Letters to the Editor

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Field Dependent Fluorescence of Vitreous Zn_2SiO_4 Phosphor

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(Received July 31, 1952)

AT the March, 1952, Massachusetts Institute of Technology Conference on Physical Electronics we reported on the behavior of field dependent fluorescence of zinc silicate phosphor. Fluorescence could be obtained only when the electric field had an ac component. The fluorescence observed in our samples was interpreted as being due to field emission, either cold emission or Zener tunneling at regions of high field intensity. The need for the presence of an ac component was ascribed to the existence of space charge associated with traps in the semiconducting vitreous phosphor. These assumptions also explained the anomalous behavior of the radiation as the temperature of the semiconductor was increased above 200°C.

Additional experimental results have now been obtained. The samples consist of a thin strip of glass, 0.01 cm wide and about 2 cm long placed between two conducting electrodes so that the electric field is applied across the width of the strip. The glass has a low softening point, and the Zn_2SiO_4:Mn phosphor is imbedded in it. The radiation is observed from a cross section in a plane perpendicular to the plane of the strip. Aluminum, silver, and graphite were used for the electrodes, the graphite giving the best performing sample as far as the efficiency of fluorescence is concerned. The vitreous mixture is a semiconductor with a resistance between 5 and 100 megohms/cm^2 at room temperature. However, the resistance is a function of the temperature and depends on the frequency of the applied potential.

Observation with a low power microscope shows that the radiation is emitted from the interface between the electrode and the vitreous phosphor.

The lowest potential for which radiation is observed varies between 100 v and 500 v depending on the thickness and other parameters of the sample. At a fixed potential the light output varies slightly with the frequency. For a frequency variation of the applied field from 120 cps to 16 kc/sec the light output varies by a factor less than 5. At 60 cps the light output varies roughly as the square of the potential in the range from 100 v above the low voltage cutoff to the crystal breakdown potential. The low voltage cutoff is defined arbitrarily as the potential at which radiation is first observed. Possibly a more sensitive photocell arrangement, such as a photomultiplier, would detect radiation at a potential lower than the presently observed cutoff.

These observations further substantiate the hypothesis that field emission is responsible for the phenomena. The transport of charge from deep-lying energy levels across the interface barriers excites the phosphor component of the glass matrix near the potential barrier at the interface. The value of this electric field across the interface will depend, of course, on the dielectric constant of the glass matrix and on the rate of conduction of the charge through the semiconducting glass matrix to the opposite electrode.

It is interesting to note that Piper and Williams[1] in their recent studies on the electroluminescence of single crystals of ZnS:Cu have arrived at a similar conclusion.

[1] W. W. Piper and F. E. Williams, Phys. Rev. **87**, 151 (1952).

Paramagnetic Resonance Absorption in Additively Colored Crystals of Alkali Halides*

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(Received August 4, 1952)

SOME time ago one of us[1] observed paramagnetic resonance absorption in crystals of alkali halides colored by irradiation with neutrons. Subsequently, techniques were developed for studying simultaneously the optical and magnetic absorptions in such crystals as a function of time of irradiation or of time of thermal bleaching. No satisfactory correlation between the two types of absorption could be established, presumably due to the presence of a very great variety of color centers and paramagnetic species and the consequent complexity of both types of absorption. We have undertaken the study of additively colored crystals, in which case the situation may be made much simpler. Under optimum conditions the color centers and paramagnetic species present in such crystals may be predominantly of one type, the F-center.[2]

Tinkham and Kip[3] have also observed paramagnetic resonance absorption in crystals of KBr colored electrolytically and with x-rays.

We have observed paramagnetic resonance absorption at room temperature and at 9.0×10^9 cycles sec^{-1} in KCl which contained excess K and in KBr which contained excess K. The paramagnetism of such crystals in static fields has been studied by Jensen[4] and by Scott, Hrostowski, and Bupp.[5] The KCl with excess K was prepared by heating a single crystal in the presence of redistilled K in a glass capsule with a stainless steel liner.[6–8] The crystal was maintained at 965°K for about 4 hr and then cooled very rapidly in air to room temperature. Subsequent chemical analysis showed that it contained 4.4×10^{-6} mole of excess K per g of crystal (5.3×10^{18} atoms of K per cm^3). A piece of this crystal weighing 1.28 g was placed with a cubic axis parallel to the static magnetic field at the midpoint of a rectangular box cavity operated in the TE_{102} mode at a frequency of approximately 9.0×10^9 cycles sec^{-1}. The reflection from the cavity was measured using a magic tee bridge. The magnetic field was modulated at 40 cycles sec^{-1} and phase sensitive detection was employed. The static field strength was measured by means of the proton resonance.

The variation with field strength of energy absorbed by the sample, as determined by numerical integration of the output of the phase sensitive detector, was a Gaussian within the error of the measurement. The area under this absorption curve was found to be only about one tenth that under the curve for an amount of $CuCl_2\cdot2H_2O$ equal in number of moles to the excess K in the colored crystal. This may be indicative of colloidal aggregation of a large fraction of the K. The full width between points of maximum slope was found to be 49.3 ± 0.8 gauss as a result of five measurements. However, the Van Vleck theory of dipole-dipole broadening applied to a face-centered cubic crystal assuming Gaussian line shape, random location of single electrons at Cl^- sites, and a concentration of electrons equal to the excess K concentration gives a full width between points of maximum slope of only 23 gauss. (If the electron concentration is as much lower than this as is indicated by the intensity measurements, the width would be only 7.3 gauss.) This difference is probably in agreement with the fact that at the concentrations concerned relatively very large amounts of higher aggregates of F-centers are present.[7]

The spectroscopic splitting factor was found to be 1.995 ± 0.001. This is considerably lower than the value, 2.0023, of the g-factor for a free electron.

Further studies of this resonance as a function of temperature and of concentration of excess K are in progress. We are also planning an investigation of the effect on the resonance of illumination of the crystal in the F-band to produce the F'-centers which would be expected to be diamagnetic. The method of paramagnetic resonance absorption offers advantages over the measurement of static susceptibilities for the study of magnetic color centers in

crystals. The paramagnetic resonance phenomenon is peculiar to the unpaired spins, and the magnetic centers result in the primary effect observed, not in a small change in the effect of the large amount of diamagnetic material present.[5,9] Paramagnetic resonance absorption will probably permit counting color centers in regions of concentration inaccessible to the optical methods.

We thank Clarence Arnow for the development and construction of part of the electronic equipment and Edward A. Bartal for construction of some of the apparatus employed in these experiments.

* This work was supported by the ONR.
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Disintegration of Cr^{51}†

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(Received August 4, 1952)

SPECTROMETER studies made by previous investigators have established that Cr^{51} decays entirely by orbital electron capture partially accompanied by gamma-radiation. Kern *et al.*[1] list the γ-ray energies as 0.32 Mev and 0.267 Mev. Bradt *et al.*[2] find the gamma-energies to be 0.320 and 0.237 Mev, and in addition suggest that the decay proceeds 97 percent directly to the ground state, 3 percent through the 0.32-Mev excited state, and ~1 percent through the 0.237-Mev level. By use of Cr^{51} supplied by the Operations Division of the Oak Ridge National Laboratory, the branching ratio of this nuclide has been investigated with the aid of coincidence counting, x-ray counting, and NaI crystal spectrometry.

Very little β^- or e^- was found associated with the decay, in agreement with the data of Bradt.[2] By use of a helium filled tube as a negatron detector 3.0×10^{-4} e^-/x-ray disintegration was found. The x-rays observed, therefore, are essentially all from orbital capture, and no interference from a conversion process is encountered. A measured aliquot of Cr^{51} was coincidence counted using a krypton-methane filled, thin end window, β-proportional counter as an x-ray detector and an anthracene crystal counter as a γ-detector. X-ray γ-coincidence data were taken as a function of Be absorber placed before the x-ray counter. The disintegration rate of the source so measured was calculated and found to be constant and independent of Be absorber.

A source of Mn^{54}, the disintegration rate of which was known through coincidence counting and ion chamber measurements, was used to determine the efficiency of a Kr-methane counter for Cr K x-rays. (2.29A). A measured aliquot of Cr^{51} (V x-rays, 2.50A) was then counted on this counter, and using the previously determined efficiency, the disintegration rate of the Cr^{51} was obtained. Agreement between this value and that obtained by coincidence counting was within 3 percent. A source of Cr^{51} of known disintegration rate was then placed on a previously calibrated NaI crystal scintillation spectrometer and the gamma-spectrum of this nuclide was obtained. The presence of only one gamma-ray of energy 0.32 Mev was observed. The area beneath this gamma-peak was obtained and multiplied by an appropriate efficiency factor. This total corrected area in disintegrations per minute was then compared to the known decay rate of the sample and the branching ratio obtained. Eight percent of the Cr^{51} disintegrations were found to proceed through the 0.32-Mev excited state. Sunyar[3] has recently stated that the lower energy γ-ray reported by workers can be ascribed to impurities. A preliminary figure ~10 percent branching has been given by him. Decay of a Cr^{51} source has been followed for five half-lives on both a GM counter and an ion chamber. A value for the half-life of 27.75±0.3 days is indicated.

Acknowledgment is made to A. R. Brosi and B. H. Ketelle for advice and assistance in this work and to E. I. Wyatt who aided in the decay measurements.

† Based on work performed for the AEC.
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Similarity Properties of the Two-Fluid Model of Superconductivity

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(Received July 23, 1952)

RECENT measurements[1–3] on superconducting tin isotopes have shown that the threshold curves for the different isotopes are all of the form, $H_c=H_0(T/T_c)$, where H_0 is the critical field at absolute zero of temperature and T_c is the zero-field transition temperature. These form a family of geometrically similar curves, that is, a uniform expansion or contraction of scale transforms one into another. As a consequence of this fact, it can be shown[3] that the corresponding electronic entropies of the superconducting state, $S_{s(el)}(T)$, are also geometrically similar functions of the form

$$S_{s(el)}=\gamma T f(T/T_c), \tag{1}$$

where γ is a parameter and $f(T/T_c)$ a function, both of which are invariant with respect to the isotopic mass. The function is represented within experimental error by either a polynomial in T/T_c or by a single term of the type $(T/T_c)^n$, where n is a positive but not necessarily integral number. This result is significant because it is consistent with features of the two-fluid model of a superconductor not previously subjected to experimental test.

In the two-fluid model proposed by Gorter and Casimir,[4] the electron assembly is visualized as consisting of two phases, a "gaseous" phase of normal electrons having the properties of a Sommerfeld electron gas and a "crystallized" phase of superconducting electrons in a lower energy state. It is assumed that the normal fraction alone contributes entropy and that the superconducting fraction has zero entropy. The fractional concentration of normal electrons x varies continuously from zero to unity as the temperature goes from zero to T_c. The free energies and entropies of the two electron "phases" are given by

$$F_g=\tfrac{1}{2}\gamma T^2x^\alpha; \quad F_c=-\beta(1-x); \tag{2}$$

$$S_g=\gamma T x^\alpha; \quad S_c=0. \tag{3}$$

The subscripts g and c refer to the "gaseous" and "crystalline" phases, respectively, and $\beta=(H_0^2/8\pi)V_m$, the molar free energy difference between the normal and superconducting states at the absolute zero, (V_m is the molar volume) and γ has the usual significance as the coefficient of T in the electronic entropy of a Sommerfeld electron gas. α is a parameter, characteristic of the metal but not given by the theory. (Empirically it is found that $\alpha\sim\frac{1}{2}$.) The condition that the total free energy of the electron assembly be a minimum determines the temperature dependence of x as

$$x=(H_0^2V_m/4\pi)^{1/(\alpha-1)}T^{-2/(\alpha-1)}. \tag{4}$$

This two-fluid model was originally proposed to explain some of the thermodynamic properties which had been observed in real superconductors. These are the facts: that the free energy difference between the normal and superconducting states vanishes at T_c, and that the electronic entropy of the superconducting state varies as (approximately) the third power of temperature and contains no term linear in the temperature. In addition to these, however, it may be shown that the model also implies the simi-