frequency ω_s can be related to the usual transverse optical frequency ω_t in large crystals (which interacts strongly with radiation) by the expression

$$(\omega_s/\omega_t)^2 = (\epsilon_0 + 2)/(\epsilon_\infty + 2), \quad (1)$$

where ϵ_∞ and ϵ_0 are the high- and low-frequency dielectric constants. The radius R of the small

crystal should fulfill the condition

$$a_0 \ll R \ll \lambda_t, \quad (2)$$

where a_0 , the lattice parameter, is of the order of 10^{-4} microns and λ_t , the wavelength in the medium of electromagnetic radiation⁵ corresponding to ω_t , is of the order of 20 microns. The lattice dynamics of crystals of finite size has been discussed more extensively by Rosen-

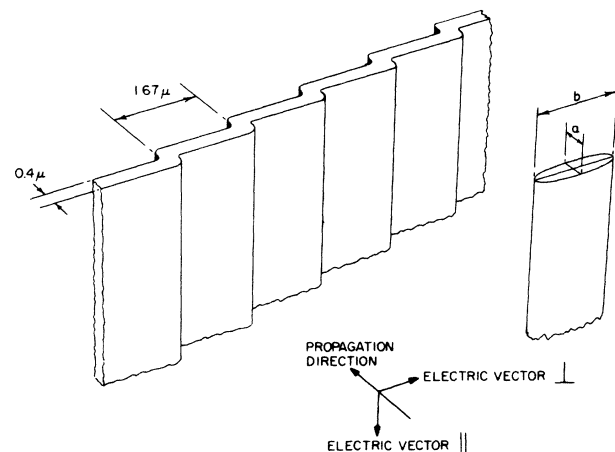


FIG. 1. Presumed shape of thin film evaporated on a diffraction grating, and elliptical-cylinder approximation.

stock,² Maradudin and Weiss,³ and Barron,⁴ and it has been possible to calculate the dispersion curves of a spherical ionic crystal and to obtain Fröhlich's result in the limiting case of long-wavelength phonons.³ However, a number of fundamental questions have been raised about the lattice dynamics of finite crystals and it is of great interest to obtain experimental evidence relating to this matter.⁶

In an attempt to reveal effects due to finite

size, samples were prepared by evaporating alkali-halide films on a substrate consisting of a transmission diffraction grating⁷ whose spacing of 1.67 microns/groove is small compared to λ_f . The presumed shape is shown in Fig. 1. Since the thickness is less than one micron, the sample can be considered much smaller than λ_f in two dimensions and much larger than λ_f in the direction parallel to the grooves. By studying the dependence of the resulting lattice ab-

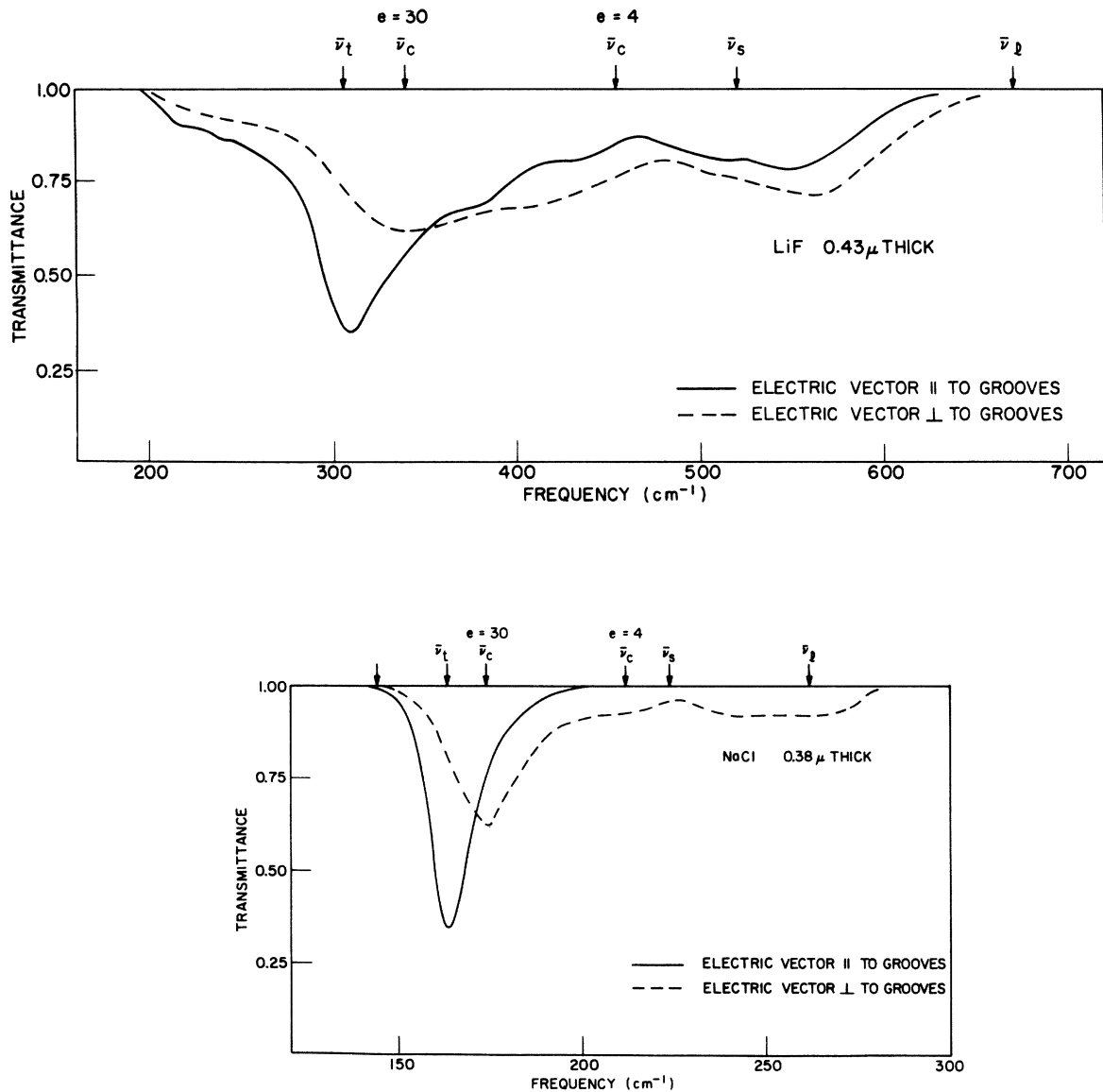


FIG. 2. Transmittance of thin films of NaCl and LiF evaporated on a grating relative to an uncoated grating. The arrows at the top indicate the frequencies for the usual transverse and longitudinal modes, and for spherical and cylindrical modes discussed in the text. The thickness quoted has been obtained by measuring the thickness of a film on a flat glass surface placed next to the grating during the evaporation.

sorption on the polarization, it should be possible to show a size and shape dependence. That is, the lattice absorption with the electric vector parallel to the grooves should correspond to the well-known case of the thin flat crystal and the absorption with the electric vector perpendicular to the grooves should be related to the situation discussed by Fröhlich. The results are shown in Fig. 2 for LiF and NaCl. For the parallel case, the absorption is relatively sharp and occurs at ω_f , as expected. For the perpendicular case, the absorption is broadened asymmetrically and shifted to higher frequencies.

Since the size and shape of the samples used here differs markedly from a sphere, it is not possible to employ Eq. (1). However, a rough approximation to the actual situation may be obtained by considering the material on one strip of the grating as an infinitely long elliptical cylinder, as shown in Fig. 1. For a cylinder of axial ratio e ($e = b/a$), the cylindrical frequency ω_c for vibrations perpendicular to the long axis of the cylinder and parallel to the axis b of the ellipse can be related to ω_f by

$$(\omega_c/\omega_f)^2 = (\epsilon_0 + e)/(\epsilon_\infty + e). \quad (3)$$

Similar results for a one-dimensional chain of alternating positive and negative ions with nearest-neighbor interactions have been obtained by Rosenstock.⁸ As an approximation to the actual sample shape, the value for $e = 4$, which corresponds to the grating spacing divided by the thickness, is shown by arrows in Fig. 2. However, the data seem to be more in accord with a value of $e \sim 30$. This is not too surprising as there is not a complete separation of material in adjacent grooves. The fact that the sample is not an elliptical cylinder (or, in the general case, an ellipsoid) will result in a nonuniform electric field in the sample and may be the reason for

the broadening and structure in the absorption spectrum.

The significance of these experimental results lies in the fact that they provide evidence for the existence of modes in crystals which depend upon the size and shape and whose frequencies are noticeably different from those of infinite crystals.

The author gratefully acknowledges many fruitful discussions with Dr. H. B. Rosenstock, Dr. A. A. Maradudin, and Dr. R. F. Wallis. The films were evaporated by M. O'Hara and the measurements were carried out by L. J. Gallagher. The gratings used were made available through the kindness of J. D. Purcell of the U. S. Naval Research Laboratory.

¹H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, Oxford, England, 1948), 2nd ed., pp. 153-155.

²H. B. Rosenstock, *Phys. Rev.* **121**, 416 (1961).

³A. A. Maradudin and G. H. Weiss, *Phys. Rev.* **123**, 1968 (1961).

⁴T. H. K. Barron, *Phys. Rev.* **123**, 1995 (1961).

⁵The wavelength λ_t in the medium can be much smaller than the corresponding wavelength in vacuum when the index of refraction is high, as it can be near ω_f . However, it should still be possible to satisfy the condition (2).

⁶Actually, a well-known case of lattice absorption in finite (in one dimension) crystals occurs for thin flat crystals of thickness much less than λ_t . Here absorption occurs at the frequency ω_f . Under certain conditions absorption at the longitudinal frequency ω_l can be observed also, according to D. W. Berreman, *Phys. Rev.* **130**, 2193 (1963). In these situations the boundary conditions are such that the infrared active modes in the finite thin flat crystal occur at characteristic frequencies of infinite crystals.

⁷This grating was prepared by Johns Hopkins University. A grating with a strong blaze is necessary to show the effect reported here.

⁸H. B. Rosenstock, *Phys. Rev.*, to be published.