may be observable in polar semiconductors. Unfortunately ΔE_t has been computed[1] only at $T=0°$, 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 ΔE_0 here differs from ΔE_t, for the energy shift ΔE_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 ΔE_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,[2] we have computed[3] ΔE_0 as a function of temperature (ω_t is restrahl frequency, ϵ_0 and ϵ_s are optical and static dielectric constants):

$$(\Delta E_0)^3 = \frac{me^4\omega_t^2}{2}\left(\frac{\epsilon_s}{\epsilon_0}\right)\left(\frac{1}{\epsilon_0}-\frac{1}{\epsilon_s}\right)^2\left(\exp\frac{\hbar\omega_t\epsilon_s^{\frac{1}{2}}}{kT\epsilon_0^{\frac{1}{2}}}+1\right)^2\left(\exp\frac{\hbar\omega_t\epsilon_s^{\frac{1}{2}}}{kT\epsilon_0^{\frac{1}{2}}}-1\right)^{-2}.$$

It may be hoped that the polaron effect can thus be observed as a dependence of the frequency of maximum absorption ω on T, and it is, in fact, observed that ω 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,[4] arises from the fact that an electronic state subject to a collision frequency ν_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

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

These results may be compared with some experimental observations[4] which very likely represent the rate of shift of ω with T:

$(d\hbar\omega/dT)$ in 10^{-4} ev/°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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[1] Fröhlich, Pelzer and Zienau, Phil. Mag. 41, 221 (1950).
[2] H. Callen, Phys. Rev. 76, 1394 (1949).
[3] We had computed ΔE_0, ΔE_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 ΔE_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 ΔE_0 so as to take advantage of this improvement in the perturbation method.
[4] A. Radkowsky, Phys. Rev. 73, 749 (1948).

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

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 Cu^{++} and 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 $H = I \cdot T \cdot S$ where I is the nuclear spin ($\frac{3}{2}$ for Cu, 5/2 for Mn), S the total electronic spin ($\frac{1}{2}$ for Cu^{++}, 5/2 for 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} cm^{-1}):

Copper Tutton salts

Exper.[1] $|T_{11}| \simeq |T_{22}|$; $2 < |T_{11}| < 6$ according to the salt; $|T_{33}| \simeq 13$
Theoret.[2] $T_{11} \simeq T_{22} \simeq 13$; $T_{33} \simeq -6$

Copper fluosilicate

Exper.[3] $|T_{11}| \simeq |T_{22}| = 2.1$; $|T_{33}| = 2.8$
Theoret.[4] $T_{11} = T_{22} = T_{33} = 7$

Manganese Tutton salts and fluosilicate

Exper.[5] $|T_{11}| \simeq |T_{22}| \simeq |T_{33}| \simeq 9$
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 Mn^{++} no state ^6S with unpaired $4s$-electron can be constructed by exciting one or two $3d$-electrons. For Cu^{++} the first excited state $3d^84s\,^2D$ gives for T a positive isotropic correction ΔT 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 $3s3p^63d^94s\,^2D$ and $3s3p^63d^54s\,^6S$. 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 Mn^{++} the $3s$-electron gives an isotropic h.f.s. of the right order of magnitude. For Cu^{++} it is possible to make the correction ΔT 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.

[1] D. J. E. Ingram, Proc. Phys. Soc. London A62, 664 (1949).
[2] A. Abragam and M. H. L. Pryce, Nature 163, 993 (1949).
[3] B. Bleaney and D. J. E. Ingram, Proc. Phys. Soc. London A63, 408 (1950).
[4] A. Abragam and M. H. L. Pryce, Proc. Phys. Soc. London A63, 409 (1950).
[5] B. Bleaney (to be published).

Properties of Tl^{209}

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PREVIOUS investigations at this laboratory[1] of the decay products of U^{233} showed that Bi^{213} undergoes branching disintegrations, 98 percent decaying by beta-emission and two percent by alpha-emission. Canadian workers[2] who carried out parallel but independent studies also detected such alpha-branching. The product of alpha-disintegration of Bi^{213} would be 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