PHYSICAL REVIEW VOLUME 122, NUMBER 3 MAY 1, 1961

# Study of the Internal Fields Acting on Iron Nuclei in Iron Garnets, Using the Recoil-Free Absorption in $Fe^{57}$ of the 14.4-kev Gamma Radiation from $Fe^{57m}$†

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(Received December 22, 1960)

The shape of the recoil-free absorption spectrum obtained in iron garnet absorbers has been investigated, using, as a source, a $Co^{57}$ source embedded in stainless steel. The results confirm the existence of two iron sublattices each showing a Zeeman structure characterized by different parameters. No significant differences have been detected between the Zeeman structure in yttrium iron garnet and dysprosium iron garnet. The values obtained for the effective magnetic field at the $Fe^{57}$ nuclei at room temperature are $3.90\times10^5$ oe and $4.85\times10^5$ oe for the $d$ and $a$ iron lattice sites, respectively. At liquid air temperature the corresponding fields are $4.6\times10^5$ oe and $5.4\times10^5$ oe, respectively. The mean value of the chemical shift for the $d$ sites relative to stainless steel is about $0.04\pm0.005$ cm/sec and about $0.06\pm0.005$ cm/sec for the $a$ sites.

## INTRODUCTION

THE phenomenon of recoil-free resonance absorption (Mössbauer effect)[1] of nuclear gamma rays has already been shown to constitute a powerful tool for investigating the properties of the internal fields acting on nuclei in solids. In particular, the 14.4-kev gamma rays of $Fe^{57m}$ have been employed in a striking way to study the internal fields at iron nuclei in ferro and antiferromagnetic materials.[2–4]

In these cases the Zeeman splitting patterns obtained in the absorption spectra can be simply interpreted.[5] From a knowledge of the nuclear magnetic moment of the nuclear ground state, values for the effective magnetic fields at the iron nucleus can be obtained and also in some cases the magnitude of the quadrupole interactions.

In the magnetic materials investigated so far, the iron atoms occupy equivalent lattice positions and the local fields at the iron nuclei are characterized by a single set of parameters. In the present investigation, a study has been made of the local fields in a ferrimagnetic material in which the iron atoms occupy two nonequivalent sets of positions. It was thought that this might result in a difference in the effective magnetic fields at the iron nuclei in the two sites. The ferrimagnetic materials studied were the iron garnets (stoichiometric formula 5 $Fe_2O_3\cdot3M_2O_3$, where M indicates a rare earth ion or yttrium). The magnetic properties of these materials have been studied intensively in recent years.[6] Pauthenet has shown that in order to explain these properties it is necessary to assume that the two iron sublattices in this structure have opposite and unequal magnetizations. The garnets have a body-centered cubic structure, space group $O_h^{10}$, the unit cell containing 96 oxygen ions in the general lattice positions, with 16 $Fe^{3+}$ ions in the $a$ special positions (octahedral sites) and 24 $Fe^{3+}$ ions situated in the $d$ special positions (tetrahedral sites). These constitute the two iron sublattices. The yttrium or rare earth ions occupy the 24 $c$ dodecahedral sites. The unit cell edge is about 12 A.

Two representative garnets of the above type were studied, yttrium iron garnet and dysprosium iron garnet. The yttrium ion is diamagnetic, whereas the dysprosium ion is strongly paramagnetic. It is known that in these garnets there is an exchange field which tends to align the rare earth ions relative to the magnetization of the iron ions. Although this exchange interaction is known to be small relative to the dominant exchange interaction, which occurs between the two iron sublattices ($10^5$ oe compared to $6\times10^6$ oe),[7] it was thought of interest to see whether this could give rise to a difference in the effective field at corresponding iron nuclei for the yttrium and dysprosium garnets, respectively, at a given temperature.

Since the magnetization of the garnets is a function of temperature[6] it was also considered interesting to try to correlate the effective fields at the nucleus with temperature.

## EXPERIMENTAL

In these experiments the absorption of the 14.4-kev gamma ray of $Fe^{57m}$ bound in stainless steel was measured in polycrystalline garnet absorbers, containing iron enriched in $Fe^{57}$, as a function of the relative velocity between source and absorber. A stainless steel source containing $Co^{57}$ has already been shown to give a relatively narrow unsplit emission line.[3,4] Such a source can be used very effectively to explore the absorption spectrum of an absorber containing $Fe^{57}$. A large argon-filled proportional counter was used to detect the 14.4-kev radiation and provided a better resolution of this radiation against background than a thin

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† Supported in part by the U. S. Air Force, Air Research and Development Command through its European Office.

[1] R. L. Mössbauer, Z. Physik, **151**, 124 (1958).

[2] S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and D. H. Vincent, Phys. Rev. Letters **4**, 177 (1960).

[3] G. K. Wertheim, Phys. Rev. Letters **4**, 403 (1960).

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[5] G. DePasquali, H. Frauenfelder, S. Margulies, and R. N. Peacock, Phys. Rev. Letters **4**, 71 (1960).

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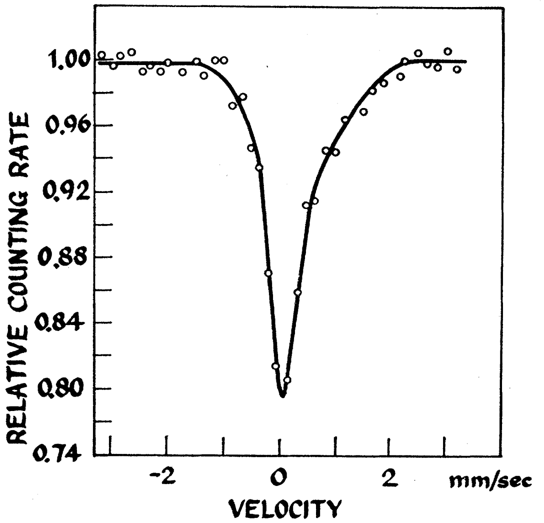

FIG. 1. The absorption by stainless steel of the 14.4-kev gamma ray emitted in the decay of $Fe^{57m}$ embedded in stainless steel, as a function of relative velocity between source and absorber.

NaI(Tl) scintillation counter. As absorbers, two types of garnets were used in this work, yttrium iron garnet and dysprosium iron garnet. These were synthesized from $Y_2O_3$ or $Dy_2O_3$ and $Fe_2O_3$, containing iron enriched in $Fe^{57}$ (70%) in order to maximize the Mössbauer absorption relative to competing processes. X-ray photographs taken by Mr. Kallman of this laboratory showed a unique crystal structure for the samples. The samples were ground fine, spread out to an average thickness of about 10 mg/cm$^2$ and held rigidly between thin Lucite disks, and in this form used as absorbers.

At first, the Doppler shift between source and absorber was provided by a mechanical device[8] consisting of a uniformly rotating eccentric wheel driving a carriage bearing the source, whose speed could be varied via a coupling. Later an instrument was developed which enabled the counting rate to be automatically recorded as a function of the relative velocity,[9] and the final results presented here were carried out in this way. The source was mounted on a loudspeaker membrane and vibrated sinusoidally at 65 cycles/sec. The amplitude of the output of the pulse-height selector, channelled on the 14.4-kev peak recorded in the proportional counter, was modulated in appropriate phase with the sinusoidal motion, so that the modulated part of the amplitude would be proportional to the source velocity at the time of emission of the corresponding photon. The spectrum of modulated pulses was displayed on the first 128 channels of a 256-channel pulse-height analyzer. As a consequence of the harmonic motion, the time the source spends in each velocity channel is itself a function of velocity. In order to obtain the true spectrum of counting rate as a function of velocity, the spectrum recorded on the analyzer was normalized in the following way. The output pulses from an independent scintillation counter and radioactive source were treated in an identical fashion as described above for the pulses from the proportional counter and displayed on the second half of the multichannel analyzer. The output of the two counters were alternately switched every half-minute into the single-channel analyzer equipped with modulated output and the two spectra stored in the two halves of the analyzer. Identical counting rates were arranged in order to insure similar counting losses in the two halves of the multichannel analyzer. The normalized spectrum was obtained by dividing the number in a given channel of the first half of the analyzer by the number in the corresponding channel in the second half. This method of normalization ensured good stability over long periods of time against drift in the electronic instrumentation. In practice, a scale of velocities was established by using as a calibration the absorption spectrum of antiferromagnetic $Fe_2O_3$ and relying on the velocity assignments to the peaks in the Zeeman pattern obtained by Kistner and Sunyar[4] and as confirmed, also, by measurements in this laboratory, using the mechanical device providing uniform relative velocity mentioned at the beginning of this section. In both the latter measurements the relative velocities were measured directly. A typical absorption spectrum of $Fe_2O_3$, using $Co^{57}$ embedded in stainless steel, is shown in Fig. 2. Figure 1 shows the results obtained using a stainless steel absorber with the same source and confirms that an unsplit emission line is indeed obtained. The width of the absorption line is about four times the natural linewidth. Assuming an emission and absorption line of the same shape in the stainless steel source and stainless steel absorber, respectively, one concludes that the width of the emission line is about twice the natural width.

Measurements were carried out for both types of garnet absorbers at room temperature and also at the temperature of liquid air. The latter experiments were carried out with the garnet absorbers immersed in liquid air contained in a Styrofoam container.

## RESULTS AND DISCUSSION

Figures 3 and 4 show the results obtained with the yttrium garnet absorber at room and liquid air temperatures, respectively. These spectra should be compared with the spectrum obtained with antiferromagnetic $Fe_2O_3$ shown in Fig. 2. The latter spectrum has already been investigated by Kistner and Sunyar[4] and analyzed in terms of a Zeeman splitting of the nuclear levels produced by a single magnetic field at the iron nucleus ($5.15\times10^5$ oe) somewhat modified by a quad-

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[8] S. Ofer, P. Avivi, R. Bauminger, A. Marinov, and S. G. Cohen, Phys. Rev. **120**, 406 (1960).

[9] The instrument used was similar to a device constructed recently by Dr. E. Sunyar of Brookhaven National Laboratory. We are indebted to him for information concerning his instrument, particularly the electronic circuits.

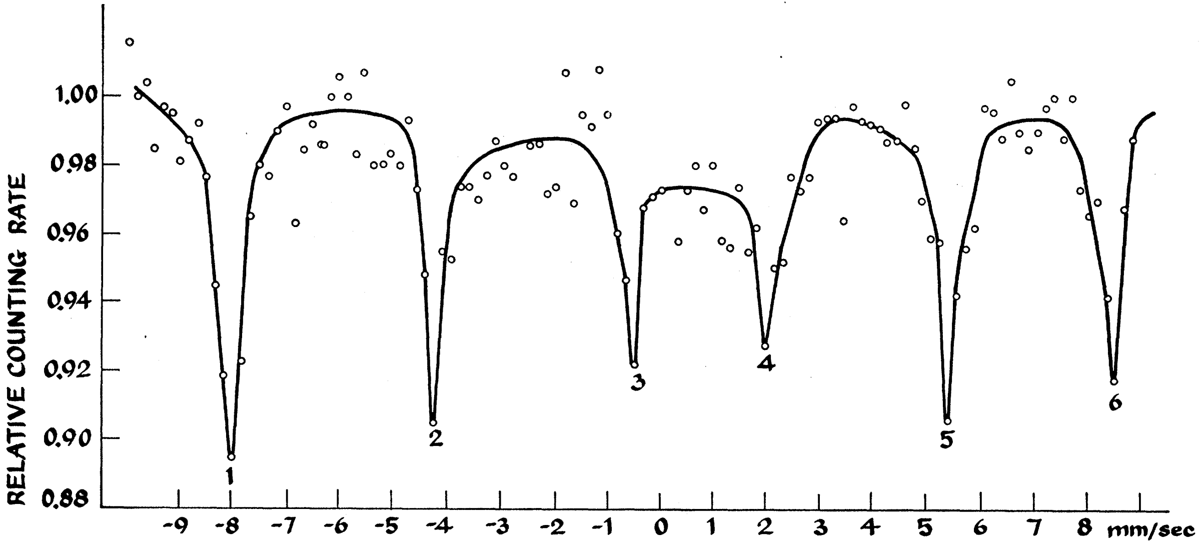

FIG. 2. The absorption at room temperature by $Fe_2O_3$ of the 14.4-kev gamma ray emitted in the decay of $Fe^{57m}$ embedded in stainless steel, as a function of relative velocity between source and absorber.

rupole interaction of the $Fe^{57}$ nucleus with a finite electric field gradient at the nucleus.

It is seen that there is an essential difference between the garnet spectra and the $Fe_2O_3$ spectrum, the garnet spectra consisting of a series of doublets, but otherwise resembling the $Fe_2O_3$ spectrum. An actual splitting is not apparent in the lines close to zero velocity (i.e., for the two "3" and "4" lines in Fig. 3 and for the three "2", "3" and "4" lines in Fig. 4) but these lines are wider than would be expected assuming a single field. This pattern in the garnets is in fact exactly that to be expected if the conjecture mentioned in the Introduction is correct, namely, that the iron nuclei situated in the two different lattice sites experience local fields which are appreciably different. One would then expect to obtain a superposition of two patterns, whose intensities are in the ratio of 3:2 (ratio of iron atoms in the two nonequivalent sites) and each resembling in shape that of $Fe_2O_3$ to a first approximation, but characterized by spacings determined by different parameters. The spectra have been analyzed in accordance with this interpretation.

In the cases when the doublets are resolved, the stronger component is assigned to the *d* sites (which are more numerous than the *a* sites in the ratio 3:2) and are labeled *d* in the figures, and the weaker component is assigned to the *a* sites. For the spectrum taken at room temperatures (Fig. 3) the positions of the four resolved lines "1*d*," "2*d*," "5*d*," and "6*d*" were used to calculate the four parameters determining

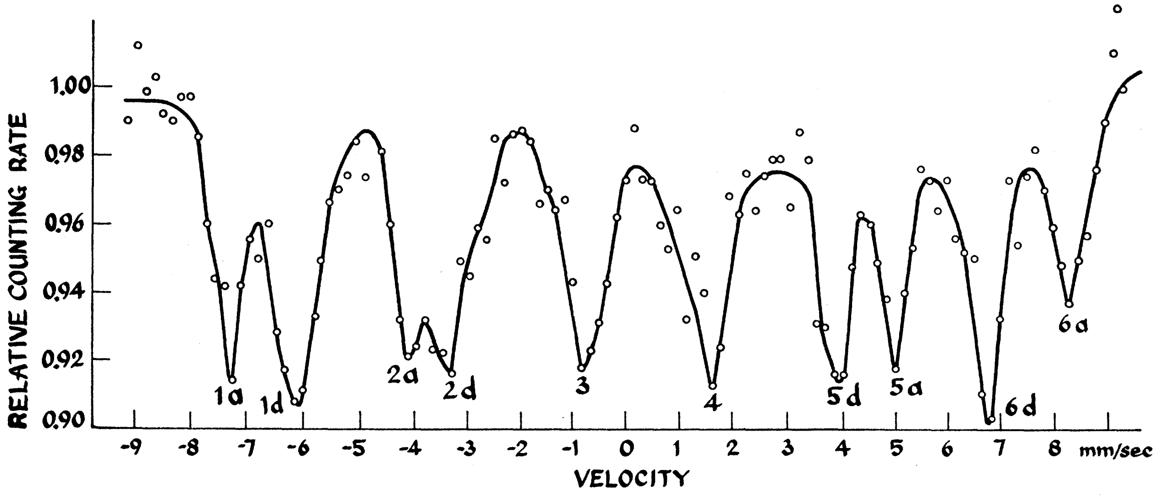

FIG. 3. The absorption at room temperature by yttrium iron garnet of the 14.4-kev gamma ray emitted in the decay of $Fe^{57m}$ embedded in stainless steel, as a function of relative velocity between source and absorber.

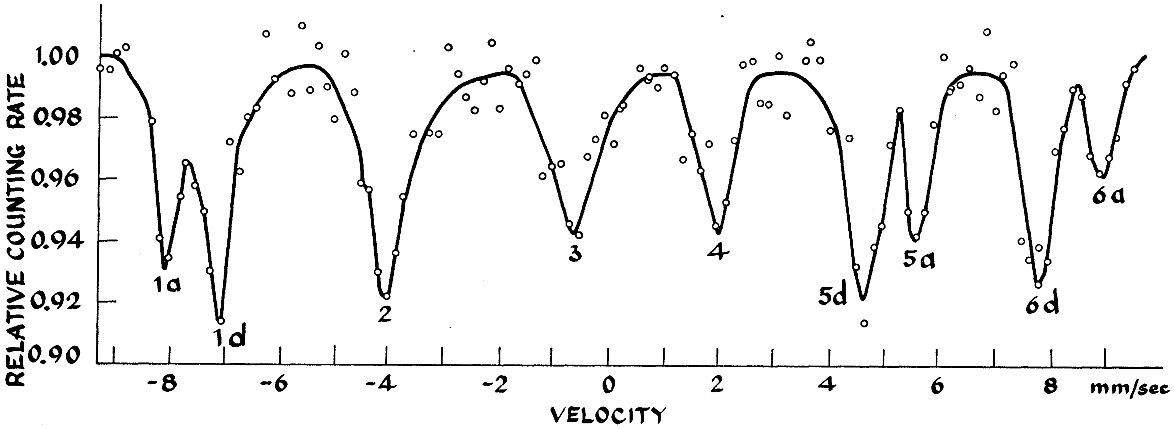

FIG. 4. The absorption at liquid air temperature by yttrium iron garnet of the 14.4-kev gamma ray emitted in the decay of $Fe^{57m}$ embedded in stainless steel, as a function of relative velocity between source and absorber.

the Zeeman pattern of the iron nuclei in the *d* sites, and the positions of the four corresponding *a* lines to calculate the parameters of the nuclei at the *a* sites. As described in the work of Kistner and Sunyar,[4] the Zeeman spectrum is characterized by four parameters and these are uniquely determined by the position of four peaks. The parameters are, in the notation of Kistner and Sunyar: $g_0$ and $g_1$, the magnetic splitting parameters for the $\frac{1}{2}$ and $\frac{3}{2}$ nuclear levels, respectively; $\Delta E$, the shift between the center of gravity of the absorption lines and the emission lines of $Fe^{57}$ in stainless steel; and $\epsilon$, the quadrupole interaction parameter, shifting only the substates belonging to the upper $\frac{3}{2}$ level. When the parameters were found in this way, the expected positions of the lines "3*a*" and "3*d*," "4*a*" and "4*d*" were calculated, and found to be in very good agreement with the position of the experimentally unresolved lines "3" and "4," thus demonstrating the consistency of the analysis. Moreover, the values of $g_0/g_1$ (equal to the ratio of the nuclear *g* factors in the $\frac{1}{2}$ and $\frac{3}{2}$ states) obtained are in satisfactory agreement with the value obtained by Hanna *et al.*[2] and Kistner and Sunyar.[4]

In the analysis of the spectrum taken at liquid air temperature (Fig. 4) in which only three clearly resolved doublets are seen, the four characteristic parameters for each site were calculated, assuming a value of 1.77 for $g_0/g_1$ and using the position of the three resolved lines appropriate to each lattice site, i.e., "1*d*," "5*d*," and "6*d*" for the *d* sites, and "1*a*," "5*a*," and "6*a*" for the *a* sites. As in the previous example, the expected positions of the remaining lines were calculated from these parameters thus obtained and found to be in good agreement with the position of the observed unresolved peaks "2," "3," and "4."

The spectra obtained with the dysprosium garnet absorber are not shown since they so closely resemble those obtained with yttrium garnet at the same temperature. They were analyzed in a similar way. The final values of the characteristic parameters $g_0$, $g_1$, $\Delta E$, and $\epsilon$ for the two sites in the various experiments are given in Tables I and II. Table I, showing the results obtained at room temperatures, also shows the values of $g_0/g_1$ obtained directly from the experiments in each case. The value of the effective magnetic field at the nucleus, $H_{\mathrm{eff}}$, in each case was calculated from the value obtained for $g_0$ using a value[10] of $+(0.0903 \pm 0.0007)$ nm for the magnetic moment of the nuclear ground state of $Fe^{57}$. The values of $H_{\mathrm{eff}}$, determined in this way, are given in Tables I and II.

The results demonstrate that the *a* and *d* sites are indeed characterized by considerably different values of $H_{\mathrm{eff}}$. Thus the values obtained for $H_{\mathrm{eff}}$ at room temperature are $3.9\times10^5$ oe at the *d* sites and $4.85\times10^5$

TABLE I. Results of analysis of measurements on yttrium and dysprosium iron garnets at room temperature.

| | $Y_3Fe_5O_{12}$ (yttrium iron garnet) at 300°K | | $Dy_3Fe_5O_{12}$ (dysprosium iron garnet) at 300°K | |
|---|---|---|---|---|
| | Strong spectrum *d* sites | Weak spectrum *a* sites | Strong spectrum *d* sites | Weak spectrum *a* sites |
| $g_0$ (cm/sec) | $0.46\pm0.02$ | $0.58\pm0.02$ | $0.460\pm0.025$ | $0.580\pm0.025$ |
| $g_1$ (cm/sec) | $0.270\pm0.015$ | $0.325\pm0.015$ | $0.275\pm0.020$ | $0.325\pm0.020$ |
| $\Delta E$ (cm/sec) | $0.035\pm0.010$ | $0.055\pm0.010$ | $0.05\pm0.01$ | $0.06\pm0.01$ |
| $\epsilon$ (cm/sec) | $0.00\pm0.01$ | $0.00\pm0.01$ | $0.00\pm0.01$ | $0.00\pm0.01$ |
| $g_0/g_1$ | $1.7\pm0.1$ | $1.8\pm0.1$ | $1.7\pm0.1$ | $1.75\pm0.1$ |
| $H_{\mathrm{eff}}$ (oe) | $(3.90\pm0.1)\times10^5$ | $(4.85\pm0.15)\times10^5$ | $(3.95\pm0.15)\times10^5$ | $(4.85\pm0.20)\times10^5$ |

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[10] G. W. Ludwig and H. H. Woodbury, Phys. Rev. **117**, 1286 (1960).

TABLE II. Results of analysis of measurements on yttrium and dysprosium garnets at liquid air temperature.

| | $Y_3Fe_5O_{12}$ (yttrium iron garnet) at 85°K | | $Dy_3Fe_5O_{12}$ (dysprosium iron garnet) at 85°K | |
|---|---|---|---|---|
| | Strong spectrum<br>*d* sites | Weak spectrum<br>*a* sites | Strong spectrum<br>*d* sites | Weak spectrum<br>*a* sites |
| $g_0$ (cm/sec) | $0.550\pm0.015$ | $0.635\pm0.015$ | $0.545\pm0.020$ | $0.64\pm0.02$ |
| $g_1$ (cm/sec) | $0.31\pm0.01$ | $0.36\pm0.01$ | $0.310\pm0.015$ | $0.360\pm0.015$ |
| $\Delta E$ (cm/sec) | $0.04\pm0.01$ | $0.06\pm0.01$ | $0.030\pm0.015$ | $0.060\pm0.015$ |
| $\epsilon$ (cm/sec) | $0.00\pm0.01$ | $-0.010\pm0.01$ | $0.00\pm0.015$ | $-0.010\pm0.015$ |
| $H_{\mathrm{eff}}$ (oe) | $(4.60\pm0.15)\times10^5$ | $(5.35\pm0.15)\times10^5$ | $(4.6\pm0.2)\times10^5$ | $(5.4\pm0.2)\times10^5$ |

oe at the *a* sites. The results at liquid air temperature give higher values for $H_{\mathrm{eff}}$, but still different for the two sites $-4.6\times10^5$ oe and 5.35 oe for the *d* and *a* sites, respectively.

Nagle *et al.*[11] have recently shown that in ferromagnetic iron, $H_{\mathrm{eff}}$, which has a well-defined value for temperatures below the Curie temperature, shows the same functional dependence on the temperature as the relative saturation magnetization $M_s$, from temperatures at which the magnetization is almost saturated up to the Curie temperature. This remarkably simple result seems to demand that the fluctuations in the value of the nuclear field at a particular iron nucleus must take place in a time short compared to the Larmor precession period of the nucleus in the magnetic field produced by the extranuclear electrons.

These fluctuations may be expected to follow the fluctuations of the magnetic moment of the extranuclear electrons. The temperature dependence of the expectation value of the extranuclear moment in the direction of magnetization will then determine the temperature dependence of both the microscopic $H_{\mathrm{eff}}$ at the nucleus and the macroscopic magnetization. It is of interest to test these ideas in the case of the garnets and to see whether the values of $H_{\mathrm{eff}}$ at different temperatures are proportional to the values of the partial spontaneous magnetizations of the appropriate sublattice. The partial magnetizations cannot of course be directly measured for ferrimagnetic materials. Pauthenet, however, starting from the experimental results for the relative saturation magnetization of the garnets as a function of temperature, and using the Néel two-sublattice model,[12] has calculated the partial spontaneous magnetization for yttrium ion garnet as a function of temperature for the two iron sublattices.[13]

Table III shows a comparison between the ratio of the values of $H_{\mathrm{eff}}$ at 85°K and 300°K in yttrium iron garnet for the *a* and *d* sites and the corresponding ratio of the spontaneous magnetization per ion ($m$) as calculated by Pauthenet.[6]

The agreement is seen to be quite good and suggests that in this case, also, $H_{\mathrm{eff}}$ follows the variation in magnetization. It should be pointed out that the calculations of Pauthenet, based on the Néel model, indicate that at liquid air temperatures the partial magnetizations of the *a* and *d* lattices should both be very close indeed to saturation, corresponding to a value of 5 $\mu_B$ per ferric ion. Nevertheless, the values of $H_{\mathrm{eff}}$ remain different for the *a* and *d* sites. Assuming saturation really occurs at liquid air temperature, this behavior implies a difference in the extranuclear electronic configurations determining the nuclear field in the two sites.

As seen from the results in Tables I and II, no significant difference in the values of $H_{\mathrm{eff}}$ and the other parameters between the corresponding sites in yttrium and dysprosium garnets has been detected. The local fields at the corresponding sites in the two garnets cannot differ by more than a few percent. This is not unreasonable in view of the relatively small value of the exchange interaction acting between the rare earth ions and the ferric ions.

It is not to be expected that a reliable value of the quadrupole interaction can be obtained from measurements on polycrystalline materials, since the shift in the sublevels due to the quadrupole interaction is a function of the angle between the magnetic field and the direction of the field gradients which are well defined with respect to the crystallographic axis. In fact, for the case of an axially symmetric field gradient and completely random orientation between the direction of magnetic field and the field gradient, the average quadrupole shift, to first order, would be zero, and only a line broadening would be produced. In ferromagnetic and ferrimagnetic materials the correlation which in general will exist between the orientation of a crystallite and the orientations of the domains within this crystallite may very well lead to an average value of the quadrupole shift different from zero. The present results show no evidence of an appreciable quadrupole *shift*, but in view of the above, little can be deduced

TABLE III. Comparison of ratio of value of $H_{\mathrm{eff}}$ at 85°K and at 300°K, with ratio of partial magnetizations at these temperatures as calculated by Pauthenet, for yttrium iron garnet.

| | *d* sites | *a* sites |
|---|---|---|
| $H_{\mathrm{eff}}(85°\mathrm{K})/H_{\mathrm{eff}}(300°\mathrm{K})$ | 1.16 | 1.11 |
| $m(85°\mathrm{K})/m(300°\mathrm{K})$ | 1.17 | 1.08 |

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[11] D. E. Nagle, H. Fraunfelder, R. D. Taylor, D. R. F. Cochran, and B. T. Matthias, Phys. Rev. Letters **5**, 364 (1960).

[12] L. Néel, Ann. Phys. **3**, 137 (1948).

[13] See reference 6, Fig. 12 and p. 454.

concerning an upper limit for the quadrupole interaction at the iron nucleus.

Concerning the chemical shifts, there is no evidence of any temperature dependence. The values of the chemical shift however, do seem to be consistently greater at the $a$ sites than the value at the $d$ sites. Noting that $H_{\text{eff}}$ is greater at the $a$ sites than at the $d$ sites, one might speculate on a possible correlation between chemical shift and the saturation value of $H_{\text{eff}}$. If an appreciable part of the chemical shift is due to an isotope shift, as has been suggested by Kistner and Sunyar,[4] such a correlation may arise since the isotope shift should certainly be influenced by changes in the value of $s$ wave functions at the nucleus and it is possible that $H_{\text{eff}}$ will also be influenced by these changes.

## ACKNOWLEDGMENTS

The authors would like to thank M. Schieber of the department of electronics, the Weizmann Institute, for preparing the garnets, E. Sunyar of Brookhaven National Laboratory for information concerning electronic circuits, E. Segal for help in constructing the apparatus, and A. Mustachi for help in chemical problems.

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PHYSICAL REVIEW VOLUME 122, NUMBER 3 MAY 1, 1961

# Photoconductivity and Trapping in Silver Chloride Crystals*

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(Received December 15, 1960)

Photoconductivity and trapping were investigated in pure, cuprous-chloride-doped, nickel-chloride-doped, and darkened silver chloride crystals. The photoconductivity was measured primarily at 88°K. The initial photoresponse increases with rising absorption constant, peaks at wavelengths for which the absorption constant is 3 to 5 cm$^{-1}$, and falls rapidly to 1/20 to 1/10 of the peak value at wavelengths at which the absorption constant is 50 to 100 cm$^{-1}$. This decrease in photoresponse at short wavelengths is explained in terms of trapping and recombination through centers in a surface region. The effect of irradiation and the filling of traps was investigated. Values of the schubweg for electrons in the bulk material were obtained from these experiments. The cuprous-chloride-doped samples had a long-wavelength tail on the photoresponse curve corresponding to the long-wavelength tail observed in the optical absorption. The photoconductivity does not show any peaks in the infrared. There was, however, a photoresponse with a threshold at approximately 10 000 A in samples irradiated at 88°K and a peak for those irradiated at room temperature. This response was attributed to photoemission from free silver introduced unavoidably during the preparation of the samples. The warming of samples irradiated at 88°K to fill traps produced no measurable thermoluminescence. Electrical warming curves (measurement of current as a function of time during warming) disclosed a number of trapping levels. All samples except the nickel-chloride-doped sample showed peaks at 115°, 140°, and 180°K related to activation energies of approximately 0.20, 0.28, and 0.45 ev. The nickel-chloride-doped sample showed only peaks at 115° and 180°K. The cuprous-chloride-doped samples and the darkened pure sample showed a peak at 160°K corresponding to a thermal activation energy of approximately 0.36 ev. On some samples another peak was visible at 240°K with a thermal activation energy of approximately 0.62 ev. Possible interpretations for these various peaks are discussed.

## I. INTRODUCTION

PHOTOCONDUCTIVITY in silver chloride crystals at low temperatures is a well-known phenomenon. Early measurements by Lehfeldt[1] and Hecht[2] showed that photoconductivity could be produced by the absorption of light in the region of the fundamental absorption edge. The results could be interpreted by attributing a finite range to the electrons. Later photoconductivity measurements[3,4] showed that the contribution of hole motion at temperatures below 200°K is insignificant in comparison with that of electron motion. These observations also indicated that the schubweg (range per unit field) was not constant over the entire crystal but had different values depending on whether the electron traveled in the surface region or in the bulk. The schubweg in the surface region was either smaller or larger than in the bulk region depending upon the sample preparation.

The existence of such a surface layer is of wider interest since it may give a clue to the unsuccessful attempts in this laboratory to observe photoconductivity in the alkali halides during irradiation in the region of fundamental absorption.[5] A comparison of the optical absorption spectra for the alkali[6] and the silver[7] halides demonstrates a striking difference in

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* Submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy at Cornell University, Ithaca, New York, 1961. This work was in part supported by a research grant from the Eastman Kodak Company, Rochester, New York.

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