

Letters to the Editor

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New Absorption Lines of Crystals in Submicrowave Region

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IN the course of studying pure quadrupole spectra of iodine nuclei in silver iodine powder, many absorption lines different from those of the nuclear quadrupole resonance have been found by the aid of a super-regenerative detector with a transmission-line tuned circuit, which was working in the frequency range between 150 Mc/sec and 350 Mc/sec. The absorption lines were not affected by a magnetic field sufficient to cause a Zeeman effect of the nuclear quadrupole resonances. The absorption appeared strongly when the sample was put in an electric radiation field, i.e., at the voltage loop of the transmission line. The first observation was made at liquid air temperature. However, after the sample was heated to 150°C, which is above the transition point of the crystals, it showed the same absorption as at room temperature. The frequency of the lines changed with temperature, having a temperature coefficient, $\nu^{-1}d\nu/dt$, of about $-3 \times 10^{-4}/^\circ\text{C}$.

A similar absorption was found in phosphorescent zinc sulfide powder in the frequency range between 24 Mc/sec and 500 Mc/sec and in barium chlorate powder (which was previously heated) between 20 Mc/sec and 500 Mc/sec at room temperature. Silver bromide at liquid air temperature and zinc oxide and cadmium sulfide at room temperature were examined, but such an absorption was not observed. In zinc sulfide it was found that the absorption disappeared when the powder was immersed in a liquid of carbon tetrachloride and that it decreased when the sample was kept in the dark for several days.

For the precise measurement of the spectra, two autodyne detectors with a LC tuning circuit covering the frequency range from 3 Mc/sec to 120 Mc/sec were used. About 10 cc of zinc sulfide, which were put into the gap of the condenser, yielded a spectrum composed of numerous lines with an average spacing of about 10 kc/sec.

A similar absorption was found in powders of quartz crystals and Rochelle salt. These experiments may be seen as an extension of the powder method¹ for piezoelectric materials, and some of the absorption lines may be a result of the piezoelectric vibration of individual crystals. But the absorption seems to be not completely explained by this mechanism.²

Single crystals of potassium bromide, thallium-activated sodium iodide, zinblend, calcites, rock salt, and Rochelle salt were examined, and the absorption appeared in only rock salt and Rochelle salt. Most of the rock salt crystals yielded a spectrum similar to that of zinc sulfide. The crystals showing no absorption became active by an irradiation of x rays.

A block of quartz with dimensions $1.305 \times 1.285 \times 4.260$ cm³, a block of Rochelle salt with dimensions $0.965 \times 0.525 \times 1.980$ cm³, and a plate of Rochelle salt with dimensions $2.015 \times 1.975 \times 0.490$ cm³ showed very strong and sharp absorption lines which accompanied "wiggles." These lines disappeared when the crystal was broken into pieces. In the case of Rochelle salt they were

strongly observed outside of the ferroelectric range of temperature. These sharp lines, which were measured with the autodyne detectors, formed a spectrum composed of several series of equidistant lines with almost equal intensity. The wiggles of the lines disappeared when the crystal was immersed in oil. Furthermore, it was found in the quartz crystal that a drop of oil adhering to a special point on the surface could extinguish a series of the absorption lines. That the absorption occurred in a small region of the crystal was revealed also by the following experiment: when the crystal was cut into two parts, one of them showed exactly the same absorption as before and the other showed nothing.

Although the absorption occurs in piezoelectric crystals and may accompany mechanical vibrations, it does not seem to be caused by the higher modes of the ordinary piezoelectric vibration, in view of the intensity distribution of the lines in a wide-frequency range and of the sharpness of the lines. The absorption is characterized by the fact that it depends on crystal imperfection and occurs in a very narrow region of the crystals. In order to study the origin of the absorption, further experiments are now in progress. Irrespective of the mechanism, this absorption must be considered as an aspect of the field of radio-frequency or microwave spectroscopy of solids.

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¹E. Geibe and A. Scheibe, *Z. Physik* **33**, 760 (1925); also see W. G. Cady *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

²Four groups of quartz powders with dimensions of about 5 mm, 1 mm, 0.5 mm, and 0.1 mm were tested. At several Mc/sec, resonances of individual crystals were observed corresponding to the grain sizes. But all groups showed almost the same absorption in the neighborhood of 300 Mc/sec.

Liquid Helium Films

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THE Polanyi potential theory¹ is now believed to provide a satisfactory approach to the problem of multilayer adsorption.^{2,3} As a first approximation, therefore, the helium film can be considered as a distribution of a continuous fluid in a potential field obtained by combining the earth's gravitational field with the field arising from the van der Waals forces between the helium and the vertical wall on which the film is formed. It follows that the hydrostatic pressure inside the film at a distance z from the wall and at a height y above the surface of the bulk liquid is⁴

$$p = p_0 + \rho(\alpha/z^3 - gy), \quad (1)$$

where p_0 is the vapor pressure, α depends upon the strength of the van der Waals forces, and ρ is the density of the liquid, which is assumed constant in a first approximation. At the surface of the film, $p = p_0$, and the variation of thickness d with height H is

$$H = \alpha/gd^3, \quad (2)$$

which is the result already obtained by Schiff⁵ and Frenkel.⁶

Equation (1) gives a qualitative explanation of several properties of the unsaturated film.⁷ The pressure p increases as the wall is approached and is equal to the solidification pressure at a distance of about 7×10^{-8} cm from the wall; this explains why the first one or two layers are solid. The entropy of liquid helium I decreases with increasing pressure, whereas the opposite is true of liquid helium II, so it is easy to see why the differential entropy of the film less the entropy of the bulk liquid should be negative above the λ point but positive below the λ point. Between 1.75°K and the λ point there is a point in the film at which the pressure crosses the λ curve, and the film must then be visualized as a solid inner portion, an intermediate portion of helium I and an outer portion of helium II. This conception may lead towards an understanding of the specific heat of the film and the flow of unsaturated films.

Arguments somewhat similar to these have already been