0.088 m_0, when the magnetic field was along a bisectrix axis, but did not observe the second effective mass expected for the crystallographic orientation. We cannot explain the apparent disagreement with our results which were obtained with the magnetic field in the plane of the surface.

An independent determination of electron Fermi-surface parameters from cyclotron-resonance data in antimony requires a value of the cyclotron mass for a trigonal-directed magnetic field which lies in the plane of the surface. A bisectrix-trigonal plane in the sample surface would permit the determination of this cyclotron mass as well as an accurate value of the tilt angle.

We are still trying to prepare a satisfactory surface by electropolishing techniques.

Magnetic Field at the Nucleus in Spinel-Type Crystals*

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Measurements of the magnetic field at the Fe^{57} nucleus were obtained on powder samples at room temperature using the Mössbauer effect for the spinel-type ferrites γ-Fe_2O_3, "ordered" lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$), and "disordered" lithium ferrite giving values of $|496\pm20|$ koe, $|508\pm20|$ koe, and $|510\pm20|$ koe. These compounds contain only trivalent and no divalent iron. The Mössbauer spectra of all of these compounds were very similar and no difference could be detected between the "ordered" and "disordered" compounds. Only one set of lines was observed indicating that the fields at the octahedral and tetrahedral sites are about the same value. The value of the hyperfine interaction constant A obtained from electron paramagnetic resonance spectrum of the divalent Mn^{55} (isoelectronic with trivalent Fe) impurity in single crystals of the isomorphous spinel-type crystal "disordered" lithium aluminate ($Li_{0.5}Al_{2.5}O_4$) was found to be $|77.2\pm1.0|$ $\times 10^{-4}$ cm^{-1}. The angular variation of the spectrum indicated that the divalent Mn^{55} ions were located substantially on octahedral sites. The corresponding magnetic field for the Mn^{55} nucleus is around 550 koe, which is close to the value obtained elsewhere for the Mn^{55} nucleus located on a tetrahedral site in a spinel-type aluminate. This is in good agreement with the Mössbauer results.

INTRODUCTION

THE determination of the magnetic field at the nucleus of magnetic ions in crystals can be carried out by several different methods. A direct determination can be achieved for ions in ferromagnetic and antiferromagnetic crystals by measurements of the Mössbauer effect or nuclear magnetic resonance (NMR). The results of such measurements can be related to the hyperfine interaction parameter A obtained from the electron paramagnetic resonance (EPR) spectrum of

magnetic impurity ions in diamagnetic crystals. To a first approximation, the hyperfine spectrum can arise only through the anomalous interaction of the s electrons with the nuclear spin (Fermi contact interaction)

TABLE I. Crystallographic parameters and symmetries.

Compound	Ordering	Lattice constant (angstroms)	Space group	A-site symmetry (tetra.)	B-site symmetry (octa.)
γ-Fe_2O_3		8.338[a]	$O_h(7)$ -$Fd3m$[a,b]	$\bar{4}3m$	$\bar{3}m$
$Li_{0.5}Fe_{2.5}O_4$	Ordered	8.33[c,d]	$O(6)$ -$P4_33$[c] or $P4_13$	3	2
$Li_{0.5}Fe_{2.5}O_4$	Disordered	8.33[c,d]	$O_h(7)$ -$Fd3m$[c]	$\bar{4}3m$	$\bar{3}m$
$Li_{0.5}Al_{2.5}O_4$	Disordered	7.92[d]	$O_h(7)$ -$Fd3m$[c]	$\bar{4}3m$	$\bar{3}m$

[a] I. David and A. J. E. Welch, Trans. Faraday Soc. **52**, 1642 (1956).
[b] Some investigators (see, for example, reference 14) have reported superstructure lines indicating the $O(6)$ -$P4_33$ space group and ordering.
[c] P. B. Braun (reference 14).
[d] Values obtained on powders prepared from single crystals grown at the Naval Research Laboratory.

for S-state ions located in cubic environments in insulators. The trivalent Fe^{57} ion, which is an S-state ion, is conveniently employed for the Mössbauer and NMR measurements. Values of the hyperfine interaction parameter A for the isoelectronic ions trivalent Fe^{57} and divalent Mn^{55} have been reported for a number of compounds. It is of interest to compare the results of various experiments[1-11] with each other and with theory.[12,13] In this article the field at the nucleus of the trivalent Fe^{57} ion in the spinel-type crystals γ-Fe_2O_3 and lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$) is obtained from measurements of the Mössbauer effect. The results are compared with the field deduced from the value of A for the divalent Mn^{55} impurity in the isomorphous compound lithium aluminate ($Li_{0.5}Al_{2.5}O_4$). Further comparison is made with other data reported using the Mössbauer effect,[1-3] EPR,[4-10] and NMR,[11] and with theory.[12,13]

In spinel-type crystals the magnetic ions can be located on either octahedral or tetrahedral sites, with the possibility of a different magnetic field on each site. In some crystals variations in the distribution of the cations can occur resulting in local fluctuations in the environment of each magnetic cation. Such fluctuations could result in slight variations in the fields at the nuclei in these sites. In order to investigate this possibility, we have studied the magnetic field at the nucleus in the isomorphous crystals lithium ferrite and lithium aluminate in which long-range ordering of the lithium and trivalent ions on octahedral sites can occur as a result of heat treatment.[14] We have also obtained results for γ-Fe_2O_3 in which vacancies occur in the spinel-type lattice and are believed to be located on octahedral sites.[15,16] These ferrimagnetic compounds are particularly suitable for study since they contain only ferric and no ferrous ions. In addition, lithium ferrite is the only ferrite in which the transition metal ion is present only as trivalent iron and can be prepared
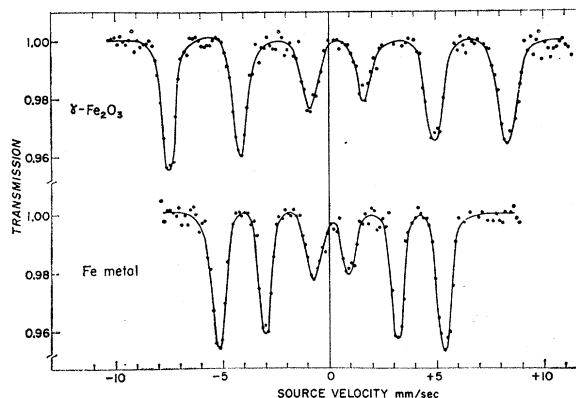

Fig. 1. Resonant absorption of the 14.4-kev gamma ray of Fe^{57} in γ-Fe_2O_3 and Fe metal at room temperature. The source was Co^{57} diffused into stainless steel. Positive velocities are for the source approaching the absorber.

in "ordered" crystals. The relevant crystallographic data for the compounds studied are shown in Table I.

EXPERIMENTAL

The experimental arrangement for the Mössbauer studies was similar to that of Ruby et al.[17] consisting of a loudspeaker driven by a sinusoidal signal at a frequency of 25 cps. A rigid rod attached to the voice coil oscillated a velocity pickup coil and the source. The induced voltage in the pickup coil was used to command a 256-channel pulse height analyzer to store counts in addresses corresponding to the appropriate instantaneous velocity. It was found most convenient to calibrate the system with an iron foil absorber. The compound absorbers were interchanged with the iron metal reference absorber at frequent intervals. The source consisted of a 0.001-in. thick nonmagnetic stainless steel foil in which radioactive Co^{57} had been diffused.[18] The γ-Fe_2O_3 absorber consisted of several layers of acetate magnetic video tape with a total effective thickness of 26 mg/cm^2 of γ-Fe_2O_3. The lithium ferrite absorber consisted of powder of approximately 25 mg/cm^2 suspended in collodion film.

The "disordered" lithium aluminate single crystal used in the EPR experiments was grown from a combined PbO-PbF$_2$ flux. The EPR measurements were carried out on both divalent Mn^{55} and trivalent Fe (natural abundance) at 24 kMc/sec. The microwave apparatus consisted of a Pound stabilized klystron and a TE_{011} circular transmission cavity. The applied magnetic field was sinusoidally modulated at 1000 cps and the transmitted cavity signal was detected with a 1N26 silicon crystal and amplified with a narrow-band amplifier. The output of the amplifier was phase-detected and finally recorded as the first derivative of the resonance absorption. The magnetic field was meas-

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TABLE II. Summary of results obtained from the Mössbauer experiments.

	γ-Fe$_2$O$_3$	Li$_{0.5}$Fe$_{2.5}$O$_4$ (ordered)	Li$_{0.5}$Fe$_{2.5}$O$_4$ (disordered)	Fe metal[a]
Peak positions[b] (mm/sec) (all ±0.09 mm/sec)	−7.58, −4.16, −0.86, +1.66, +4.99, +8.41	−7.74, −4.36, −0.94, +1.66, +5.10, +8.49	−7.82, −4.27, −0.82, +1.92, +5.06, +8.50	−5.21, −2.99, −0.72, +0.97, +3.23, +5.43
Derived quantities g_0, ground state splitting (mm/sec)	5.85±0.13	6.03±0.13	6.06±0.13	3.95±0.13
g_1, excited state splitting (mm/sec)	3.37±0.07	3.41±0.07	3.40±0.07	2.24±0.07
ΔE, isomer shift (relative to stainless steel) (mm/sec)	+0.41±0.09	+0.37±0.09	+0.43±0.09	+0.11±0.09
Magnetic field at Fe nuclei at room temp. (koe)	|496±20|	|508±20|	|510±20|	−333±10

[a] Used for calibration purposes employing splitting parameters of Hanna *et al.* (reference 19).
[b] Zero position is that of maximum absorption of stainless steel source and stainless steel absorber.

ured using proton and lithuim nuclear resonance. The accuracy of the determination of the field differences corresponding to the hyperfine line separation was approximately one gauss.

RESULTS

The room temperature Fe[57] hyperfine spectra obtained by the Mössbauer effect in γ-Fe$_2$O$_3$ and lithium ferrite are very similar to those of iron metal. Typical spectra for iron metal and γ-Fe$_2$O$_3$ are shown in Fig. 1. The lithium ferrite spectra were practically identical to that of γ-Fe$_2$O$_3$. Since only one set of lines was observed, it was concluded that the fields at the octahedral and tetrahedral sites are the same to within a few percent. A small asymmetry in line width and amplitude can be seen between the right and left half of the spectra. Further tests indicated that this is largely instrumental. The observed linewidths for all the compounds studied was about 1.0 mm/sec and no significant differences could be observed for the linewidths between the various compounds. An analysis of the data indicated an absence of any quadrupolar interaction in contrast to that found for α-Fe$_2$O$_3$ [1] and yttrium iron garnet[2] (YIG) (single crystal). It has been pointed out[4] that quadrupolar interaction in ferrimagnetic powders may be difficult to observe because to a first approximation it would only result in line broadening. No quadrupolar interaction can be deduced from the YIG powder data[4] although it has been observed in single crystals.[2]

The results of a least-squares analysis of the data obtained in the Mössbauer investigations are summarized in Table II in which the velocity calibration is based on the splittings in iron metal reported by Hanna *et al.*[19,20] All errors quoted include those of the reference value. The field at the nucleus in iron metal has been used to calculate the magnitudes of the fields

in the compounds which are given in Table II. The isomer shifts, ΔE, are also reported and are approximately the same as those found for other trivalent iron compounds.[21,22]

The EPR measurements were carried out on a "disordered" lithium aluminate single crystal oriented so that the magnetic field (H) was in the (1$\bar{1}$0) plane. The spectrum of the six hyperfine lines corresponding to the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ electronic transition. The line positions were nearly isotropic and the line intensities diminished with increasing angle of H with respect to the [111] direction. The full width for H in the [111] direction was about 11.5 gauss and was larger in the [001] and [110] as well as in intermediate directions. The magnitude of the hyperfine constant ($|A|$) obtained from these measurements was 82.6±1.0 oe or (77.2±1.0)×10^{-4} cm^{-1}. The measured g parameter was 2.0023±0.0010. The symmetry of angular variation of the line intensities and widths with respect to the [111] direction was found to be in accord with the crystallographic trigonal symmetry of the octahedral site in "disordered" spinels. Consequently, it is reasonable to assign a substantial portion of the divalent Mn[55] to this site in lithium aluminate. Additional measurements of the EPR spectrum of the divalent Mn[55] and trivalent Fe[57] ions and their relation to the magnetic properties of ferrites will be published separately.[23]

DISCUSSION

A summary of the fields obtained by various methods for the isoelectronic ions, divalent Mn[55] and trivalent Fe[57], is shown in Table III. For the trivalent oxides the magnitude of the fields are about 500 koe. For lithium ferrite, the magnitude of the field at 0°K can be estimated if it is assumed that the field at the nucleus

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TABLE III. Comparison of fields at the nucleus by various methods.

Ion	Compound	A $(10^{-4}$ cm$^{-1})$	H (koe)	Method	Temperature (°K)	Reference
Fe^{3+}	γ-Fe_2O_3		|496ᵃ|	Mössbauer	room	Present
Fe^{3+}	$Li_{0.5}Fe_{2.5}O_4$ "ordered"		|508|	Mössbauer	room	Present
Fe^{3+}	$Li_{0.5}Fe_{2.5}O_4$ "disordered"		|510|	Mössbauer	room	Present
Fe^{3+}	α-Fe_2O_3		|515|	Mössbauer	room	1
	YIG tetrahedral		|390|	Mössbauer	room	2
Fe^{3+}			|460|	Mössbauer	85°K	4
	YIG octahedral		|470|	Mössbauer	room	2
			|540|	Mössbauer	85°K	4
Fe^{3+}	$NiFe_2O_4$		|510ᵃ|	Mössbauer	room	3
Mn^{2+}	$Li_{0.5}Al_{2.5}O_4$ octahedral	|77.2|	|547|	EPR	room	Present
Mn^{2+}	$ZnAl_2O_4$ tetrahedral	|74.9|	|530|	EPR	room	5
Mn^{2+}	MgO	−81	−574	EPR	290.4	5
Fe^{3+}	MgO	|10.1|	|550|	EPR		6
Mn^{2+}	ZnO	−76	−538	EPR	77	7
Fe^{3+}	ZnO	|9.0|	|490|	EPR		8
Mn^{2+}	CaF_2	|95.5|	|677|	EPR	4.2	5
Mn^{2+}	NaCl	−81.2	−576	EPR	290	9
Mn^{2+}	ZnS	−63.0	−446	EPR	290	10
Fe^{3+}	Fe_3O_4		|490ᵃ|	NMR	room	11
Mn^{2+}	free ion		−696	theory		12
Fe^{3+}	free ion		−626	theory		13

ᵃ Very recent Mössbauer experiments by R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer. and E. Segal, Phys. Rev. 122, 1447 (1961), give excellent agreement with these values.

varies with temperature in a way which is proportional to the sublattice magnetization. This was pointed out by Bauminger et al.[4] who have presented experimental evidence in support of this assumption. For ferromagnetic metals, the temperature dependence of the field at the nucleus has been observed to vary as the saturation magnetization (except for small lattice dilation effects).[24,25] For lithium ferrite the ratio of the sublattice magnetization at room temperature to that at 0°K is 0.974 for the A site and 0.951 for the B site. This was calculated using the Néel theory and the magnetization data and molecular field coefficients obtained by Rado and Folen.[26] As a result the field at 0°K for the lithium ferrites (and probably the closely related compound γ-Fe_2O_3) may be expected to be less than 5% different from the room temperature value.

The fields measured at 0°K by the Mössbauer effect can be compared with fields deduced from the value of A using the relation[27,28]

$$H = AS/g_n\mu_n,$$

where S is the spin of the ion ($\frac{5}{2}$ for Fe^{3+} and Mn^{2+}), g_n is the nuclear gyromagnetic ratio of the ion, and μ_n

is the nuclear magneton. The values of A and H for the divalent Mn^{55} and trivalent Fe^{57} impurities in oxides and a few compounds are listed in Table III. It can be seen that where measurements of the sign have been obtained, the fields are negative and range from −450 koe to −680 koe, depending on the covalency of the host lattice. For the oxides a field of around 500 to 550 koe magnitude seems prevalent. However, in the garnet-type ferrimagnetic crystals, the field on the tetrahedral site has been observed by the Mössbauer effect to be lower in magnitude than the field at the octahedral site. This is in contrast to spinel-type ferrites where no difference in the field at each site can be observed. In view of the dependence of the field at the nucleus on covalency, it is not strictly rigorous to compare fields obtained by the Mössbauer effect with those obtained by EPR even if both are measured with the same type ion, e.g., trivalent Fe^{57}. This is because the Mössbauer measurements are obtained with magnetic crystals. On the other hand, the EPR results are obtained on diamagnetic host crystals which would, in general, have a different degree of covalency.

In spinel-type diamagnetic crystals the value of A for divalent Mn^{55} on a tetrahedral site in zinc aluminate has been reported by Stahl-Brada and Low[5] and for an octahedral site in lithium aluminate in the present paper. It is interesting to note that these corresponding fields at the nucleus agree to within 20 koe. Data using the trivalent Fe^{57} impurity would be more suitable for the comparison with the Mössbauer results. However, these data were not available. Existing data on the field

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at the nucleus by EPR for both divalent Mn^{55} and trivalent Fe^{57} are available for MgO [5,6] and ZnO [7,8] host crystals. In the case of MgO, the field for trivalent Fe^{57} is only about 5% lower in magnitude than the field for divalent Mn^{55}. In the case of ZnO, the field for trivalent Fe^{57} is about ten percent lower than that for divalent Mn^{55}. In spite of all of these complications, it is interesting to note that the field at the nucleus obtained by Mössbauer and EPR experiments are remarkably constant for various host crystals and for the isoelectronic ions divalent Mn^{55} and trivalent Fe^{57}.

The values of the field at the nucleus obtained by nuclear magnetic resonance have been reported recently by Boyd, Bruner, Budnick, and Blume[11] for various garnets and ferrites. They report two fields for magnetite of 460 and 490 koe magnitude in which the higher value is believed to correspond to the tetrahedral site which contains only Fe^{3+} ions.

Also, we note that the theoretical value of the field can be predicted from the spin-polarized Hartree-Fock calculations of Freeman and Watson[12,13] for free ions. In their treatment the s electrons are polarized by the $3d$ electrons. The difference in the electron spin density at the nucleus is conveniently given in terms of a function χ which has a value of -3.34 atomic units for Mn^{2+} and -3.00 atomic units for Fe^{3+}. These correspond to fields at the nucleus of -696 and -626 koe, respectively. This is considered to be very good agreement in view of the approximations involved in the calculations.

In addition, the occurrence of covalent bonding and crystalline (Coulomb) field effects could reduce the magnitudes in solids compared to those of the free ion.

The Mössbauer results given here indicate that the field at the trivalent Fe^{57} nucleus in the spinel-type ferrites studied is the same to within a few percent at both the octahedral and tetrahedral sites. No changes in the Mössbauer spectrum can be observed between "ordered" and "disordered" crystals. It is not too surprising that no difference can be found between "ordered" and "disordered" crystals since the largest differences may be expected to be manifested in the quadrupolar interaction which is difficult to observe in powder ferrimagnetic samples. The magnitude of the field obtained by Mössbauer effect is in good agreement with that deduced from the hyperfine interaction parameter obtained from the electron paramagnetic resonance spectrum of the isoelectronic divalent Mn^{55} impurity in isomorphous crystals for both sets of sites.

Diffusion of Zinc and Tin in Indium Antimonide*

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The diffusion of zinc and tin in single-crystal and polycrystalline InSb has been studied with the radio-tracer technique. The temperature dependence of the diffusion coefficients can be represented by: $D(Zn) = 1.4 \times 10^{-7} \exp(-0.86/kT)$ cm²/sec and $D(Sn) = 5.5 \times 10^{-8} \exp(-0.75/kT)$ cm²/sec in single-crystal InSb; and $D(Zn) = 1.1 \times 10^{-6} \exp(-0.85/kT)$ cm²/sec in polycrystalline InSb, the activation energies being in electron volts. From the penetration curves, it appears that in polycrystalline InSb the zinc diffusion is a volume diffusion while the tin diffusion is mainly a grain boundary diffusion. The different behaviors of zinc and tin in InSb are discussed on the basis of one-type and two-type vacancy mechanisms.

INTRODUCTION

IN recent years, indium antimonide has been a subject of intense study. However, little has been reported on the solute diffusion in it. This is not without reason. Unless specially prepared, an InSb crystal used to

contain undesired impurities of no less than 10^{14}/cc. For diffusion studies in this kind of crystal, the p-n junction method, which relies on conductivity measurements, would be less reliable. The radio-tracer technique, on the other hand, could produce dependable results if the half-life of the tracer as a diffusant is not too short compared with the diffusion time. Unfortunately, the time required for diffusion in InSb is relatively long (from several days to a few weeks). This would render experiment rather difficult if and when the