

### III. SOLID STATE PHYSICS

Prof. J. C. Slater	C. F. Davis, Jr.	W. H. Kleiner
Prof. G. G. Harvey	E. M. Gyorgy	M. Tinkham
Prof. A. F. Kip	R. H. Kingston	R. Weinstein
Prof. L. Tisza		H. C. White

#### A. THEORY OF SUPERCONDUCTIVITY

The application of symmetry considerations to the theory of superconductivity has been considered further. The problem consists of extending the methods recently advanced (1) so as to include the interaction of the electrons with the lattice vibrations. (See Quarterly Progress Report, April 15, 1951.)

It now appears that the difficulties which have been blocking progress are not of a formal mathematical, but rather of a conceptual nature. In other words, symmetry considerations may be expected to provide essential qualitative information on the nature of superconductivity, since both the quantum mechanical presentation of electronic currents and the parameters describing transitions of the second kind are closely connected with the translational symmetry of the crystal in question (2). The simple structure of the group of translations is responsible for the mathematical simplicity. The difficulty arises from the traditional way of describing the electronic wave functions of solids as the solutions of the wave equation with a potential energy of fixed periodicity. Not only does this approach lack any quantum mechanical justification, but it actually eliminates the type of wave functions which seem to be required for the description of superconductivity.

Our procedure is to approach the problem from the point of view of the so-called adiabatic approximation adapted to the case of crystals, and to simplify the procedure by means of the concepts of macro- and micro-coordinates introduced in connection with the theory of phase transitions (2). The theory leads without ad hoc assumptions to the possibility of the establishment of a superstructure with a lattice constant which is the  $\omega$ -fold of the lattice constant of the crystal. This superstructure leads to a splitting of the Brillouin zone and  $\omega$  is determined from the condition that the subzone should be completely filled by the available electrons. Superconducting behavior obtains for  $\omega \geq 3$ , whereas  $\omega = 2$  would imply the transition into an insulating state.

This interpretation of the number  $\omega$  in terms of the band theory is equivalent to the one given in Ref. 1 in terms of atomic wave functions. It seems to tie in also with Slater's (3) discussion of antiferromagnetism.

The correlation of these theoretical possibilities with experimental facts (including the resistance minimum measurements) is suggestive, although hypothetical at the present time. We hope to substantiate the theory from more specific calculations which are at present in the planning stage and, quite particularly, from experiment. Although the

### (III. SOLID STATE PHYSICS)

superstructure mentioned above is not stationary as in the classical case of alloys, but runs through the lattice with sound velocity, it should be observable through X-ray methods. This experiment might well be crucial for the clarification of the nature of superconductivity.

#### References

1. L. Tisza: Phys. Rev. 80, 717, 1950
2. L. Tisza: Technical Report No. 127, Research Laboratory of Electronics, M.I.T. June, 1949
3. J. C. Slater: Phys. Rev. 82, 538, 1951

L. Tisza

### B. SOFT X-RAY VACUUM SPECTROGRAPH

The study of the emission bands of potassium and calcium has been completed and the results will be described in forthcoming Technical Report No. 193. Since both these metals gave sharp emission edges we are returning to a study of the transition group, i.e. the metals scandium through nickel in the periodic table. Previous to the study of potassium and calcium we had attempted, with poor results, to obtain the emission band of manganese. The work on the former metals, however, has indicated that the contamination of the surface of the metal is very rapid in calcium and, from tentative results, in chromium. It is also important to realize that manganese exhibits an anomalous behavior in comparison with its neighbors in the transition group: for example, there are more than 50 atoms in the unit cell. It seems possible, therefore, that the emission bands of the transition metals may also show sharp edges if the evaporation procedure can be perfected to produce clean surfaces. This entails redesign to provide more rapid evaporation of the metal, so that it has less time to become contaminated.

G. G. Harvey, E. M. Gyorgy, R. H. Kingston

### C. PARAMAGNETIC RESONANCE EXPERIMENTS

We have put in considerable effort on our apparatus to increase its sensitivity in order to allow measurement of microwave resonance in certain low-intensity absorption materials including crystals containing F-centers and dilute solutions of paramagnetic ions. A brief summary will be given of the modifications and their effectiveness, and of some preliminary results of new measurements.

#### 1. Apparatus

Earlier Progress Reports explain our technique for making measurements involving a 60-cps magnetic field sweep. This method allows the direct plotting on a

### (III. SOLID STATE PHYSICS)

cathode ray oscilloscope of absorption vs. magnetic field. A signal depending on the instantaneous value of the external applied field is put on the horizontal plates of the cathode ray oscilloscope and a signal dependent on the instantaneous paramagnetic absorption of microwave power by the sample is placed on the vertical plates. This latter signal is obtained from amplitude-modulated microwave power reflected from the resonant cavity containing the sample, as picked up by a crystal detector placed in a magic tee. The resultant audio-frequency signal is amplified on a narrow-band amplifier, detected and fed to the cathode ray oscilloscope.

In order to improve signal-to-noise ratio, a variable sweep frequency, reducible to as low as 1/7 cps, was applied to the magnetic field. In effect this low sweep allows the averaging out over a much longer time of the random fluctuations due to noise. In order to take advantage of this slower sweep we have adopted the amplifier-filter circuit developed by M. W. P. Strandberg and his group in this Laboratory for use in microwave spectroscopy. This circuit involves demodulation of the signal, filtering through a low-pass filter and remodulation before final presentation on the cathode ray oscilloscope. The circuit now in use represents a considerable improvement over our earlier circuit, particularly in the case where the absorption curve is complicated by fine structure. However, for threshold signals at the limit of observability it proves to be of less value than expected, and probably no better than the earlier system. This is understandable on the following basis: a prominent part of the noise spectrum involves changes in amplitude of the signal which are slow compared to the 60-cps sweep but more rapid than the slow sweep. Using the earlier system, this noise causes a jitter of the position of the beam on the cathode ray oscilloscope which, however, does not prevent the observation of a very small absorption peak on the cathode ray oscilloscope. With the new method involving slow sweep such noise may appear similar to an absorption peak and can be distinguished from true absorption only because it is not reproduced on each sweep. The eye has tremendous power of smoothing out the noise on the high-frequency sweep, but little ability to do the same on the low-frequency sweep. The new method is much better than the old for making photographic records, since one cannot take advantage of the eye's ability to smooth out the noise, regardless of the circuit used.

There is some evidence that a major fraction of the noise originates in the resonant cavity and sample. If this is true, an increase in the microwave power available will greatly increase the sensitivity. Future tests with higher power are planned.

#### 2. Resonance in F-Center Crystals

Since the presence of electrons trapped in crystal imperfections in alkali halides has been observed by static susceptibility measurements, it was to be expected that paramagnetic resonance methods should show absorption at values of frequency and magnetic field corresponding closely to those for free electrons ( $g = 2$ ).

### (III. SOLID STATE PHYSICS)

The first such observations were made by Hutchison (Clyde A. Hutchison, Jr.: Phys. Rev. 75, 1769, 1949) on crystals of LiF and KCl which had been bombarded by neutrons in order to produce a very high density of structural defects. The  $g$  value was found to be 2.00 and the width at half power was 160 gauss. A perhaps unexpected result was that the absorption was not symmetrical about the peak. On the high-field side a sloping plateau about 500 gauss wide and about one-quarter the height of the peak was found.

We undertook to make measurements on crystals presumably having a much smaller density of imperfections. We first tested a single crystal of KBr prepared and loaned to us by J. G. Jelatis and E. Kloholm of the Laboratory for Insulation Research. This sample had of the order of  $10^{19}$  centers per cubic centimeter.

The sample was about 0.5 cc and our sensitivity was such that we were able only to detect the peak and not to study its shape. We later bombarded another sample of KBr with high-energy electrons and gamma rays (about 18 Mev) on the microwave linear accelerator for a total of about 4 hours. Very rough optical absorption measurements indicated a density of about  $10^{20}$  centers per cubic centimeter. In this case the shape of the resonance curve was clearly measurable. It had a half-power width of 210 gauss at room temperature and 150 gauss at 77°K and showed no asymmetry. The  $g$  value was found to be 2.00 within the experimental error of  $\pm 0.04$ .

We are tempted to conclude from our results that the plateau observed by Hutchison in his measurements was a consequence of the extreme treatment given his samples and the high density of centers. More detailed study of F-center crystals will probably have to wait for a still further increase in sensitivity of measurement.

#### 3. Measurements in Aqueous Solutions

We have begun a series of measurements on aqueous solutions of paramagnetic ions. Most of the work so far has been on  $Mn^{++}$  ions. Figure III-1 shows a cathode ray

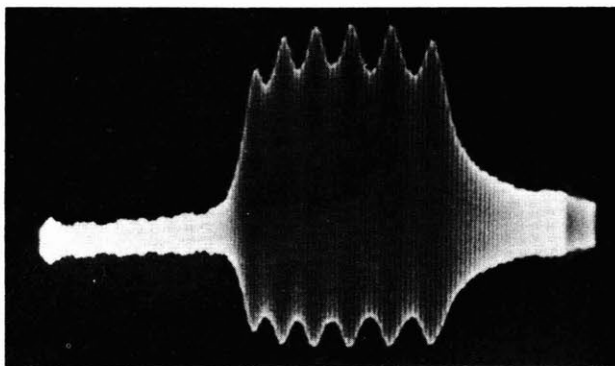


Fig. III-1

Cathode ray oscilloscope trace of  $MnSO_4$  solution showing hyperfine structure.

### (III. SOLID STATE PHYSICS)

oscilloscope tracing of a solution of  $\text{MnSO}_4$  in water, containing about  $10^{19}$   $\text{Mn}^{++}$  ions per cubic centimeter. In this presentation only the top half of the pattern is to be considered, since the bottom half is the result of the remodulation technique. The interesting effect here is the presence of hyperfine lines, due to the effect of the several magnetic levels of the nuclear magnetic moment on the levels of the orbital electrons. A further important result is that the exact shape of the lines depends on the anion present. Similar solutions of  $\text{MnCl}_2$  of the same concentration show higher resolution of the hyperfine lines. A fairly extensive program of investigations of these phenomena is in progress.

A. F. Kip, W. Kleiner, C. F. Davis, M. Tinkham, R. Weinstein, H. C. White