explain even the origin of the Van Allen radiation. This means that the particles are accelerated by variations in the earth's magnetic field. At the same time they diffuse away from the region of injection which defines the location of the maximum intensity.

The existence of two belts of radiation indicates that particles are injected in two different regions. It is natural to assume that the inner belt derives from the injection of particles from the ionosphere, possibly with some connection with the equatorial electro-jet.

The theory predicts that at a distance x from that line of force which passes through the point of injection, the spectrum should be

$$N = \frac{\text{const}}{p^{2-\varphi}} \exp\left(-\frac{x^2}{\kappa p^{1-\varphi}}\right), \tag{1}$$

where κ is a constant.

Applying this to the Van Allen radiation, we should expect a spectrum as shown by the dashed curve in Fig. 1 with a cutoff at a momentum which depends on the distance from the point of injection. A reasonable measure of this distance would be the distance in the equatorial plane from that shell of magnetic field lines, at which the injection takes place. This prediction could be checked by future observations. For a more refined comparison the homogeneous field which is used in the model of the theory should be replaced by the earth's dipole field.

---

[1] H. Alfvén, Tellus 6, 232 (1954); 11, 106 (1959); Max Planck Festschrift 1958, p. 83.

[2] S. C. Freden and R. S. White, Phys. Rev. Letters 3, 9 (1959).

OPTICAL PUMPING IN CRYSTALS

H. H. Theissing, P. J. Caplan, F. A. Dieter, and N. Rabbiner
U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey

(Received October 21, 1959)

An estimate was made of the expected population change in the ground state of a crystal due to optical pumping. Kastler's original pumping scheme[1] assumed that the ground state and an optically excited state are characterized by J values and have fairly pure m_J sublevels. Also, one needs a crystal with relatively long relaxation time T_1, as is the case for an S ground state.

Thus, Series and Taylor[2] have suggested optical pumping of Eu^{++} in $\mathrm{CaF_2}$ or $\mathrm{SrCl_2}$ and the observation of possible changes of magnetic-resonance absorption. The free Eu^{++} ion has intense lines in the 2300-2500 A region[3] ascribed to electric dipole transitions between the $4f^6 5d$ configuration and the $4f^7$ ground state $^8S_{7/2}$, presumably corresponding to the 3200 A and 2480 A bands in aqueous $\mathrm{EuCl_2}$ solution observed by Butement[4] and the 3380 A band observed in a $\mathrm{CaF_2{:}Eu^{++}}$ crystal by Series and Taylor. Although correlation between the observed absorption spectrum and specific excited states is conjectural, we shall consider, as an example, optical pumping of the transition $J = 7/2$ to $J = 7/2$ between the ground state and the $^8P_{7/2}$ excited state.[5] One knows the transition probabilities KBI (B = coefficient of absorption and $K = 7/84,\ 12/84, \ldots$[6]) between a ground-state sublevel m_1 and an excited sublevel $m_2 = m_1 + 1$ due to irradiation with circularly polarized light of intensity I. Likewise known is the relative distribution of spontaneous emission from m_2 to $m_1 = m_2 - 1, m_2, m_2 + 1$. If one assumes a common relaxation time T_1 between all ground-state sublevels, and one writes the rate of change of sublevel populations due to both pumping and relaxation, one obtains in the steady state for the ground-state populations[7]:

$$N_m - N_{m-1} = (N_m - N_{m-1})_0 + pBIT_1 N, \tag{1}$$

where $(N_m - N_{m-1})_0$ is the Boltzmann equilibrium population difference, N is the paramagnetic-ion concentration, and p is a pumping coefficient listed in Table I. Similar orders of magnitude may be expected for transitions to the other optical states ($J = 5/2, 9/2$).

Series and Taylor estimate the oscillator strength of the 3380 A band in the $\mathrm{CaF_2{:}Eu^{++}}$ crystal comparable to Butement's values[4]

Table I. Pumping factors p between levels m_I and $m_I - 1$, for Eu^{++}.

m_I	$m_I - 1$	p
7/2	5/2	1/860
5/2	3/2	1/570
3/2	1/2	1/1150
-5/2	-7/2	1/3400

$f = 6\times10^{-3}$ (at 3200 A) and $f = 3\times10^{-2}$ (at 2480 A) for $EuCl_2$ in solution. This estimate places $B = 4\pi^2e^2f/mch\nu$ between 3×10^8 and 1.5×10^9 cm^2/erg sec. For a 500-watt 11 000-lumen xenon lamp, the radiation in all directions near 3300 A is $10^{-6}\,d\nu$ erg/sec. Thus, if an efficient optical system can concentrate 1/100 of that energy on a 1-cm^2 crystal surface and half the intensity is lost by polarization, $I = 0.5\times10^{-8}$ erg/cm^2 is available. No appropriate europium samples were yet available in this laboratory for relaxation measurements; hence on the basis of measurements of Gd^{+++} at Bell Laboratories,[8] we take $T_1 \approx 10^{-3}$ sec. By taking the intermediate value for B, 9×10^8 cm^2/erg sec, we have

$$(N_{5/2} - N_{3/2})/N - (N_{5/2} - N_{3/2})_0/N = 7.9\times10^{-6}.$$

This is only 1/1600 of $(N_{5/2} - N_{3/2})_0/N \approx h\nu/8kT = 0.013$ at X band and 4.2°K.

For iron-group crystals, where the coupling between L and S is broken, the p factor can no longer be obtained from reference 6. However, the detailed work of Sugano and co-workers[9,10] on the red ruby lines R_1 and R_2 permits such a computation. The p factors of Table II are for magnetic field parallel to crystalline axis.[11] In all polarizations the necessarily simultaneous pumping of both lines is detrimental. The factor B to be used in Eq. (1) now depends on the polarization, e.g., $B_\sigma/B_\pi = 10$ for the R_1 line.[11]

From spectrographic absorption measurements it was found that $B_\sigma \approx 6\times10^3$ cm^2/erg sec for the R_2 line. Assuming that B_σ for R_1 is 5/3 as large,[11] we find that the strongest effect using both lines is obtained by pumping with σ^+ and σ^- radiation (i.e., natural light along crystalline axis), and observing the $3/2 \leftrightarrow 1/2$ paramagnetic absorption. The total effective p, referred to B_σ of R_2, is $(5/3)(-29+23)/440 + (23-5)/216 = 2/33$. With $I = 2\times10^{-8}$ erg/cm^2 available from the same xenon lamp (unpolarized light in red region) and $T_1 = 0.025$ sec,[12] $(N_{3/2} - N_{1/2})/N - (N_{3/2} - N_{1/2})_0/N \approx 1.8\times10^{-7}$. This is less than 1/100 000 of $(N_{3/2} - N_{1/2})_0/N \approx h\nu/4kT = 0.027$ for X band and 4°K, a hardly detectable change, mainly due to the very small B value. In experiments with π pumping of the red ruby lines, Wieder[13] detected no change in the microwave absorption. The light source, which used the fluorescence from the red lines themselves, provided an output of about 0.1 watt, thus giving approximately the same intensity over the linewidth as the above-mentioned xenon lamp.

From Gibson's[14] measurements of the green absorption band in ruby we find the value $B = 3\times10^7$ cm^2/erg sec. Unfortunately, the sublevel transition probabilities have not been worked out, so the p factors cannot be computed. Assuming them to be of the same order of magnitude as those in Table II, one could change the paramagnetic population differences by one or two parts in a hundred for X band and 4.2°K, which would be detectable.

In the case of F centers in a KCl crystal, the ground and excited states are mixtures of s and p states with other states and information for computing p factors is not available. But even taking pessimistic p values, one can verify that this is a better prospect than the previously discussed substances. With $B = 7\times10^{10}$ cm^2/erg sec (since $f = 0.81$[15]), $I = 10^{-8}$ erg/cm^2, $T_1 = 15$ sec at 4.2°K,[16] and $p = 1.13\times10^{-5}$, inversion is reached; if $p = 10^{-4}$, the original population difference $Nh\nu/2kT = 0.053N$ has become $-0.46N$.[7] Thus the positive result of Lambe and Baker[13] for X-

Table II. Pumping factors p for ground-state transitions between m_S and $m_S - 1$, for red ruby lines R_1 and R_2.

		p for R_1			p for R_2		
m_S	$m_S - 1$	σ^+	σ^-	π	σ^+	σ^-	π
3/2	1/2	-29/440	23/440	3/44	23/216	-5/216	-1/12
1/2	-1/2	25/440	-25/440	0	-25/216	25/216	0
-1/2	-3/2	23/440	29/440	-3/44	5/216	-23/216	1/12

irradiated KCl can very plausibly be attributed to optical pumping. Although they used unpolarized light, a net pumping effect can result because, as in Table II, the p factors for σ^+ and σ^- need not cancel.

---

[1] A. Kastler, J. phys. radium 11, 255 (1950).

[2] G. W. Series and M. J. Taylor, J. phys. radium 19, 901 (1958).

[3] Russell, Albertson, and Davis, Phys. Rev. 60, 653 (1941), Table XI.

[4] F. D. S. Butement, Trans. Faraday Soc. 44, 622 (1948), Fig. 11 and Table V.

[5] See reference 4, p. 624.

[6] See, e.g., A. E. Ruark and H. C. Urey, Atoms, Molecules, and Quanta (McGraw-Hill Book Company, Inc., New York, 1930), p. 708, Eqs. (20)-(22).

[7] Equation (1), derived for small population changes, holds good even up to inversion of a two-level system, where the error is $h\nu/kT \approx 10\,\%$. For the extreme pumping in the last paragraph a more extended calculation was required.

[8] G. Feher and H. E. D. Scovil, Phys. Rev. 105, 760 (1957).

[9] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan 13, 880 (1958).

[10] S. Sugano and I. Tsujikawa, J. Phys. Soc. Japan 13, 899 (1958).

[11] See reference 9, Sec. 5b, especially Table I, where the experimentally found relation $\sigma \approx 2\pi$ applies.

[12] C. Kikuchi et al., Project Michigan Report No. 2144-377-T, March, 1959 (unpublished), p. 8.

[13] Paper presented at the Quantum Electronics-Resonance Phenomena Conference, September 14-16, 1959 (unpublished).

[14] K. S. Gibson, Phys. Rev. 8, 38 (1916).

[15] F. Seitz, Revs. Modern Phys. 26, 49 (1954).

[16] G. A. Noble, Bull. Am. Phys. Soc. 4, 326 (1959).

PURE NUCLEAR QUADRUPOLE RESONANCES IN PARAMAGNETIC IRON-GROUP HALIDES

R. G. Barnes and S. L. Segel
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa*

(Received October 16, 1959)

Although the number of compounds in which pure nuclear quadrupole resonances have been detected now runs into the hundreds, no resonance appears ever to have been reported in a paramagnetic substance. The observation, by Shulman and Jaccarino,[1] of the nuclear magnetic resonance of F^{19} in MnF_2 and some related paramagnetic compounds demonstrated that the nuclear resonance line width was not necessarily so broad as to preclude its detection. In fact, although the dipolar field of the Mn^{2+} ions in MnF_2 is very large and the hyperfine field due to the covalent bonding is even larger, both effects are swamped by the effective exchange field responsible for the antiferromagnetic ordering at 68°K. A detailed theoretical study by Moriya[2] of the relaxation processes in the antiferromagnetic and paramagnetic states anticipated the experimental findings. The same arguments might be expected to apply equally well in the pure quadrupole case. In spite of the large dipolar fields of the magnetic ions, the quadrupole resonances ought to be sufficiently exchange-narrowed to be observable if the substance has a large exchange energy (i.e., an ordering temperature greater than a few degrees K). Indeed, Jaccarino[3] has observed the quadrupole splitting of the nuclear magnetic resonance lines of Co^{59} in antiferromagnetic CoF_2.

A considerable number of iron-group chlorides and bromides are structurally identical to or very closely similar to the BiI_3 structure.[4] In this structure, the metal ions occur in layers between layers of close-packed halogens, such "sandwiches" being stacked to form the entire crystal. The layers of metal ions are thus separated by two halogen layers. Recent neutron diffraction work by the Oak Ridge group[5] has shown that these compounds become antiferromagnetic at appreciable temperatures, the ordering being with few exceptions ferromagnetic within the metal ion layer and with alternate layers arranged antiferromagnetically. Several diamagnetic compounds also utilize the BiI_3 structure, including AsI_3, SbI_3, and BiI_3 itself. The iodine nuclear quadrupole resonances in these compounds were reported some years ago[6]; the coupling constants appear to be consistent with the view that the bonding within the halogen-metal-halogen sandwich is largely covalent. The arsenic and antimony resonances have also been detected.[7] In consequence, it seemed reasonable to search for nuclear quadrupole resonances in some of the chlorides and bromides of the iron-group ele-