

TABLE I. Rotational constants for XH_3Cl molecules.

Molecule	B_0 (mc/sec.)
$\text{C}^{12}\text{H}_3\text{Cl}^{35}$	13,292.89 ^a
$\text{C}^{12}\text{H}_3\text{Cl}^{37}$	13,088.19 ^a
$\text{C}^{13}\text{H}_3\text{Cl}^{35}$	12,796.2
$\text{C}^{13}\text{H}_3\text{Cl}^{37}$	12,590.0
$\text{Si}^{28}\text{H}_3\text{Cl}^{35}$	6673.8 ^b
$\text{Si}^{28}\text{H}_3\text{Cl}^{37}$	6512.4 ^b
$\text{Si}^{30}\text{H}_3\text{Cl}^{35}$	6485.8
$\text{Ge}^{70}\text{H}_3\text{Cl}^{35}$	4401.71
$\text{Ge}^{74}\text{H}_3\text{Cl}^{35}$	4333.91
$\text{Ge}^{74}\text{H}_3\text{Cl}^{37}$	4177.90
$\text{Ge}^{76}\text{H}_3\text{Cl}^{37}$	4146.5

^a See reference 1.^b See reference 2.

The new data obtained combined with those of Gordy *et al.*¹ and Sharbaugh² allow the molecular structures of methyl chloride, chlorosilane, and chlorogermane to be determined completely using only accurate microwave measurements. The structural parameters obtained are assembled in Table II. The structures of CH_3Cl and SiH_3Cl differ to some extent from earlier values based partially on infra-red data and on the Si—H distance in silane. The new H—Si—H angle is $110^\circ 57'$ instead of $103^\circ 57'$, which is a less drastic change from the tetrahedral angle ($109^\circ 28'$) and in close agreement with corresponding angles in CH_3Cl and GeH_3Cl . No corrections for the effect of zero-point vibration on bond distance and angles have been made. Maximum errors which zero-point vibrations are likely to produce are 0.01A in the X—H distance, 0.003A in the X—Cl distance, and $30'$ in the H×H angle.

Hyperfine structure due to the chlorine nuclei is present in GeH_3Cl . The quadrupole coupling constant for Cl^{37} in this molecule is given in Table II.

Dipole moments of SiH_3Cl and GeH_3Cl have been obtained by measurement of Stark displacement as a function of field strength and are also listed in Table II.

The shortening of the Si—Cl and Ge—Cl bonds, the considerably smaller Cl quadrupole coupling in SiH_3Cl and GeH_3Cl than in CH_3Cl , as well as the irregular progression of dipole moments indicate clearly that the Si and Ge compounds involve importantly some electronic structure which does not occur in CH_3Cl . This structure is very probably of the type $\text{H}_3\text{Si}^-\text{Cl}^+$, involving use of a d orbital to form five Si bonds and a doubly bonded Cl. The d orbitals are of course not available in C. The occurrence of structures of this type in molecules involving the heavier elements has been discussed by Pauling³ and suggested by Gilliam *et al.*⁴ as an explanation for the small SiH_3Cl dipole moment and the H—Si—H angle of $103^\circ 57'$ reported by Sharbaugh.²

A rather satisfactory semiquantitative correlation of the data of Table II can in fact be obtained by assigning 20 percent ionic

TABLE II. Structural data for XH_3Cl Molecules.

Molecule	CH_3Cl	SiH_3Cl	GeH_3Cl
Dipole moment (Debye units)			
Microwave value	1.88 ^a	1.31	2.13
Previous value	1.86	1.28 ^c	2.03 ^e
X-Cl distance (angstroms)			
Measured value	1.781	2.048	2.147
Sum of single bond radii	1.76	2.16	2.21
H—X distance (angstroms)			
Measured value	1.12	1.50	1.52
Sum of single bonded radii	1.07	1.47	1.52
HXH angle	$110^\circ 50'$	$110^\circ 57'$	$111^\circ 4'$
Quadrupole coupling const. eqQ for Cl^{37} (mc/sec.)	-59.03 ^b	-30 ^d	-34

^a R. Karplus and A. H. Sharbaugh, Phys. Rev. **75**, 1449 (1949); R. G. Shulman, private communication.^b See reference 1.^c L. O. Brockway and I. E. Coop, Trans. Faraday Soc. **34**, 1429 (1938).^d See reference 2.^e Smyth, Grossman, and Ginsburg, J. Am. Chem. Soc. **62**, 192 (1940).

character to the C—Cl bond, 40 percent ionic and 30 percent double bond character to the Si—Cl bond, and 45 percent ionic and 15 percent double bond character to the Ge—Cl bond. These numbers fit the quadrupole coupling constants,⁵ X—Cl distances, and dipole moments, as well as agreeing with the general principles of dependence of ionic character on electronegativity differences and the tendency for the lighter elements to form double bonds more easily than their heavier congeners.

Hyperfine structure caused by a Ge^{73} nuclear quadrupole coupling in the molecule GeH_3Cl has been observed. Although this hyperfine structure is not yet completely analyzed, it is clear that the quadrupole coupling constant is large. This is very good evidence for ionic character of the Ge—Cl bond, since other electronic structures suggested for this bond would give only a very small quadrupole coupling to the germanium nucleus.

Studies of other halogen derivatives of silane and germanium as well as further examination of possible hyperfine structure due to Ge and Si nuclei are being undertaken.

* Work supported jointly by the Signal Corps and the ONR.

¹ W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).² A. H. Sharbaugh, Phys. Rev. **74**, 1870 (1948).³ L. C. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, p. 228.⁴ O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. **75**, 1014 (1949).⁵ Cf. C. H. Townes and B. P. Dailey, J. Chem. Phys. to be published.

Ferromagnetic Resonance Absorption Magnetite*

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THE previously reported¹ results of ferromagnetic resonance absorption experiments on natural single crystals of magnetite have been substantially confirmed with synthetic single crystals in both the 3 cm and 1 cm wave-length regions.

The experiments were made with thin circular disks cut from the (100) crystal plane. For the purpose of calculating demagnetizing effects, they were regarded as oblate spheroids. The disks, one side of which had been copper-plated, were soldered to a rotatable portion of the wall of a rectangular resonant cavity. This allowed a change in the orientation of the crystal axes with respect to the applied d.c. magnetic field. From two measurements of the resonance magnetic field, one with the [100] and the other with the [110] crystal direction parallel to the field, one can calculate the first order anisotropy constant K_1 and the g -factor by means of Kittel's equations.² In order to allow measurements to be made at low temperatures, the cavity was thermally insulated from the rest of the wave-guide system.

Table I gives typical experimental results. Figure 1 shows values of g and K_1 calculated from these results. These values are esti-

TABLE I. Experimental results for synthetic magnetite single crystal.

Temperature (°C)	Saturation magnetization (c.g.s.)	Resonance field (gauss)		Frequency (mc/sec.)	g factor	K_1 (ergs/cc)
		[100]	[110]			
Sample diameter: 0.1246"; thickness: 0.0036"						
+20	461	1775	980	8923	2.17	-1.12×10^5
-143	492	1330	1330	8945	2.08	0
-153	494	1200	1450	8946	2.06	$+3.65 \times 10^4$
Sample diameter: 0.0705"; thickness: 0.0030"						
+20	461	6300	5680	23957	2.13	-1.11×10^5
-143	492	5850	5850	23986	2.09	0

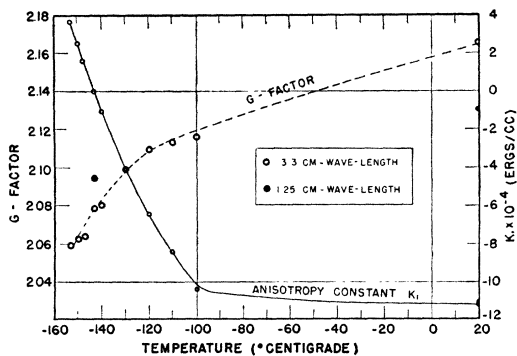


FIG. 1. Anisotropy constant and g -factor for synthetic magnetite single crystal as a function of temperature.

mated to be accurate to within 2 percent, including the probable error in values of magnetization.

Above -143°C the anisotropy constant is negative, indicating that $[111]$ is the direction of easy magnetization, while below -143° , $[100]$ is the direction of easy magnetization. At -143° the resonance magnetic field is independent of orientation, indicating that the material is magnetically isotropic.

The initial permeability of magnetite is known to go through a maximum near -140°C . The effects seems to have been attributed directly to the second-order phase transition which magnetite undergoes in the region of -160°C .³ The behavior of the magnetic crystal anisotropy makes it seem reasonable that such is not the case. The initial permeability should be high when the crystal anisotropy is low; therefore a maximum in the initial permeability is to be expected near the temperature at which the anisotropy goes through zero. Measurements of the initial permeability of the same natural crystals of magnetite used in the resonance experiments showed the maximum to be at -146°C , which is within a few degrees of the anisotropy point. It is also interesting to note that the anisotropy point occurs at the same temperature for both natural and synthetic crystals, whereas the transition occurs 10°C higher for the synthetic crystal than for the natural.

Published results of the measurement of magnetite's anisotropy constant by other methods are not abundant. The room temperature value obtained from the resonance experiments agrees reasonably well with a value of -1×10^6 erg/cc given by Snoek.⁴ Li⁵ published some torque curves for magnetite at -155°C . He apparently failed to notice that these curves showed the direction of easy magnetization to be different from what it is at room temperature. On the basis of measurements of magnetization in weak fields, Okamura and Ogawa⁶ concluded that the direction of easy magnetization changes near -100°C .

The writer has reported¹ previously that the resonance absorption at 3.3 cm wave-length disappears below the transition. It has now been found that at 1.25 cm the resonance appears below the transition, shifted to appreciably lower field strengths. This effect is being studied in detail.

The synthetic single crystals used in these experiments were grown by J. Smiltens and D. H. Fryklund of this laboratory. The mol ratio of FeO to Fe_2O_3 was found by Smiltens to be 1:0.998. Values of saturation magnetization used in the calculations were obtained by C. Domenicali from pendulum magnetometer measurements.

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¹ L. R. Bickford, Jr., Phys. Rev. **75**, 1298 (1949).

² C. Kittel, Phys. Rev. **73**, 155 (1948).

³ J. L. Snoek, *New Developments in Ferromagnetic Materials* (Elsevier, Amsterdam, 1947), p. 25.

⁴ Reference 3, page 21.

⁵ C. H. Li, Phys. Rev. **40**, 1002 (1932).

⁶ T. Okamura and S. Ogawa, Proc. Physico-Math Soc. Japan, **23**, 363 (1941).

On the Sign of the Electric Quadrupole Moment of Li^7

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THIS note presents data which show that the nuclear electric quadrupole moment of Li^7 is positive. The result is entirely unexpected on the basis of all nuclear models which have been proposed and which predict a negative electric quadrupole moment for Li^7 .

The present experiments determine the sign of the coupling energy of the quadrupole moment of a nucleus with the gradient of the electric field produced at that nucleus by the electrons and the other nucleus in certain diatomic molecules. The sign of the quadrupole moment is then derived from experimental results by a theoretical calculation of the gradient of the electric field. While exact wave functions for molecules containing Li are not, of course, available, the calculation nevertheless leads to a positive sign for the quadrupole moment of Li^7 without ambiguity.

The lines observed in the molecular beam magnetic resonance method which result from the re-orientation of the nucleus within a diatomic molecule in an applied magnetic field are complex spectra consisting of a large number of closely spaced lines arising in the rotational states J, m_J . From an observation of the structure of the pattern it is possible¹ in some cases, to determine the magnitude of the interaction energy of the nuclear electric quadrupole moment with the gradient of the electric field at the nucleus. If the nuclear spin is $\frac{3}{2}$, the line $\Delta m_I = \pm 1$ exhibits three maxima corresponding to the three possible transitions. At sufficiently high magnetic fields the central maxima ($1/2, -1/2$) occurs at the frequency $g_I \mu_0 H/h$ and the two satellite maxima ($3/2, 1/2$) and ($-1/2, -3/2$), are symmetrically disposed about the central line. The frequency interval between the two extreme maxima is $1/2 e^2 q Q/h$. The general details of the spectrum are the same² in heteronuclear and homonuclear molecules.

It is not possible from an observation of the spectrum alone to identify the two satellite maxima in terms of the quantum numbers, m_I , of the terminal states. To determine the sign of the quadrupole interaction it is necessary that this identification be made.

The various diatomic molecules in the beam describe different trajectories in the apparatus, depending principally on the magnetic quantum numbers m and m' of the two nuclei. It is, accordingly, possible to interpose in the beam an obstacle which will predominantly remove molecules of positive m or of negative m from the beam which finally reaches the detector. It is possible to achieve a complete separation of states of positive and negative m only if the second nucleus has a very small g value. The extent to which the separation can be achieved in a general case depends on the relative values of g and g' . If the obstacle is interposed into that portion of the beam in which states of positive m preponderate, then the satellite maximum arising from the transition ($3/2, 1/2$) will have its intensity reduced relative to the other maximum. If the maxima are not resolved from the central peak, the center of gravity of the pattern will shift in the direction of the line ($-1/2, -3/2$).

The effect of interposing a wire at an appropriate point along the path of the beam has been investigated for the Li^7 line in Li_2 and LiBr . In each of these two cases the high frequency satellite of the central line corresponds to the transition ($-1/2, -3/2$). For the Na line in Na_2 and in NaI and for the Cl^{35} line in KCl the high frequency satellite corresponds to the transition ($3/2, 1/2$).

Feld and Lamb¹ give as that portion of the energy of the levels which depends on the m_I of a single nucleus the expression:

$$E = m_I g_I \mu_0 H + \left[\frac{e^2 q Q}{4J(2J-1)I(2I-1)} \right] \times [3m_I^2 - J(J+1)] \times [3m_I^2 - I(I+1)].$$

In all cases under consideration the value of g_I is negative since the nuclear magnetic moment is positive. The satellite maxima