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OBSERVATION OF SOLID-STATE PHOTOEMISSION FROM TIN INTO GERMANIUM

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The process of photoemission of electrons from one solid into another in contact with it has been postulated by several workers. Mott and Gurney¹ suggested the existence of an internal photoelectric effect to explain certain data for sodium metal in contact with rock salt crystals. Gilleo² investigated the existence of this effect in more recent work with silver on alkali halide crystals. Most recently, Williams and Bube³ proposed that photoemission from copper and other metals plated on cadmium sulfide crystals takes place. All the above experiments required relatively energetic radiation (greater than 1 ev) to produce effects.

Recently we observed an extended spectral response for photovoltaic and photoconductive effects in tin-plated germanium. The test specimen was a slice of "n"-type 30-ohm-cm germanium 20 mils thick, on opposite faces of which were electroplated tin contacts. The contacts were $\frac{1}{4}$ inch \times $\frac{1}{4}$ inch square and were displaced with respect to one another by $\frac{1}{8}$ inch. In the test setup, radiation from a monochromator was made to pass through the germanium and impinge on the tin metal. The photovoltaic or photoconductive signal across the contacts was measured. The radiation was chopped at 450 cps, and the signal was amplified by a narrow-band ac amplifier. Room-temperature measurements on this and many similar specimens failed to show any extended spectral response. However, at liquid-nitrogen and liquid-helium temperatures, an extended spectral response several hundred times smaller than the peak intrinsic responses was detected.

To ensure that intrinsic excitation processes and short-wavelength scattered light did not produce the observed signals, germanium filters of various thicknesses were interposed in the exit beam of the monochromator. Typical results are

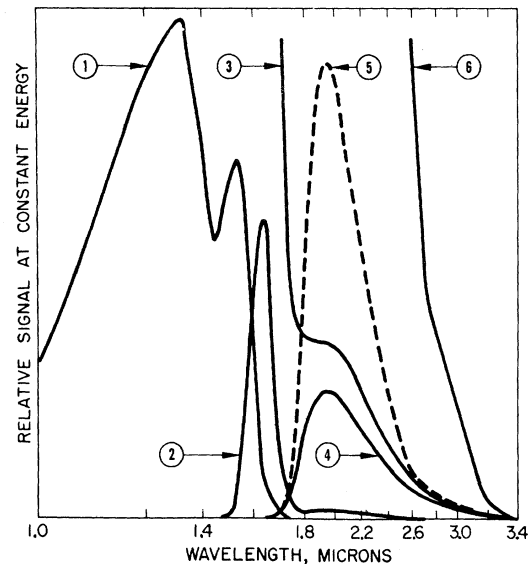


FIG. 1. Photovoltaic signals at constant energy for electroplated tin-on-germanium cell No. 1. Curve 1: the "intrinsic" photovoltaic response with no filtering of the monochromator radiation. Curve 2: radiation is filtered by a 10-mil-thick germanium filter; amplifier gain is ten times that used for curve 1. Curve 3: 10-mil-thick germanium filter is used again, but amplifier gain is ten times that used for curve 2. Curve 4: same gain as that for curve 3, but a 100-mil-thick germanium filter is used. Curves 1 through 4 were taken at liquid-nitrogen temperature. Curve 5: same gain as that for curves 3 and 4, 100-mil-thick filter, but liquid-helium cooled. Curve 6: same conditions as those for curve 5, but amplifier gain increased ten times. The extended spectral response lies at wavelengths greater than 1.8 microns approximately.

illustrated in Fig. 1, which shows that the use of filters differing in thickness by a factor of ten caused no significant decrease in long-wavelength

response. Two thick filters were used, and the signal response decreased only by a factor attributable to the transmission losses (primarily by reflection) of the filters. Use of these filters demonstrates that intrinsic processes cannot be responsible for the long-wavelength signal. In any case, many measurements of intrinsic absorption coefficients⁴ showed no values even approaching those required to produce a measurable signal at the wavelengths involved. Short-wavelength radiation was almost completely eliminated as a source of excitation, and in any case, its intensity would be strongly dependent of filter thickness.

The only other sources of excitation of which the writer can conceive are free-carrier absorption and impurity excitation. The former does not seem capable of producing signals. Furthermore, the absorption coefficient for this process is low, especially at low temperatures where few free carriers are available. Similarly, impurity photoconduction is most improbable. One observes from Fig. 1, curves 3 and 4, that on the short-wavelength side the extended spectral response dropped off rapidly when the thick filter is used (curve 4), but remained approximately constant at 1.8 microns (curve 3) when the thin filter was used. The ratio of the filter transmissions will change rapidly for absorption coefficients in the range 1 to 10 (cm^{-1}); therefore, such values for absorption coefficients are necessary to account for the extended spectral response in terms of an impurity photoconduction process. Neither shallow impurities (which are mostly ionized at liquid-nitrogen temperature) nor deep-lying impurities are present in the near-intrinsic germanium in a concentration sufficient to give an absorption coefficient of one per centimeter. The electroplated tin-on-germanium received no heat treatment so that significant alloying or diffusion could not have occurred. The signal strength depends on the intensity of the light incident on the tin, although these measurements are a little difficult to interpret exactly because of the high reflectivity and refractivity of the germanium which causes much scattering of light within the samples. Finally, the character of the spectral response curves at long wavelengths strongly suggests the photoemission process; one expects a rapid drop in response with an increase in wavelength as a result of the finite mean free paths of excited photoelectrons within the tin cathode, just as for the external photoelectric effect.

Measurements on several tin-plated germanium

samples showed that the current-voltage characteristics were variable, although extended spectral responses were obtained in most cases. This variability is not surprising considering that tin is not a specific "dope" for germanium and therefore the exact barriers at contacts may depend on the presence of minute amounts of impurity. Since the current-voltage characteristics were variable, it has been difficult to determine conclusively the effects of applied electric fields on the spectral response. Also, noise resulting from the application of voltage to the cells has frequently interfered with measurements, and the effects of light scattering within samples sometimes obscured results. The

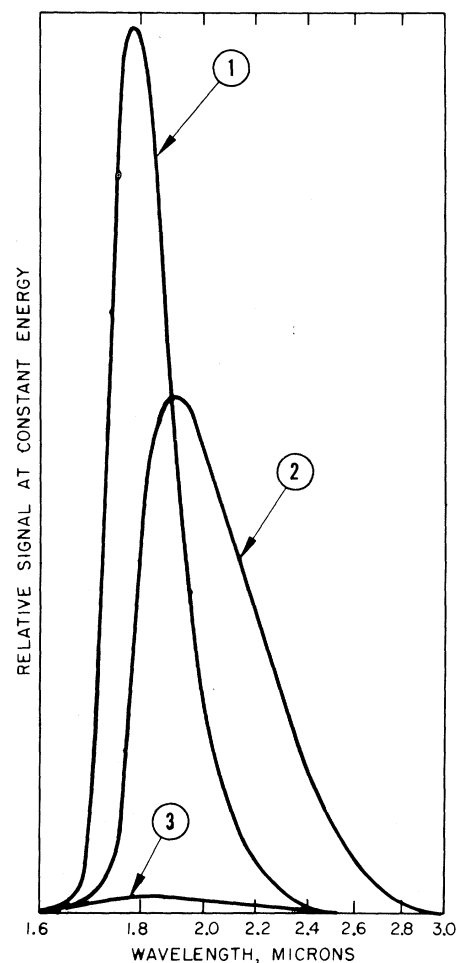


FIG. 2. Photovoltaic and photoconductive signals for electroplated tin-on-germanium cell No. 3 at liquid-nitrogen temperature. Curve 1: photovoltaic signal; amplifier gain is ten times that for curves 2 and 3. Curve 2: photoconductive signal for negative voltage applied to "cathode." Curve 3: photoconductive signal for a positive voltage on the cathode. For all curves, a 100-mil-thick filter was used.

evidence in general, however, supports the expectation that fields which push the electrons away from the metal cathode into the germanium produce larger signals and some extension of the spectral response. Figure 2 shows some particularly good data illustrating these field effects.

With the present electroplated tin-on-germanium specimens, the spectral responses extend to about 3.4 microns. The quantum yields are typically a few tenths of a percent, and significant improvement in these yields may be anticipated. In principle, potential barriers between solids may be very small, and thus photoemission at much longer wavelengths may be ultimately achieved.

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NUCLEAR MAGNETIC RESONANCE OF Cr⁵³ IN ANTIFERROMAGNETIC CrCl₃†

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The metamagnetic properties of the anhydrous iron group chlorides have been the subject of many investigations in the past. Recently, several of these hexagonal layer type compounds were shown to become antiferromagnetic at low temperatures.¹ The magnetic ordering consists of ferromagnetically aligned moments within each hexagonal layer. The antiferromagnetic coupling between adjacent layers is relatively weak and as a consequence steep net magnetization curves are obtained even for small external magnetic fields.² This effect suggests that an enhancement mechanism similar to that found in ferromagnets³ might make it feasible to measure the temperature dependence of the sublattice magnetization in some of these compounds by nuclear magnetic resonance (NMR) techniques.

In this Letter we wish to report the observation of the Cr⁵³ NMR in CrCl₃ in the temperature range of 1.23°K–4.02°K and zero external field. Results of precision measurements of the frequency for resonance are in excellent agreement with the predictions of simple spin-wave theory for a two-dimensional ferromagnetic system in the presence of anisotropy.

CrCl₃ has a hexagonal unit cell, of space group *D*₃⁵, containing 6 molecules.⁴ It exhibits a λ -type specific heat anomaly at 16.8°K⁵ and a magnetic susceptibility maximum around 20°K. Neutron diffraction studies⁶ give an ordered structure in which the axes of magnetization are directed per-

pendicular to the *c* axis. Polycrystalline samples for the present study were prepared by vacuum sublimation of the dehydrated salt at 700°C. The nuclear resonance spectra are sensitive to the crystallographic purity of the samples. Resonances in addition to those reported here were observed in samples which exhibited a large number of stacking faults and other imperfections.

The resonance was observed with a frequency-swept FM marginal oscillator.⁷ As in the case of ferromagnetic CrBr₃,⁸ the spectrum consists of a well-resolved triplet due to a nuclear electric quadrupole interaction. From the separation of the satellites, $I = \frac{3}{2}$, and the assumption that the electric field gradient at the Cr positions has cylindrical symmetry about the *c* axis, we obtain $h^{-1}e^2q_{zz}Q = 0.882 \pm 0.010$ Mc/sec. The central component of the spectrum is shifted by the second order effect to slightly higher frequency (~6 kc/sec) relative to the satellites. This shift agrees in magnitude and direction with the previous assumptions.

A comparison of the intensities of the Cr⁵³ resonances in CrBr₃ and CrCl₃ showed that the enhancement factor in these two compounds is of the same order of magnitude. However, since the quadrupole splitting in CrCl₃ is insensitive to the orientation of the magnetization in the hexagonal plane it is not yet certain whether the resonance is excited by domain rotation or domain wall displacement. The observed linewidths are