on interactions with near neighbors, and its associated spread and displacement in frequency is confirmed in the interpretation of Pershan's experiment.

IV. COMPUTATIONAL NOTE

This study has involved a sizeable mass of numerical detail. The generation and manipulation of large pair matrices, the tabulation of the various χ functions, the evaluation of different convolution integrals, to mention only the more obvious computational tasks, have had to be performed on a mass-production basis. The use of the Bell Telephone Laboratories IBM-7090 computer has proved indispensable. The computer programs were written by the author.

Molecular Field Model and the Magnetization of YIG*

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The susceptibility and magnetization of YIG of high purity have been measured from 4.2 to 650°K by means of a precision vacuum balance. The spontaneous magnetization has a saturation value of 37.90 emu/g at 4.2°K and 27.40 emu/g at 292°K. The Curie point is at 559°K as determined by both the vanishing of the spontaneous moment and the discontinuity in the susceptibility curve. Using a program written for the IBM 7090, the molecular field coefficients were determined by fitting the experimental total magnetization curve. The sublattice magnetizations and the exchange interactions are calculated and compared with other results. On the basis of the molecular field model the intrasublattice interactions must be larger than previously supposed.

INTRODUCTION

ACCURATE sublattice magnetization data are required for an adequate description of such quantities as the magnetic anisotropy and magnetostriction in ferrimagnetics. The first calculations of the sublattice magnetizations in the garnets were made by Pauthenet in 1957 based on the molecular field model.[1] Though his results have been the only ones available it has long been apparent that they could be improved upon by using purer samples and a better method of solving the molecular field equations. An alternative approach is to measure the magnetization of a sublattice indirectly by observing the magnetic resonance frequency or the Mössbauer absorption of nuclei situated in that sublattice. This was first done for YIG by Solomon[2] and Robert[3] and has been repeated by several others,[4-9]

some of whose results will be discussed in a later section. It may be said here, however, that the NMR measurements have not been extended to sufficiently high temperatures to represent any real improvement over Pauthenet's results.

In this present study the total spontaneous magnetization was obtained by subtracting the field-dependent magnetization from the measured values for high-purity YIG over the temperature range from 4.2 to 650°K. These values of the spontaneous magnetization were fed into a program written for the IBM 7090 by Gerhard Heiche of this laboratory and the molecular field equations were solved for all temperatures. The molecular field coefficients computed in this manner are used to calculate the sublattice magnetizations and the exchange interaction energies for YIG. Similar results for the three sublattice garnets will be the subject of a separate paper.

EXPERIMENTAL APPARATUS

The technique used for the measurements reported here is a modification of the Curie method.[10] Briefly, the sample is placed in a magnetic field having a large gradient and the force on the sample is measured by a sensitive balance. The essential unit is an automatic vacuum balance and recorder which can weigh accurately to 3×10^{-5} g. A quartz sample holder is suspended from one pan of the balance so that the sample

* This work is an excerpt from a thesis submitted to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The research was performed at the U. S. Naval Ordnance Laboratory.

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[2] I. Solomon, Compt. Rend. **251**, 2675 (1960).
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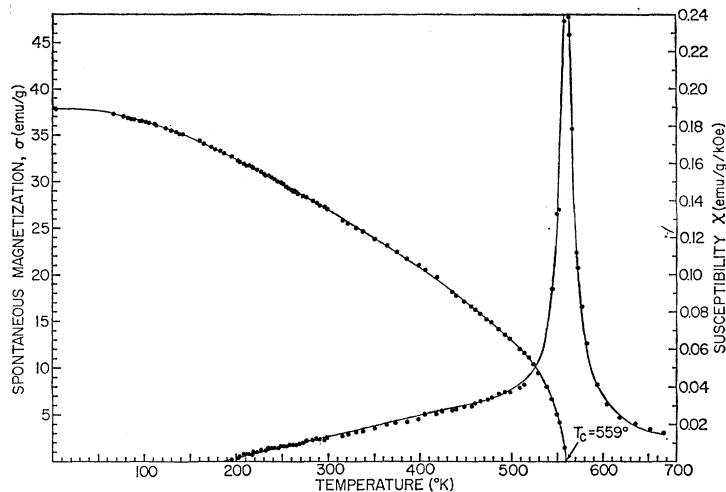[10] P. Curie, Ann. Chim. Phys. (7) **5**, 289 (1895).

FIG. 1. Spontaneous magnetiza-
tion and susceptibility of YIG.

is at the point where the magnetic field gradient is a maximum. The sample holder is protected by a vacuum-tight glass tube which may be either evacuated or subjected to a helium atmosphere at any desired pressure. For low-temperature measurements a stainless-steel double Dewar is used. High temperatures are achieved by using a noninductive wire-wound heater whose magnetoresistance coefficient is extremely low. The temperature of the sample is monitored by two thermocouples which are mounted close to the sample on the inside of the protective tube. In the interval from 50 to 250°K the maximum temperature error is esti-mated at ±0.5°C and above room temperature it is probably less than ±0.2°C. The magnetic field is pro-vided by an electromagnet having parabolic pole pieces situated so as to produce a large gradient in the vertical direction. The maximum field attainable is 10 kG and the corresponding gradient is 1241 G/cm at the optimum sample position. The latter was deter-mined by mapping the field of the magnet and choosing the point where $\partial^2 H/\partial z^2 = 0$. Ideally, if $\partial H/\partial z$ is the only nonzero derivative, then the force per gram of sample is given by

$$F = \sigma(\partial H/\partial z). \tag{1}$$

The gradient was determined for each value of magnet current from measurements on spectroscopically pure nickel (Johnson Matthey Code 890) using the value of 54.39 emu/g for nickel at 20°C.[11] The precision of this calibration is better than ±0.1% and includes any errors due to sample weight, sample position, and field current setting. It also includes any uncertainties due to sample shape since spherical and nonspherical sam-ples were used to make the calibration runs.

SAMPLES

YIG single crystals were grown from the melt by J. Richard Cunningham, Jr., of this laboratory using

oxides of 99.99% purity. Polycrystalline samples were made by ceramic techniques using ultrapure yttrium oxide (Lindsay Code 1118). The single crystals were ground into spheres and were x-ray oriented so that the applied field could be directed along a [111] axis. Measurements on the polycrystalline samples were made on sintered powders as well as on spheres ground from toroids of high density. X-ray diffraction patterns were obtained for all of the polycrystalline materials using a Norelco high-angle goniometer spectrometer. The scanning rate was $\frac{1}{4}°$ per minute using unfiltered chromium radiation. None of the samples showed any unwanted phases or impurities and the powders ap-peared to be homogeneous and completely reacted.

MOLECULAR FIELD THEORY OF YIG

On the basis of the two sublattice model for ferri-magnetics [12] the molecular field equations for YIG may be expressed as follows:

$$\sigma = \sigma_d - \sigma_a,$$
$$\sigma_a = 75.70 B_{5/2}(3.359 \times 10^{-4}/T) H_a,$$
$$\sigma_d = 113.55 B_{5/2}(3.359 \times 10^{-4}/T) H_d,$$
$$H_a = \lambda_{aa}\sigma_a - \lambda_{ad}\sigma_d,$$
$$H_d = -\lambda_{ad}\sigma_a + \lambda_{dd}\sigma_d. \tag{2}$$

In Eqs. (2), σ is the total magnetization, σ_a is the magnetization of the octahedral sublattice and σ_d is the magnetization of the tetrahedral sublattice, all ex-pressed in emu/g. $B(x)$ is the Brillouin function, T is the absolute temperature, and $H_{a,d}$ is the molecular field in gauss. The molecular field coefficients λ_{ij} are related to the n_{ij} of Pauthenet[1] by

$$\lambda_{ij} = 92.25 n_{ij}.$$

They may also be expressed in terms of the three

[11] R. M. Bozorth, Ferromagnetism (D. Van Nostrand Company, Inc., New York, 1951), p. 867.

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

FIG. 2. Spontaneous magnetization of YIG. The solid curve is the experimental curve of Fig. 1 with data points omitted. The broken curve is the molecular field solution using the coefficients in line 2 of Table I.
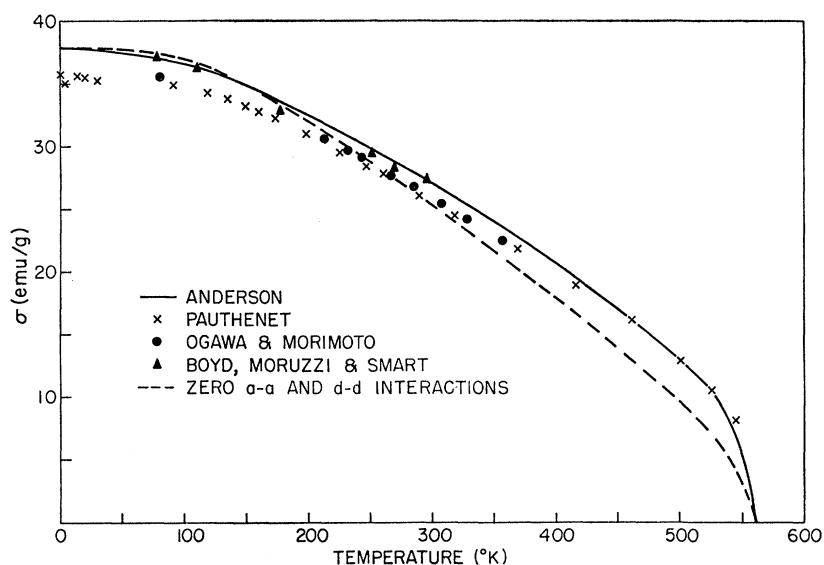
exchange energies as follows:

$$\lambda_{aa} = 5661 J_{aa},$$
$$\lambda_{dd} = 1887 J_{dd},$$ (3)
$$\lambda_{ad} = 2821 J_{ad},$$

where the J_{ij} are in units of cm^{-1}.

Equations (2) were solved by means of a computer program designed to determine the molecular field coefficients by fitting the experimentally determined total magnetization curve.

EXPERIMENTAL RESULTS

The spontaneous magnetization and the susceptibility of YIG are shown in Fig. 1 in units of emu/g. The value of 37.90 emu/g at absolute zero corresponds to slightly over 5 Bohr magnetons and is in excellent agreement with the value of 5.01 reported by Geller et al.[13] This is about 5% higher than Pauthenet's value and attests to the purity and homogeneity of these samples. The Curie temperature is 559°K and is indicated by the discontinuity in the susceptibility curve as well as the vanishing of the magnetic moment. There is little question about the shape of the magnetization curve as is evidenced by the smoothness of the data. The points shown in Fig. 1 represent only about one-fourth of those measured and the omitted points fit the curve just as smoothly. The total magnetization is again shown in Fig. 2, where it is compared with the data of Pauthenet and the NMR results. The latter, unfortunately, do not extend much above room temperature and thus shed no light on the region where the magnetization changes most rapidly. The broken curve in Fig. 2 is the molecular field solution obtained

[13] S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, Phys. Chem. Solids **23**, 1525 (1962).

by assuming that the a–a and d–d interactions are zero. Adjusting the a–d interaction coefficient to give the experimental Curie temperature of 559°K, one obtains the results shown in line 3 of Table I. However, the experimental curve (solid line) of Fig. 2 is best fit by the two sets of coefficients in lines 1 and 2 of Table I. The coefficients of line 1 were obtained by assuming them to be independent of temperature while those of line 2 were given Aléonard's temperature dependence, namely,

$$\lambda(T) = \lambda(o) \cdot (1 - 1.3 \times 10^{-4} T).$$

The magnetization curve calculated from each of these sets of coefficients is extremely close to the experimental values. The relative error is generally less than a few tenths of a percent except near the Curie point. Two factors probably contribute to the latter: (1) The spontaneous magnetization in this region is quite small and the measured magnetization consists largely of the field-dependent contribution. Thus, a small error in the susceptibility will produce a large relative error in spontaneous moment. (2) The molecular field model neglects short-range order which is known to play an ever increasing role as the long-range order disappears.

TABLE I. Molecular field coefficients for YIG (J_{ij} in cm^{-1}).

	λ_{ad}	λ_{aa}	λ_{dd}	J_{ad}	J_{aa}	J_{dd}	T_c °K
Anderson	71 505	47 820	22 394	25.36	8.45	11.86	559
Anderson	71 505	44 200	20 700	25.36	7.8	11.0	559
Anderson	38 371	0	0	13.61	0	0	559
Aléonard[a]	71 100	34 500	19 500	25.2	6.1	10.3	612
Pauthenet[b]	68 500	32 500	19 700	24.3	5.7	10.4	600
Wojtowicz[c]	68 500	0	0	24.3	0	0	>900

[a] Reference 14.   [b] Reference 1.   [c] Reference 15.
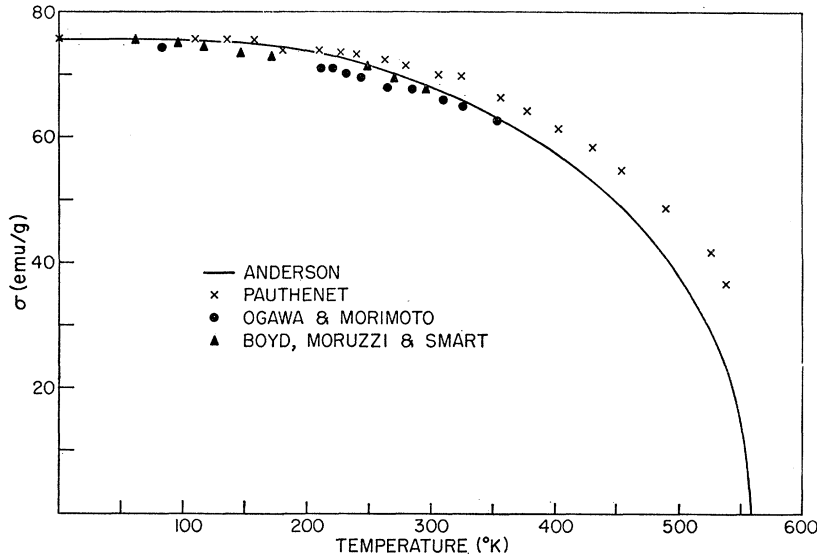
FIG. 3. Magnetization of the octahedral sublattice of YIG. The solid curve was calculated using the coefficients in line 1 of Table I.

DISCUSSION

It is evident from Fig. 2 that the shape of the total magnetization curve is not very sensitive to the values of the a–a and d–d interactions provided the a–d interaction is constrained to satisfy the Curie temperature. Thus, scattered data can be approximately fitted by a wide range of values for the coefficients. The curve in Fig. 1, however, is sufficiently smooth to give the unambiguous sets of molecular field coefficients of lines 1 and 2, Table I. These coefficients and the calculated exchange energies are compared with earlier values in the table. The tabulated values for the Curie temperature are all calculated values which were obtained from the solution of Eqs. (2) using the corresponding sets of coefficients. Note that the coefficients of lines 1–3 are the only ones that give a Curie temperature which agrees with the experimental value of 559°K. Pauthenet obtained a Curie temperature of 560°K experimentally but his temperature-dependent coefficients predict a value 40° higher.

Applying the results of spin-wave theory[16–18] to YIG, the dispersion constant D and the Landau-Lifshitz exchange constant A are related to the J's as follows:

$$\omega\hbar = Dk^2 = (a^3 A/4S)k^2$$

$$= \tfrac{5}{16}(5J_{ad} - 8J_{aa} - 3J_{dd})a^2 k^2. \quad (4)$$

Using $a = 12.376 \times 10^{-8}$ cm and $S = \tfrac{5}{2}$,

$$D = 4.787 \times 10^{-15}(5J_{ad} - 8J_{aa} - 3J_{dd}),$$

$$A = 2.525 \times 10^7 (5J_{ad} - 8J_{aa} - 3J_{dd}).$$

A summary of the values of D and A that have been obtained by magnetization, specific heat[19–22] and microwave measurements[23,24] is given in Table II. The values calculated from lines 1 and 2, Table I are smaller than the earlier magnetic results and are much less than those obtained from specific heat measurements. The discrepancy with the other magnetic results arises

TABLE II. Summary of exchange coefficients for YIG.

	$5J_{ad} - 8J_{aa} - 3J_{dd}$	D(erg-cm^2)	A (erg/cm)
Magnetization			
Line 1, Table I	4.69×10^{-15} erg	22.5×10^{-30}	11.8×10^{-8}
Line 2, Table I	6.24	29.9	15.8
Line 3, Table I	13.5	64.6	34.1
Pauthenet	8.9	43.	22.
Aléonard	9.2	44.	23.
Wojtowicz	24.1	115.	61.
Specific heat			
Edmonds and Petersen		51.	27.
Meyer and Harris		63.	33.
Kunzler, Walker, and Galt		83.	44.
Shinozaki		83.	44.
Microwave			
Turner		99.	53.
LeCraw and Walker		96.	52.

[14] R. Aléonard, Phys. Chem. Solids 15, 167 (1960).
[15] P. J. Wojtowicz, J. Appl. Phys. 33, 1257 (1962).
[16] C. Herring and C. Kittel, Phys. Rev. 81, 869 (1951).
[17] R. L. Douglass, Phys. Rev. 120, 1612 (1960).
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[19] D. T. Edmonds and R. G. Petersen, Phys. Rev. Letters 2, 499 (1959).
[20] J. E. Kunzler, L. R. Walker, and J. K. Galt, Phys. Rev. 119, 1609 (1960).
[21] S. S. Shinozaki, Phys. Rev. 122, 388 (1961).
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[24] R. C. LeCraw and L. R. Walker, J. Appl. Phys. Suppl. 32, 167S (1961).

principally from the differences in the values for J_{aa}. The disagreement with the specific heat data is probably due to differences in the spin wave and molecular field models.

Figures 3 and 4 show the octahedral and tetrahedral sublattice magnetizations for all temperatures as calculated using the coefficients of line 1 (solid line) and line 3 (dashed line) of Table I. The dashed line is not shown for the octahedral sublattice since it nearly coincides with the solid curve. The calculations of Pauthenet and some of the NMR results are also shown.

In Mössbauer and NMR experiments in magnetic materials it is assumed that the temperature dependence of the effective field at the nucleus is due entirely to the temperature dependence of the sublattice magnetization. This is probably not a bad assumption since it has been shown[25] that the hyperfine interaction is the dominant contributor to the effective field at the nucleus.

The hyperfine term of the Hamiltonian may be written in the form

$$H = -g_I \beta_I \mathbf{I} \cdot \mathbf{H_{eff}}, \tag{5}$$

where

$$\mathbf{H_{eff}} = (8\pi/3)\rho(o)g\beta \mathbf{S} \tag{6}$$

is the effective field seen by the nuclear spin. Since $\rho(o)$ is nonzero only for s electrons, it is not obvious why Fe^{3+}, which has no unpaired s electrons, should have an effective field at the nucleus. Sternheimer[26] suggested that a net unpaired spin density at the nucleus is produced by a polarization of the core electrons due to the spin of the d electrons. If this core polarization is essentially constant up to the Curie temperature, then H_{eff} and the hyperfine energy will show the same temperature dependence as the sublattice magnetization. That this assumption is valid, at least up to 430°K in YIG, is borne out by the NMR data in Figs. 3 and 4.

SUMMARY OF RESULTS

(1) The saturation moment of YIG is 37.90 emu/g (5.01 Bohr magnetons) at absolute zero and 27.40 emu/g (3.62 Bohr magnetons) at 292°K. The Curie temperature is 559°K. The magnetic susceptibility vanishes below 190°K.

[25] R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960); J. Appl. Phys. Suppl. **32**, 118S (1961).
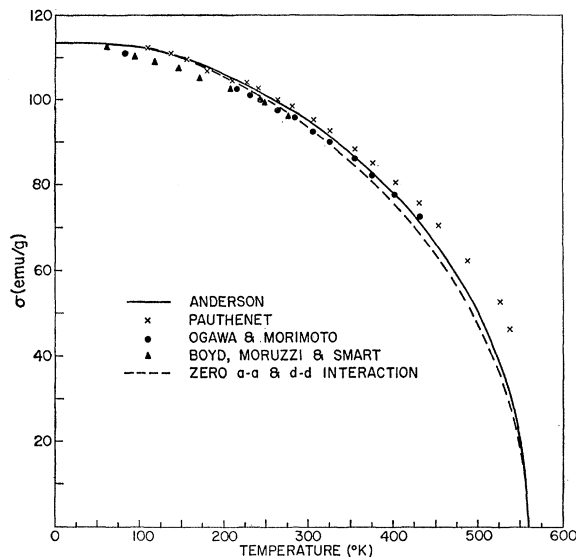[26] R. Sternheimer, Phys. Rev. **86**, 316 (1952).

FIG. 4. Magnetization of the tetrahedral sublattice of YIG. The solid curve was calculated using the coefficients in line 1 of Table I, the broken curve using line 3.

(2) The experimental magnetization curve can be reproduced by means of the molecular field model. However, a unique set of interaction coefficients cannot be obtained by this method if there is much scatter in the data.

(3) The sublattice magnetizations are less sensitive than the total magnetization to the exact values of the interaction coefficients.

(4) The sublattice magnetizations reported here are in good agreement with available NMR results.

(5) On the basis of this model the $a-a$ interaction must be larger than previously supposed.

Note added in proof. A. B. Harris [Phys. Rev. **132**, 2398 (1963)] gives the following values for the molecular field coefficients of YIG: $\lambda_{ad} = 89\ 700$, $\lambda_{aa} = 35\ 950$ and $\lambda_{dd} = 11\ 980$. However, this set of coefficients results in a Curie temperature that is greater than 900°K.