power even when the sample was in liquid nitro-
gen. It is believed that more careful filtering of
the light source to remove all but the useful
pumping radiation will permit low-temperature
operation at greatly reduced pump power.

It has thus been shown that optical maser oper-
ation at the wavelength of the 7009A line (N_2)
does occur in concentrated ruby as predicted.[6]
Moreover, simultaneous maser oscillations at
7041 A (N_1) show that these two lines are not
closely related, and probably come from differ-
ent kinds of chromium ion pairs.

We wish to thank W. L. Bond for polishing the
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portance of sample heating by the flash, and to
A. M. Clogston and D. L. Wood for helpful dis-
cussions on the origin and properties of the
satellite lines.

[1]Deutschbein labelled these lines N_1 and N_2, where
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INTERPRETATION OF THE Fe57 ISOMER SHIFT

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We have made a systematic study of the Möss-
bauer effect[1] of Fe57 in di- and tri-valent iron
compounds and in d-group metals. The observed
"isomer shift"[2] measures the total s-electron
density at the nucleus. The shift in compounds
is shown to depend mainly upon the $3d$ configura-
tion of iron involved and to a lesser extent upon
the "chemical" bond. The Hartree-Fock calcula-
tions of Watson[3] on the various $3d$ configurations
of iron are combined with the data on the shifts
in the most ionic compounds to obtain a calibra-
tion of the shift in terms of s-electron density.
This enables us to estimate the difference in
charge radius of the ground state and isomeric
state of Fe57. We associate the shift of an Fe
solute ion in a d-group metal with the addition of
some fraction of a $4s$ electron to an Fe $3d^7$ con-
figuration; an estimate of the $4s$-electron wave
function density at the nucleus from the Fermi-
Segrè-Goudsmit (FSG) formula[4] enables this
fraction to be determined.

Kistner and Sunyar[5] first observed in the recoil-
free emission and resonant absorption of the
14.4-kev nuclear gamma ray of Fe57, that the

energies of the emitted and absorbed gamma rays
were noticeably different if the emitter and ab-
sorber were two dissimilar lattices containing
iron. The origin of this effect is as follows.

The ground and isomeric levels of the nucleus
have different effective charge radii; the elec-
trostatic interaction with the electronic charge
is then different in the two states and the gamma-
ray energy is consequently changed (relative to
its value for a point nucleus) by an amount pro-
portional to the s-electron density at the nucleus.
If the s-electron density is different for the ab-
sorber and emitter, the difference in gamma-
ray energies, $E_a - E_e$, is defined as the isomer
shift.

$$E_a - E_e = \tfrac{2}{5}\pi Ze^2[R_{is}^2 - R_{gr}^2][|\psi(0)_a|^2 - |\psi(0)_e|^2], \quad (1)$$

where R_{is} and R_{gr} are the radii of the isomeric
and ground states and $|\psi(0)_a|^2$ and $|\psi(0)_e|^2$ are
the total s-electron densities at the nucleus for
absorber and emitter, respectively.[6] It is to be
noted that the sign of the shift has its origin in
the fact that the level energy is lower the more

compact the charge distribution.

An examination of the restricted Hartree-Fock calculations of Watson[3] shows that there are significant differences in the value of $|\psi_{3S}(0)|^2$ for different $3d$ configurations of iron; the change in $|\psi_{1S}(0)|^2$ and $|\psi_{2S}(0)|^2$ is substantially smaller.

It is perhaps worthwhile to point out that un-restricted Hartree-Fock calculations, which exhibit the imbalance of up and down spin density (exchange polarization effect), appear to give the same total density at the nucleus as the restricted procedure.[7] The variation of $|\psi_{3S}(0)|^2$ is such as to correspond to different degrees of shielding of $3s$ by $3d$ electrons. To calibrate the observed shifts in terms of total s-electron density, we associate the difference in the shifts for the most ionic Fe^{2+} and Fe^{3+} compounds with the difference in Watson's values of $\sum_{n=1}^{3} |\psi_{nS}(0)|^2$ for $3d^6$ and $3d^5$ configurations. When an Fe atom is introduced into a d-group host metal, $\sum_{n} |\psi_{nS}(0)|^2$ will also contain a contribution from $4s$ conduction electrons. Hartree-Fock calculations do not exist for single $4s$ electrons outside $3d^n$ configurations, but the FSG[4] formula, combined with the known term value of $3d^n 4s$ configurations,[8] provides an entirely adequate estimate of $|\psi_{4S}(0)|^2$.

In Fig. 1 is shown a possible interpretation of the observed shifts making use of the above ideas. The total s-electron density in atomic units is plotted as ordinate. Watson's values for $2\sum_{n=1}^{3} |\psi_{nS}(0)|^2$ for the Fe $3d^n$ configurations from $n=4$ to $n=8$ are indicated on the left. The scale on the right for Mössbauer center-of-gravity shifts relative to stainless steel is established by identifying the shifts in the most ionic Fe^{2+} and Fe^{3+} with Watson's densities for $3d^6$ and $3d^5$, respectively. The solid straight lines represent s-electron densities for hypothetical $3d^n 4s^x$ configurations. They are drawn on the assumption that the density for such a configuration is of the form $|\psi(3d^n)|^2 + x|\psi_{4S}(0)|^2$, where $|\psi_{4S}(0)|^2$ is calculated from the FSG formula for a single $4s$ electron outside the $3d^n$ configuration. This assumes no screening of inner s electrons by the single $4s$ electron.[9] Curves for the configurations $3d^{8-x}4s^x$ and $3d^{7-x}4s^x$ are indicated by dashed lines and were obtained by extrapolation and interpolation of the FSG formula. The experimental data are given in Table I.

The shifts for Fe in various metals have been represented as horizontal lines of a length sufficient to cover what appear to be the most plausible configurations. Since for Fe in Fe metal there are certainly 8 electrons to be accounted
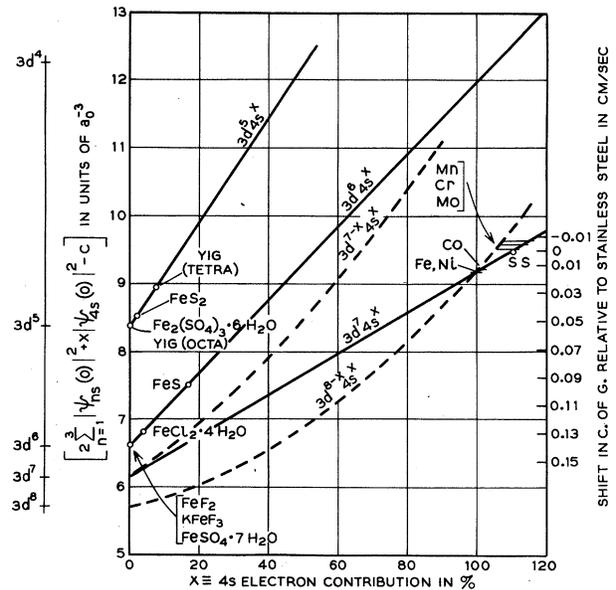

FIG. 1. A possible interpretation of the Fe^{57} Mössbauer isomer shifts in various solids. The total s-electron density is plotted as a function of the percentage of $4s$ character for various d-electron configurations. The reasons for placing the experimental data on given theoretical curves are discussed in the text. The constant $C = 11\,873\ a_0^{-3}$.

for, the evidence seems to point clearly to the configuration $3d^7 4s$ for this case. The smallness of the spread in shifts between the different metals indicates strongly that the configuration of the solute Fe is substantially the same in the metals investigated. For the Fe^{2+} and Fe^{3+} compounds, the experimental data are entered upon the $3d^6 4s^x$ and $3d^5 4s^x$ curves, respectively. This is consistent with the idea that in these covalent compounds the $4s$ atomic orbitals are partially occupied by electrons from the ligand ions (bonding orbitals).[10,11] The data for the "ferro" and "ferri" cyanides of potassium have not been plotted since it is not clear how to fit them into the above scheme. Indeed, since they have ground states which do not follow Hund's rule, it is unlikely that Watson's calculations are applicable to them. The fact that the isomer shifts in both cyanides are very small relative to each other and to stainless steel appears to be fortuitous.

From the observed isomer shift and the calculated difference in $|\psi(0)|^2$ for the d^5 and d^6 free-ion configurations we may compute the difference of the excited and ground-state charge

Table I. Observed shifts in gamma-ray energy in various iron compounds and d-group metals measured relative to type 310 stainless steel. (Source and absorber at room temperature.) The measured shifts contain contributions from the second-order Doppler shift and the zero-point energy shift in addition to the isomer shift discussed here. Measurements at 77°K[a] indicate that the second-order Doppler shift contributions are small compared to the total shift. Moreover, since the Doppler shifts are likely to be of similar magnitudes in the compounds considered, they will cancel, since we are ultimately concerned only with differences in the shifts between similar materials. The same is true of the zero-point energy shift. The uncertainty in comparing metals with salts is considerably greater. To convert the shifts from cm/sec to Mc/sec, one should multiply the values by 116. The errors indicated reflect the uncertainty in the last significant figure.

		Shift (cm/sec)
$3d^6$	FeF_2 (single crystal)	0.140 ±5
$3d^6$	$KFeF_3$	0.139 ±5
$3d^6$	$FeSO_4 \cdot 7H_2O$	0.140 ±5
$3d^6$	$FeCl_2 \cdot 4H_2O$	0.130 ±5
$3d^6$	FeS	~0.11 ±1
$3d^5$	$Fe_2(SO_4)_3 \cdot 6H_2O$	0.052 ±5
$3d^5$	Fe_2O_3[b]	0.047 ±5
$3d^5$	Yttrium-iron garnet, octahedral	0.057 ±5
$3d^5$	Yttrium-iron garnet, tetrahedral	0.026 ±5
	FeS_2 (pyrites)[c]	0.048 ±5
	FeS_2 (marcasite)	0.048 ±5
Metals	Fe[b]	0.015 ±5
	Co	0.012 ±5
	Ni	0.015 ±5
	Mn	-0.008 ±2
	Cr	-0.005 ±2
	Mo	-0.001 ±2
Cyanides	$K_4Fe(CN)_6 \cdot 3H_2O$	0.0083 ±10
	$K_3Fe(CN)_6$	0.0000 ±10

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[b]See reference 5.

[c]See reference 6.

radii using Eq. (1), assuming the usual charge radius dependence on mass number, i.e., $R = 1.20A^{1/3} \times 10^{-13}$ cm. We obtain $\delta R/R = 1.8 \times 10^{-3}$ as the fractional change in the charge radius, with the effective radius of the ground state larger than that of the excited state. This result is not unexpected[12] in sign and magnitude. The shell model predicts that the ground state for 3 odd neutrons outside a closed shell (28 neutrons), corresponding to a hole in the $2p_{3/2}$ shell, is one for which $I = 3/2$, as is the case for the 14-kev excited state. The large spin-orbit coupling precludes the possibility of a $2p_{1/2}$ configuration being the ground state.

Using the radial moments for an isotropic square well[13] and even assuming a proton excitation corresponding to $\Delta l = 3$ or 4, one still obtains a value of only 2×10^{-3} for $\delta R/R$. (The more likely case of a neutron excitation would leave the charge radius unchanged in a first approximation.) It is most unlikely therefore that the ground state is a simple shell state. It is interesting to note that the charge radius change expected for the addition of one particle (isotope shift at $A = 57$) is $\delta R/R \equiv \frac{1}{3}(\delta A/A) = 5.9 \times 10^{-3}$.

In the isomeric transition of Hg^{197} ($I_{gr} = 1/2 \rightarrow I_{ex} = 13/2$), it was estimated[2] that the charge redistribution corresponded to an increase of one-fourth to one-fifth of that observed experimentally for the addition of one neutron at $A = 157$. (The excited state has the larger charge distribution in this case.) Since both states are identifiable as single-particle neutron states, it is clear that a general charge redistribution accompanies the isomeric transition.

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EVIDENCE FOR THE EXISTENCE OF SURFACE EXCITONS IN TETRACENE MICROCRYSTALS*

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During the past few years there have been a number of predictions of new types of excitons in molecular crystals.[1]

Selivanenko[2] predicted the existence of surface excitons in molecular crystals with a high heat of fusion. Ferguson and Schneider[3] observed a b-polarized shoulder in a 0.2μ anthracene film which was not observed in thicker films. These authors believed that it was unlikely that this band be due to a surface exciton. However, McClure[1] interpreted this $25\,100$-cm^{-1} band as the b-polarized factor group component of the pure electronic transition occurring in these surface molecules.

We have observed two absorption bands in thin tetracene (microcrystalline) films prepared by rapid sublimation under conditions which produce a high surface-to-volume ratio. Rapid sublimation is essential[2] to increase the density of surface states.

No absorption above 5200 A was observed in thick crystals grown from the vapor under vacuum. However, when these same crystals were sublimed rapidly, under vacuum, onto a quartz disk forming a highly imperfect surface, a band at about 5400 A was observed. The two bands in the range 530-600 mμ could not be observed in the solutions made by dissolving the films in suitable solvents. This proves that these bands were not due to an impurity produced during the preparation.

Films were prepared under a pressure of 30 μ, but with different rates of sublimation. No absorption in the range 520-600 mμ occurred in

slowly sublimed films. However, films prepared by rapid sublimation (at 130°C) exhibited one strong band when the film was about 0.5 μ and two strong bands at a thickness of 1 - 1.5 μ. The 1 μ need not be the thickness of the microcrystals involved. This observation of a critical thickness is an indication that the 5330A band (I) involves either a minimum crystalline length or a crystalline structure that can exist in stable form only above a certain thickness. Below such a thickness either the strains or the large number of imperfections, due to the high (surface/volume) ratio, make such a crystalline structure unstable. Table I summarizes sample data on the positions and extinction coefficients. Band II at 5350 A shifts continuously to about 6000 A with increasing thickness. Band I is very sharp

Table I. Dependence of the position and intensity of the surface excitons on thickness.

Wavelength (A)	Thickness (μ)	$\epsilon \times 10^{-3}$ (cm^{-1})	Bandwidth (cm^{-1})
5344 (I)	1 - 2	...	25 - 75 (80°K)
5650 (II)	0.4 - 2	...	100 - 300 (300°K)
5340 (II)	0.4	4.2	...
5410 (II)	1	4.4	...
5540 (II)	1.3	4.9	...
5680 (II)	1.5	4.4	...