

may be observable in polar semiconductors. Unfortunately  $\Delta E_t$  has been computed<sup>1</sup> only at  $T=0^\circ$ , so that the form of the dependence of the effective gap width on temperature is not known.

The situation seems somewhat more hopeful in the case of optical excitation. The frequency of maximum absorption will be  $\hbar\omega = E_G - 2\Delta E_0$ . It will be noted that the effective energy shift  $\Delta E_0$  here differs from  $\Delta E_t$ , for the energy shift  $\Delta E_t$  includes a contribution from the alteration of the form of the phonon; but, by the Franck-Condon principle, this contribution is absent in an optical process. Thus  $\Delta E_0$  must be computed by finding the change in energy of an electron in the field of a phonon, assuming the phonon states to be unaffected by the presence of the electron. Using the methods employed in the treatment of electrical breakdown in polar crystals,<sup>2</sup> we have computed<sup>3</sup>  $\Delta E_0$  as a function of temperature ( $\omega_t$  is reststrahl frequency,  $\epsilon_0$  and  $\epsilon_s$  are optical and static dielectric constants):

$$(\Delta E_0)^3 = \frac{m e^4 \omega_t^2 (\epsilon_s)}{2 \epsilon_0} \left( \frac{1}{\epsilon_0} - \frac{1}{\epsilon_s} \right)^2 \left( \exp \frac{\hbar \omega_t \epsilon_s}{k T \epsilon_0} + 1 \right)^2 \left( \exp \frac{\hbar \omega_t \epsilon_s}{k T \epsilon_0} - 1 \right)^{-2}$$

It may be hoped that the polaron effect can thus be observed as a dependence of the frequency of maximum absorption  $\omega$  on  $T$ , and it is, in fact, observed that  $\omega$  decreases with increasing  $T$  in polar crystals, but is virtually constant in non-polar crystals. Unfortunately there is a second effect which, in polar crystals, decreases the gap width with increasing temperature. This effect, which has been treated theoretically by Radkowsky,<sup>4</sup> arises from the fact that an electronic state subject to a collision frequency  $\nu_c$  has a half-width  $\frac{1}{2}\hbar\nu_c$ , resulting in a decrease in gap width of approximately  $\hbar\nu_c$ . Recomputing Radkowsky's results in accordance with the methods of reference 2 one obtains

$$2\Delta E = \hbar\nu_c = \frac{2^{\frac{1}{2}} m^{\frac{1}{2}} e^2 \omega_t^{\frac{1}{2}} \epsilon_s^{\frac{1}{2}}}{\hbar^{\frac{1}{2}} \epsilon_0^{\frac{1}{2}}} \left( \frac{1}{\epsilon_0} - \frac{1}{\epsilon_s} \right) \left( \exp \frac{\hbar \omega_t \epsilon_s}{k T \epsilon_0} - 1 \right)^{-1}$$

These results may be compared with some experimental observations<sup>4</sup> which very likely represent the rate of shift of  $\omega$  with  $T$ :

$(d\hbar\omega/dT)$ in $10^{-4} \text{ eV}/^\circ\text{K}$	KI (296°)	KI (766°)	RbBr (360°)	RbBr (766°)
Observed	11.9	9.4	7.4	7.4
Polaron effect	4.4	3.3	5.0	4.0
Radkowsky effect	7.9	8.2	11.2	11.5

It would thus appear that the shift of optical absorption frequency with temperature allows, in principle, an observation of the polaron effect, but that experimental observations and theoretical treatments must be improved before truly quantitative conclusions can be drawn.

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<sup>1</sup> Fröhlich, Pelzer and Zienau, *Phil. Mag.* **41**, 221 (1950).

<sup>2</sup> H. Callen, *Phys. Rev.* **76**, 1394 (1949).

<sup>3</sup> We had computed  $\Delta E_0$ ,  $\Delta E_t$  and the effective mass prior to the appearance of reference 1, using conventional perturbation theory and the methods of reference 2. Our results for  $\Delta E_t$  and effective mass agree with those of F.P.Z. except insofar as the results of those authors are improved by a novel variation of the perturbation technique. We have therefore recast the calculation of  $\Delta E_0$  so as to take advantage of this improvement in the perturbation method.

<sup>4</sup> A. Radkowsky, *Phys. Rev.* **73**, 749 (1948).

with greater accuracy than is generally needed in the optical spectroscopy of the free atoms or ions. In fact the h.f.s. of the paramagnetic salts of divalent copper and manganese, calculated by assuming for  $\text{Cu}^{++}$  and  $\text{Mn}^{++}$  respectively the electronic configurations  $3d^9 \ ^2D$  and  $3d^5 \ ^6S$ , suggested by the optical properties of these ions, disagree considerably with experiment.

The interaction between the electrons and the nuclear magnetic moment can be written  $H = \mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S}$  where  $\mathbf{I}$  is the nuclear spin ( $\frac{3}{2}$  for Cu,  $5/2$  for Mn),  $\mathbf{S}$  the total electronic spin ( $\frac{1}{2}$  for  $\text{Cu}^{++}$ ,  $5/2$  for  $\text{Mn}^{++}$ ) and  $T$  is a tensor representing a generalized anisotropic h.f.s. interval. The principal values of the tensor  $T$  are (in  $10^{-3} \text{ cm}^{-1}$ ):

#### Copper Tutton salts

Exper.<sup>1</sup>  $|T_{11}| \simeq |T_{22}|$ ;  $2 < |T_{11}| < 6$  according to the salt;  $|T_{33}| \simeq 13$

Theoret.<sup>2</sup>  $T_{11} \simeq T_{22} \simeq 13$ ;  $T_{33} \simeq -6$

#### Copper fluosilicate

Exper.<sup>3</sup>  $|T_{11}| \simeq |T_{22}| = 2.1$ ;  $|T_{33}| = 2.8$

Theoret.<sup>4</sup>  $T_{11} = T_{22} = T_{33} = 7$

#### Manganese Tutton salts and fluosilicate

Exper.<sup>5</sup>  $|T_{11}| \simeq |T_{22}| \simeq |T_{33}| \simeq 9$

Theoret.  $T_{11} = T_{22} = T_{33} = 0$ .

These discrepancies can be explained by assuming that the electronic wave functions contain small admixtures of excited states with unpaired  $s$ -electrons, which are also respectively  $^2D$  and  $^6S$  states.

For  $\text{Mn}^{++}$  no state  $^6S$  with unpaired  $4s$ -electron can be constructed by exciting one or two  $3d$ -electrons. For  $\text{Cu}^{++}$  the first excited state  $3d^8 4s \ ^2D$  gives for  $T$  a positive isotropic correction  $\Delta T$  which further increases the discrepancy.

As a working hypothesis we suggest the promotion of a  $3s$ -electron to a  $4s$ -orbital giving the excited configurations  $3s 3p^6 3d^9 4s \ ^2D$  and  $3s 3p^6 3d^5 4s \ ^6S$ . Energetically these configurations are far above the ground state and their admixture in this state is small, but this is compensated by the fact that  $3s$ -electron has a very wide h.f.s. For  $\text{Mn}^{++}$  the  $3s$ -electron gives an isotropic h.f.s. of the right order of magnitude. For  $\text{Cu}^{++}$  it is possible to make the correction  $\Delta T$  negative. If we take  $\Delta T = -9$  we find the new theoretical values:

#### Copper Tutton salts

$T_{11}' \simeq T_{22}' \simeq 13 - 9 = 4$ ;  $T_{33}' = -6 - 9 = -15$

#### Copper fluosilicate

$T_{11}' \simeq T_{22}' \simeq T_{33}' = 7 - 9 = -2$

which agree reasonably with experiment.

Details of these calculations will be reported elsewhere.

<sup>1</sup> D. J. E. Ingram, *Proc. Phys. Soc. London* **A62**, 664 (1949).

<sup>2</sup> A. Abragam and M. H. L. Pryce, *Nature* **163**, 993 (1949).

<sup>3</sup> B. Bleaney and D. J. E. Ingram, *Proc. Phys. Soc. London* **A63**, 408 (1950).

<sup>4</sup> A. Abragam and M. H. L. Pryce, *Proc. Phys. Soc. London* **A63**, 409 (1950).

<sup>5</sup> B. Bleaney (to be published).

## Paramagnetic Resonance and Hyperfine Structure in the Iron Transition Group

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IN the paramagnetic ions of the iron group, the orbital angular momentum is generally quenched by the crystalline field, which makes the h.f.s. much narrower than in the free ion and thereby considerably increases the perturbing influence on this h.f.s. of excited states, with unpaired  $s$ -electrons and wide h.f.s.

This fact, and the great precision of paramagnetic resonance methods, make it necessary to know the electronic wave function

## Properties of $\text{Tl}^{209}$

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PREVIOUS investigations at this laboratory<sup>1</sup> of the decay products of  $\text{U}^{233}$  showed that  $\text{Bi}^{213}$  undergoes branching disintegrations, 98 percent decaying by beta-emission and two percent by alpha-emission. Canadian workers<sup>2</sup> who carried out parallel but independent studies also detected such alpha-branching. The product of alpha-disintegration of  $\text{Bi}^{213}$  would be  $\text{Tl}^{209}$  (neptunium  $C'$ ) which, by analogy with the  $C''$  products of the natural radioactive series, should be a beta-emitter with a half-life of only a few minutes. The amount of thallium activity formed by

decay of the milligram amounts of  $U^{233}$  used in the earlier investigations was too low to permit detection. However, gram quantities of  $U^{233}$  have since become available and with this larger amount of source material it has been possible to observe directly the  $Tl^{209}$  beta-particles.

The thallium was isolated by ether extraction from a solution of  $Ac^{225}$  obtained from a stock of  $U^{233}$  which had decayed for one year. The  $Ac^{225}$  was separated from the uranium by co-precipitation with lanthanum fluoride and was thoroughly purified by a procedure involving extraction of the  $Ac^{225}$  with a benzene solution of thenoyltrifluoroacetone to separate from radium and thorium isotopes,<sup>3</sup> followed by addition of lead carrier and precipitation of lead sulfide to remove any extraneous lead, bismuth, or polonium activities.

Because of the short half-life of the thallium a method of rapid separation was necessary. The following procedure proved satisfactory. Ten milligrams of inactive thallium carrier and a small amount of bromine were added to 2 ml of 6*N* HCl containing the  $Ac^{225}$ . The solution was heated to oxidize the thallium to the extractable +3 state and the excess bromine boiled out. The solution was cooled, 2 ml of ether added and the mixture stirred for 30 sec. The ether phase was transferred to another vessel and stirred for several seconds with an equal volume of ether-saturated 6*N* HCl. After separation of the phases, the acid layer was drained through a stopcock and the washing repeated two or three times with fresh portions of acid. After the final wash the ether was transferred to a platinum dish and ignited. When the ether was consumed the platinum dish was rapidly cooled and placed immediately in the counter. The total time elapsed from start of the separation to start of counting was three to five minutes.

Decay of the thallium activity, which amounted to several thousand counts per minute initially, was followed at half-minute intervals. A small amount of long-lived activity, 20 to 30 counts/min. above the natural background, which remained after decay of the thallium was probably due to incomplete chemical separation. A typical decay curve is shown in Fig. 1. The half-life as determined by least-squares analysis of seven such decay curves was 2.20 min., with a probable error of  $\pm 0.07$  min.

An aluminum absorption curve of the  $Tl^{209}$  beta-particles (Fig. 2) was obtained by isolating a series of samples and following the

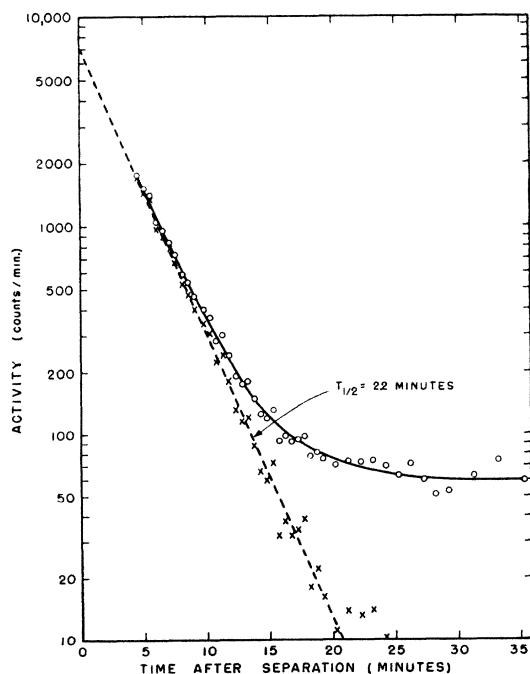


FIG. 1. Decay of  $Tl^{209}$ .

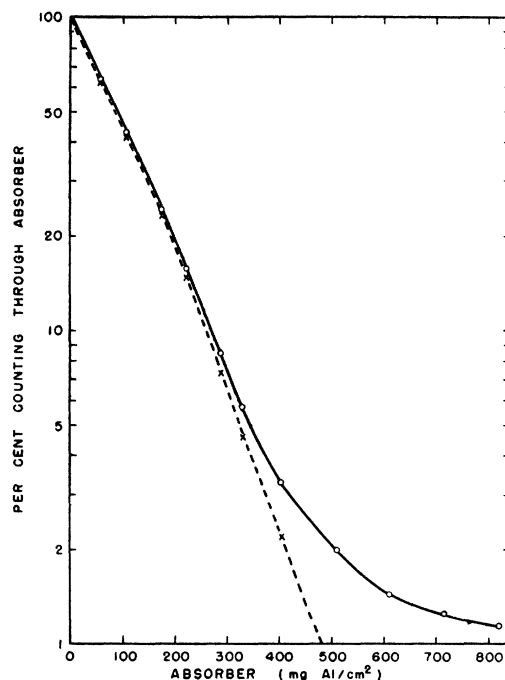


FIG. 2. Absorption of  $Tl^{209}$  beta-particles in aluminum. Feather range,  $\sim 825$  mg Al/cm<sup>2</sup> corresponding to  $E_{max} = 1.8$ . Half-thickness  $\sim 80$  mg Al/cm<sup>2</sup>.

decay of each alternately with and without a given absorber. Each sample thus yielded one point on the absorption curve which was the ratio of the extrapolated counting rate at zero time with absorber to that without absorber. A Feather analysis<sup>4</sup> of the absorption curve, after subtraction of the hard component, gave a value of about 825 mg of aluminum for the range, corresponding to a maximum energy of 1.8 Mev. The half-thickness was about 80 mg Al/cm<sup>2</sup>.

<sup>1</sup> Hagemann, Katzin, Studier, Seaborg, and Ghiorso, *Phys. Rev.* **72**, 252 (1947); *Phys. Rev.* **79**, 435 (1950), this issue.

<sup>2</sup> English, Cranshaw, Demers, Harvey, Hincks, Jelley, and May, *Phys. Rev.* **72**, 253 (1947).

<sup>3</sup> F. Hagemann, *J. Am. Chem. Soc.* **72**, 768 (1950).

<sup>4</sup> N. Feather, *Proc. Camb. Phil. Soc.* **34**, 599 (1938); L. E. Glendenin, *Nucleonics* **2**, 12 (1948).

## Resistivity of Semiconductors Containing Both Acceptors and Donors\*

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THE resistivity of impurity semiconductors has previously been explained<sup>1</sup> by the addition of  $\rho_L$ , resistivity caused by scattering by lattice ions, and  $\rho_I$ , resistivity due to scattering by impurity ions. Since the mean free path associated with lattice scattering<sup>2</sup> is inversely proportional to temperature,

$$\rho = AT^{3/2}/n, \quad (1)$$

where  $A$  is a constant characteristic of the material and  $n$  is the density of conduction electrons or holes. By assuming that carriers are subject to Rutherford scattering by impurity ions, it has been shown<sup>3</sup> that

$$\rho_I = 9 \times 10^{11} \pi^{3/2} e^2 m^{1/2} 2^{-7/2} \kappa^{-2} (kT)^{-3/2} (N_S/n) \times \ln \{1 + 36 \kappa^2 d^2 (kT)^2 e^{-4}\}, \quad (2)$$

where  $\kappa$  = dielectric constant,  $e$  and  $m$  electron charge and mass, and  $d$  one-half the average distance between the  $N_S$  scattering ions per unit volume.