our interest in the problem of studying excited states in solids by paramagnetic resonance. We are grateful to D. Linn for his extensive experimental assistance and to Professor J. Brossel, A. Javan, W. B. Mims, H. E. D. Scovil, and Professor S. Sugano for helpful discussions.

[1]Varsanyi, Wood, and Schawlow, preceding Letter [Phys. Rev. Letters 3, 544 (1959)].

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

[3]The principle of this method was also suggested independently by Professor J. Brossel.

[4]F. Bitter and J. Brossel, Phys. Rev. 86, 308 (1952).

[5]S. F. Jacobs, thesis, 1957, John Hopkins University (unpublished), earlier established the approximate $\cos\theta$ variation of the $\bar{E}(^2E)$ Zeeman pattern from the optical Zeeman spectrum. Our work confirms this with an order of magnitude greater accuracy characteristic of microwaves. We are grateful to Professor G. H. Dieke for making this work available to us.

[6]A. M. Clogston (private communication).

OPTICAL DETECTION OF PARAMAGNETIC RESONANCE IN CRYSTALS AT LOW TEMPERATURES

J. Brossel,* S. Geschwind, and A. L. Schawlow
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received November 12, 1959)

Paramagnetic resonance absorption has been extensively used to determine the structure of the ground state of paramagnetic ions in different crystal fields. As is well known, many absorption and fluorescence spectra of ions in a crystal lattice show very sharp optical lines besides the usual broad bands. The Zeeman effect of these lines has been observed in some cases, and the components are often strongly polarized.

A method of detection of magnetic resonance in the fluorescent state which utilizes the selective reabsorption of the components of the fluorescent radiation at low temperatures has been described in the preceding Letter.[1] We wish to discuss extensions of this method to other cases which may arise, as well as to indicate where the more conventional double resonance[2] techniques may be applied to the study of paramagnetic ions in crystal lattices. In addition, we want to point out that optical detection of magnetic resonances in the ground state may have some merits of its own.

The first step in doing resonance in an excited state is to obtain a population difference between the Zeeman substates. We will use the case of ruby to illustrate the different possibilities. Referring to Fig. 1 of Varsanyi, Wood, and Schawlow,[3] two cases may arise:

(A) Thermalization is fast.—This we feel will be the most common case. It is what happens in ruby, i.e., the Boltzmann distribution is reached between (a) and (b) before the atoms radiate. The fluorescent state can be reached in any convenient way and one can rely on thermal relaxation to achieve the population difference. Absorption of light in any of the broad bands is particularly convenient because it can be filtered out at detection and need not come from a preferred direction.

(B) Thermalization is slow.—In this case, a population difference between the Zeeman levels of the excited state can be achieved, just as is done in gaseous double resonance experiments, by pumping with polarized resonance light. However, in a solid at low temperatures and high enough fields, one can even use unpolarized resonance radiation, because the lowest Zeeman level of the ground state is far more populated than the others, so that absorption will populate level (a) more than level (b).

Having obtained a population difference between the Zeeman levels of the excited state, the next step is to detect the change in this population on passing through magnetic resonance by observing the fluorescent light. At low temperatures selective reabsorption may be utilized as shown in the preceding Letter.

At temperatures very much above 4°K, however, selective reabsorption will not occur. In addition, selective reabsorption will be absent from a fluorescent line whose width is greater than the total Zeeman splitting of the ground state. In these cases, it follows from the transition probabilities shown in Fig. 1 of reference 3, and as explained in the preceding Letter, that the total light output is independent of the popula-

tion difference in the upper state and so will be unaffected by microwave transitions in the excited state. However, a microwave transition can nonetheless be detected by comparing the ratio of right circular (R) to left circular (L) light emitted in fluorescence; in particular (R) light will increase at resonance. The same thing will happen for all Kramers doublets. There is the experimental difficulty of looking along the direction of the field, at high fields where the Boltzmann factor is favorable. Moreover, the crystal must be strain free so as not to depolarize the light; but the method works even when the components of the optical Zeeman pattern overlap.

In studying resonance in the excited state by the selective reabsorption method, ground state resonances will often show up also, as they did in ruby, due to the change in population of the absorbing levels arising from the microwave resonance. This may be confusing under some circumstances. A way to see only the excited state is to operate with a ruby so dilute that no reabsorption takes place, and observe its fluorescence through a selectively absorbing ruby outside the rf field, but in the same magnetic field and at the same low temperature.

At liquid helium temperatures, optical detection of magnetic resonance in the ground state can be accomplished in several ways. The change of paramagnetic to diamagnetic Faraday effect has been used previously.[4] The absorption of circularly polarized light may be used, since as is seen from Fig. 1 of reference 3, component (a) is more absorbed, i.e., circularly left light is absorbed in the ruby 6934A line, to a greater extent than other polarizations. Resonance in the ground state between level 1 and any other will increase the amount of transmitted left light. One can operate at low fields. The light source may have "broad line" characteristics, but the light must travel along the field.

The same absorption method will apply to linearly polarized (σ or π) 6934A light, traveling perpendicular to the magnetic field, or even in the absence of a field.[5] However, with the condition just defined, transitions $-\frac{1}{2}\rightarrow+\frac{1}{2}$ and $-\frac{3}{2}\rightarrow+\frac{3}{2}$ will not appear, as seen from the optical transition probabilities (although they should appear if H were not along the optic axis). They can be observed with a suitable "narrow line" light source, emitting the Zeeman components with unequal intensities. This last case requires that the Zeeman components of the line be well separated and that fairly high fields be used.

Optical detection of ground state resonances could prove useful in many cases. For example, many satellite lines have been seen in the optical spectrum of Cr^{3+} in Al_2O_3 and MgO which are attributed[6] to Cr^{3+} pairs, as well as to an added axial field component due to charge compensation in the case of MgO. Such pairs and centers have indeed been identified by standard paramagnetic resonance techniques.[7] Therefore, by doing double-resonance type experiments on these optical satellites in such a way that only ground-state transitions are observed, a correlation can be made between the particular optical satellite and the type of center with which it is associated. In addition, optical detection of ground-state resonances will be helpful in unraveling unidentified paramagnetic resonance spectra which are associated with different types of centers; for, by studying the ground-state resonances of a particular optical satellite, one selects only that part of the total paramagnetic resonance spectrum associated with only one type of center.

---

*Permanent address, Ecole Normale Supérieure, Paris, France.

[1]Geschwind, Collins, and Schawlow, preceding Letter [Phys. Rev. Letters 3, 545 (1959)].

[2]F. Bitter and J. Brossel, Phys. Rev. 86, 308 (1952); A. Kastler, J. Opt. Soc. Am. 47, 460 (1957).

[3]Varsanyi, Wood, and Schawlow, this issue [Phys. Rev. Letters 3, 544 (1959)].

[4]J. M. Daniels and H. Wesemeyer, Can. J. Phys. 36, 406 (1958).

[5]I. Wieder, Phys. Rev. Letters 3, 468 (1959).

[6]Schawlow, Wood, and Clogston, Phys. Rev. Letters 3, 271 (1959).

[7]J. E. Wertz and P. Auzins, Phys. Rev. 106, 484 (1958); J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) 73, 948 (1959); private communications from M. Peter and from J. C. Gill.