

III. SOLID STATE PHYSICS

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A. SOFT X-RAY SPECTROSCOPY

The object of this research is to study experimentally the structure of the conduction band of electrons in a series of metals, particularly the alkalis, alkaline earths, and some of the transition metals. The filled portion of such a band can be studied by observing the emission spectrum produced by transitions from this band to the nearest sharp levels below the band. For most metals this corresponds to an energy in the range of 15-250 ev (wavelengths in the range of 50-900 A) so that the technique is that of extreme ultraviolet vacuum spectroscopy. The energy width of these bands usually lies in the range of 2-10 ev.

The metal to be studied is evaporated, in very pure form, onto a clean copper target which serves as the anode of the X-ray tube. The energy range of the bombarding electrons varies from approximately 200 ev to 600 ev, depending on the metal studied. In order to minimize such extraneous effects as satellite emission and the like, it is desirable to use the lowest voltage possible consistent with a measurable intensity. Radiation from the target passes through a narrow slit onto a precision concave ruled grating of one meter focal length and 30,000 lines per inch. The detector is a fourteen-stage beryllium-copper photomultiplier. The output of the multiplier is fed directly to a pre-amplifier and thence to a counting-rate circuit the output of which is observed directly on a 0-1 ma Esterline-Angus recorder. The over-all sensitivity of the apparatus is such that with a tube current of 2 ma a complete emission curve can be plotted in about five minutes. Thus it is possible to observe the contamination rate of a freshly evaporated surface. With a vacuum of 10^{-6} mm Hg in the X-ray tube such contamination is apparent in a matter of minutes.

Studies of emission spectra provide information on the filled portion of the bands. It is ultimately planned to combine these data with measurements on absorption which yield the structure of the unfilled portion. Emission spectra of most of the "easy" metals have now been measured (see the Quarterly Progress Reports from April 15, 1951 to July 15, 1953). It would be desirable to do a few more pure metals, as well as some alloys. Although we are interested in the band structure of semiconductors, the experimental difficulties attending the measurements on such substances are much greater than for pure metals, and so far we have no measurements on semiconductors.

G. G. Harvey

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B. MICROWAVE STUDY OF SEMICONDUCTORS

As mentioned in earlier reports, measurements of the dielectric coefficient of germanium in the 10-cm region have been made by a waveguide transmission method (see E. G. Montgomery: *Techniques of Microwave Measurements*, McGraw-Hill, New York, 1947, chap. 10). These measurements have been completed and yield a value of 15.1 for $K = K_e + \sigma_i/\omega\epsilon_0$ and 18.1 ohms-cm for the resistivity. This value of the resistivity is in agreement with dc values. To obtain the inherent dielectric coefficient of the medium, K_e , we must correct the measured quantity for the $(\sigma_i/\omega\epsilon_0)$ term. (See Quarterly Progress Report, April 15, 1953, p. 12.) If we do this, using the value of 0.6 for m^*/m for electrons obtained by Benedict and Shockley (*Phys. Rev.* 89, 1152, 1953), we obtain $K_e = 16.0$. The experimental error is believed to be less than 0.6. The reproducibility of the results was good; the probable error, from a statistical analysis of the data, was 0.3.

The results of these measurements of the dielectric coefficient of germanium are in agreement with those of other workers whose measurements were made in the infrared and in the X-band and K-band regions of the microwave spectrum. They are in disagreement, however, with earlier results obtained here by the resonant cavity method (see Quarterly Progress Report, April 15, 1953, p. 12). We conclude that the results obtained by the resonant cavity method are in error. Better equipment and techniques are now available for resonant cavity studies and another experiment is being set up to repeat the experiment.

An experiment for measuring the "conductivity" effective mass of electrons in germanium will shortly be under way. Measurements of the dielectric coefficient will be made as a function of electron density. One sample will be used throughout; the electron density will be varied by heat treatment. The dielectric coefficient that is measured is $K_e + \sigma_i/\omega\epsilon_0$, where K_e is the lattice contribution. The term $(\sigma_i/\omega\epsilon_0)$ is given by

$$A \frac{ne^2}{m^*(\nu_c^2 + \omega^2)}$$

where ν_c is the collision frequency of the electrons with the phonons, and A is a known function of (ν_c/ω) , which is fairly close to unity. If the measured quantity, $K_e + (\sigma_i/\omega\epsilon_0)$, is plotted against the electron density n, the slope of the curve will yield m^* . The experiment will be performed at several temperatures, with an attempt to measure the temperature coefficient of the effective mass. If ν_c and ω are of the same order of magnitude, the term $(\sigma_i/\omega\epsilon_0)$ should be frequency-dependent. We shall attempt to demonstrate this fact.

J. M. Goldey

C. ENERGY LEVELS OF IMPURITIES IN SILICON CARBIDE

The energy levels of impurity atoms in silicon carbide will be determined by measuring the change in the dielectric constant and the conductivity at microwave frequencies as a function of temperature. Bound electrons in the higher excited states are expected to have an increased polarizability by a factor of n^6 , where n is the principal quantum number. (See J. H. Van Vleck: Electric and Magnetic Susceptibilities, Oxford, 1932, p. 205.)

An approximate treatment of impurities of the p or n type in a semiconductor considers the impurities to be analogous to a localized charge, either positive or negative, with an associated electron or hole immersed in a dielectric medium. The solution of this hypothetical case is just the solution of the hydrogen atom, with the energy levels reduced by a factor $(1/k^2)$, the radii increased by a factor k , and the polarizability increased by a factor k^4 , where k is the dielectric constant of the medium. (See Van Vleck, as given above.)

For a real semiconductor the perturbative potential is expected to approach asymptotically a coulomb potential at large distances from the impurity atom. The approximate treatment should therefore be better for the higher excited states. Since the wave functions for the higher excited states extend a considerable distance from the impurity atom, and a smaller proportion of the wave function is in the neighborhood of the impurity atom, the details of the potential near the impurity atom will have a smaller effect on the higher energy levels.

If the impurities in the semiconductor have a sufficient density, the wave functions that are associated with the impurities will overlap. Under this condition the energy levels will broaden into impurity conduction bands that are below the main conduction band. Figure III-1 shows a typical energy level for material of the n type.

For such a semiconductor it is expected that the dielectric constant can be expressed as

$$k = k_0 + N_D f \left(\frac{\epsilon_1 - \epsilon_F}{kT} \right) a_1 + N_D f \left(\frac{\epsilon_2 - \epsilon_F}{kT} \right) a_2 - N_D f \left(\frac{\epsilon_3 - \epsilon_F}{kT} \right) \frac{e^2}{\epsilon_0 m^* (\nu_c^2 + \omega^2)} - N_D f \left(\frac{\epsilon_c - \epsilon_F}{kT} \right) \frac{e^2}{\epsilon_0 m^* (\nu_c^2 + \omega^2)}$$

where k_0 is the dielectric constant for the bulk material, N_D is the number of donor impurities, a is the polarizability for the various bound energy levels, $f(x)$ is the Fermi factor $1/(e^x + 1)$, and ν_c and m^* are the collision frequency and effective mass of electrons associated with a particular conduction band.

The conductivity at the frequency ω is given by

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$$\sigma = N_D f \left(\frac{\epsilon_3 - \epsilon_F}{kT} \right) \frac{e^2 \nu_c}{m^* (\nu_c^2 + \omega^2)} + N_D f \left(\frac{\epsilon_c - \epsilon_F}{kT} \right) \frac{e^2 \nu_c}{(\nu_c^2 + \omega^2) m^*}$$

In germanium and silicon, the excited levels would be practically indistinguishable from the bottom of the conduction band because of the high dielectric constant, 16 and 10, respectively. Since silicon carbide has a dielectric constant of 7, the excited levels should be well separated from the main conduction band. (See J. T. Kendall: Electronic Conduction in SiC, J. Chem. Phys. 21, 821, 1953.)

Measurements of the dielectric constant and the conductivity will be made by measuring the change in the resonant frequency of a re-entrant cavity when the silicon carbide crystal is inserted into the cavity. The conductivity of the crystal can be determined from the change in the Q of the cavity.

It is expected that the dielectric constant and the conductivity can be written as

$$\begin{aligned} k &= k_o + N_D a_1 + N_D \exp \left(- \frac{\epsilon_2 - \epsilon_F}{kT} \right) a_2 \\ &\quad - N_D \exp \left(- \frac{\epsilon_3 - \epsilon_F}{kT} \right) \frac{e^2}{\epsilon_o m^* \nu_c^2} - N_D \exp \left(- \frac{\epsilon_c - \epsilon_F}{kT} \right) \frac{e^2}{\epsilon_o m^* \nu_c^2} \\ \sigma &= N_D \exp \left(- \frac{\epsilon_3 - \epsilon_F}{kT} \right) \frac{e^2}{m^* \nu_c} + N_D \exp \left(- \frac{\epsilon_c - \epsilon_F}{kT} \right) \frac{e^2}{m^* \nu_c} \end{aligned}$$

if the most important terms are considered. From graphs of log of the frequency shift vs (1/T), and log of the change in Q vs (1/T), the energy levels of the bound states and of the conduction bands can be determined.

Single crystals of silicon carbide which are suitable for the microwave measurements are in the process of being cut to the proper dimensions.

J. B. Thomas

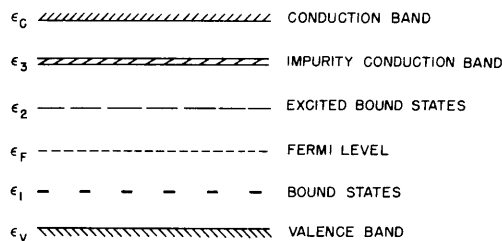


Fig. III-1

Energy-level diagram for material
of n type.