JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

The Mössbauer Effect in Some Iron Compounds

K. ÔNO, Y. ISHIKAWA AND A. ITO
Inst. for Solid State Physics, Univ. of Tokyo
Tokyo, Japan

AND

E. HIRAHARA
Tohoku Univ., Sendai, Japan

Magnetic properties of Fe_3O_4, αFe_2O_3, $FeS_{1.00}$, $FeS_{1.05}$ and Fe_3Al has been investigated with the method of the Mössbauer effect. The results obtained in this work are listed in Table I.

Mössbauer effect has been used as a tool to study many interesting phenomena in solid state physics, especially in magnetism. Measurements of the hyperfine splitting of the nuclear energy levels provide us with much fruitful information about the magnetic field at the nucleus as well as the electric field gradient tensor, which, in the case of iron, can never be measured with other methods because of Fe^{57} having $I=1/2$.

We have studied the variation of the internal magnetic field and, in particular, the electric field gradient with temperature in some antiferromagnetic and ferrimagnetic iron compounds.

Magnetite

Fe_3O_4 contains two types of sites; *A* site occupied by Fe^{3+} and *B* site occupied by Fe^{2+} and Fe^{3+}. Verwey suggested that above the transition temperature of about 120°K, there is a fast electron exchange between Fe^{2+} and Fe^{3+} on *B* site, while Fe^{2+} and Fe^{3+} are separately ordered below 120°K. The Mössbauer effect is the best method to confirm this hypothesis and measurements have been done in great details by our group. Independently of us, Anderson has also suggested the study of magnetite with Mössbauer effect and the experiment has been recently done by Israel group.[1] The results obtained by us at room temperature agree well with those obtained by Israel group. Below the transition temperature, however, our results are rather different from those of Israel group. The magnetite with enriched Fe^{57} was prepared, which was found to be single phase by X-ray analysis. A thin absorber was used in order to obtain the absorption spectrum without saturation effect, while a thick one to exaggerate weak absorption lines. The hyperfine spectrum of Fe^{57} in Fe_3O_4 obtained at 300°K for the thin absorber and that at 50°K for the thick one are shown as examples in Fig. 1 (a) and (b) respectively. Fig. 1 (a) shows that the relative intensity ratio of the two components of each partly resolved line is about 2 : 1, which corresponds to an actual ratio of ions on *B* and *A* sites. On the other hand, the strong absorption lines in a spectrum of Fig. 1 (b) are fairly saturated,

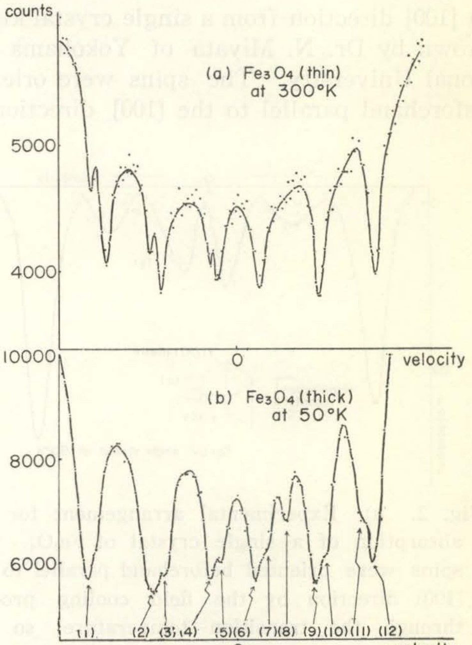

Fig. 1. a) Hyperfine spectrum of Fe^{57} in Fe_3O_4 obtained at 300°K for the thin absorber.
b) That obtained at 50°K for the thick absorber.

and a weak peak is apparently observed as is indicated at a position (8) in the figure. This weak line was not detected by Israel group. The hyperfine spectrum obtained at 220°K is very similar to that obtained at 300°K, while the spectrum taken at 90°K is the same as that at 50°K, indicating that the transition is completely accomplished even at 90°K. The hyperfine spectrum below the transition temperature is fairly complicated. Once we tried to explain this spectrum by assuming that the weak line at (8) corresponds to the 4th line of Fe^{2+} ions on B site; in other words, we attributed the peaks at (1), (2), (4), (6), (9) and (12) to the hyperfine splitting of Fe^{3+} ions on both A and B sites and the peaks at (3), (5), (7), (8), (10) and (11) to that of Fe^{2+} ions. This interpretation was very attractive, because not only we could explain whole lines consistently by assuming the Verwey order, but also the internal field of Fe^{2+} obtained from this analysis was fairly in good agreement with that of Fe^{2+} ions in the ordinary compounds. However we were compelled to give up this interpretation after careful experiments using a single crystal. The experiments were performed using, as an absorber, a thin slab of Fe_3O_4 cut normal to [100] direction from a single crystal kindly grown by Dr. N. Miyata of Yokohama National University. The spins were oriented beforehand parallel to the [100] direction by the field cooling process through the transition temperature. This slab was then arranged as shown in Fig. 2 (a). The magnetic moment was aligned in this case to the direction of observation. The result obtained at 90°K is shown in Fig. 2 (b). This figure shows clearly that the peaks at (2), (3), (9), (10) indicated in Fig. 1 (b) decrease appreciably, which suggests that these peaks contain no other lines than the 2nd and 5th ones of both Fe^{2+} and Fe^{3+} ions. According to the interpretation adopted at first, however, the 1st line of Fe^{2+} ions was considered to be situated at (3). Therefore this line must not be disappeared after magnetic annealing process. This was not actually observed and the first interpretation was found not to be correct. In the present stage, the weak peak at (8) is left unexplained, and we can not identify the hyperfine spectra of Fe^{2+} and Fe^{3+} ions correctly. Accordingly, it may only safely be said that the internal fields of both Fe^{2+} and Fe^{3+} are (510±35) KOe. The complete separation of Fe^{2+} and Fe^{3+} on B site below the transition temperature, therefore, could not be supported by this experiment. The results obtained are summarized in Table I.

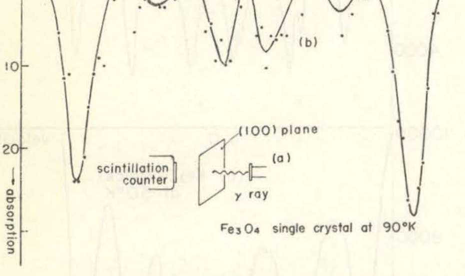

Fig. 2. a) Experimental arrangement for the absorption of a single crystal of Fe_3O_4. The spins were oriented beforehand parallel to the (100) direction by the field cooling process through the transition temperature, so the magnetic moment was aligned to the direction of observation.

b) Hyperfine spectrum of Fe^{57} obtained at 90°K in the single crystal of Fe_3O_4 with (100) parallel to the direction of observation.

α-Fe_2O_3

Kistner and Sunyar have shown that the internal magnetic field at the iron nucleus of this material is 515KOe and a small quadrupole interaction does exist.[2] We have also measured the hyperfine spectra from 90°K to 1000°K for this material. The absorption spectra observed at 300°K and 160°K are shown in Fig. 3 (a) and (b) respectively. In this figure, S_1 is the difference between the velocities at the first and the second peaks, and S_2 that between those at the fifth and sixth peaks. We found that S_1 is larger than S_2 at 300°K, while S_1 is smaller than S_2 at 160°K. (S_1-S_2) is known to correspond to $-(1/2)e^2qQ(3\cos^2\theta-1)$, where θ is the angle between the internal magnetic field, $\boldsymbol{H}_{\text{int}}$, and the axis of symmetry for the electric field gradient, q. The temperature dependence of (S_1-S_2) is shown in Fig. 4 (a). Here, the errors are fairly large. These are partly ordinary statistical errors and partly those which come from the unstability and nonlinearity of sensitivity of the loud speaker

Table I. Summary of data and derived quantities.

	Temp. (°K)	H_{eff} (KOe)			$e^2qQ/2$ (cm/sec)			δ (chemical shift) (cm/sec)		
		Fe^{2+}(B)	Fe^{3+}(B)	Fe^{3+}(A)	Fe^{2+}(B)	Fe^{3+}(B)	Fe^{3+}(A)	Fe^{2+}(B)	Fe^{3+}(B)	Fe^{3+}(A)
Fe_3O_4	300	450 (unresolved)		480	—		~0	~0.06		~0.02
〃	220	465 (unresolved)		495	—		~0	~0.06		~0.02
〃	90	510±35			—			—		
〃	50	510±35			—			—		
Fe_3O_4 (Israel group)	300	450		500	0		0	0.07		0.045
〃	85	450	510		0	0		0.115	0.065	
		Fe^{2+}	Fe^{3+}		Fe^{2+}	Fe^{3+}		Fe^{2+}	Fe^{3+}	
α-Fe_2O_3	300		515			0.04			0.05	
FeF_2 (Wertheim)	0	340			0.268					
$FeSO_4\cdot 7H_2O$	300				0.33			0.14		
$FeS_{1.00}$	300	320			~0.02			0.11		
Fe_3Al	300	295 230								

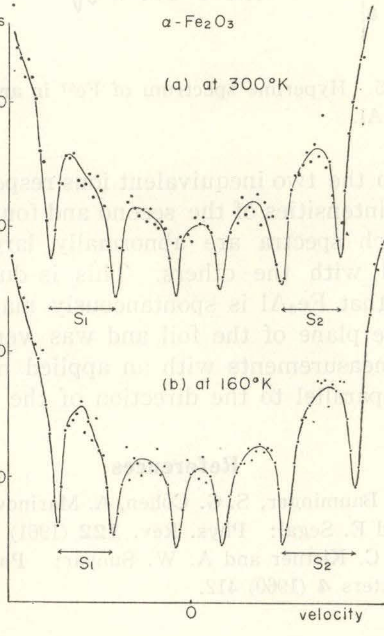

Fig. 3. a) Hyperfine spectrum of Fe^{57} in α-Fe_2O_3 observed at 300°K.
b) That obtained at 160°K.

used as a velocity detector of the radioactive source. In this figure, (S_1-S_2) are found to change rapidly from 210°K to 275°K changing its sign at 260°K. This abrupt change of (S_1-S_2) corresponds to the change of the spin direction from the *c*-axis to the *c*-plane at the transition temperature. The ratio of (S_1-S_2) at 210°K to that at 300°K is −2.0±0.2. This value corresponds exactly to the ratio of $(3\cos^2\theta-1)$ below and above the transition temperature, if we assume that the direction of q is parallel to the *c*-axis. This assumption is probable from the crystallographical consideration. This fact indicates that the magnitude of the electric field gradient tensor does not change through the transition temperature. The value of $e^2qQ/2$ obtained at 300°K was (0.04±0.01) cm/sec. The field gradient seems to increase slowly, and it increases abruptly near the Néel temperature. This anomalous increase in the electric field gradient may correspond to the anomalous change of the thermal expansion coefficient near the Néel temperature as is observed in some ordinary antiferromagnetic substances. Above the Néel temperature, we observed

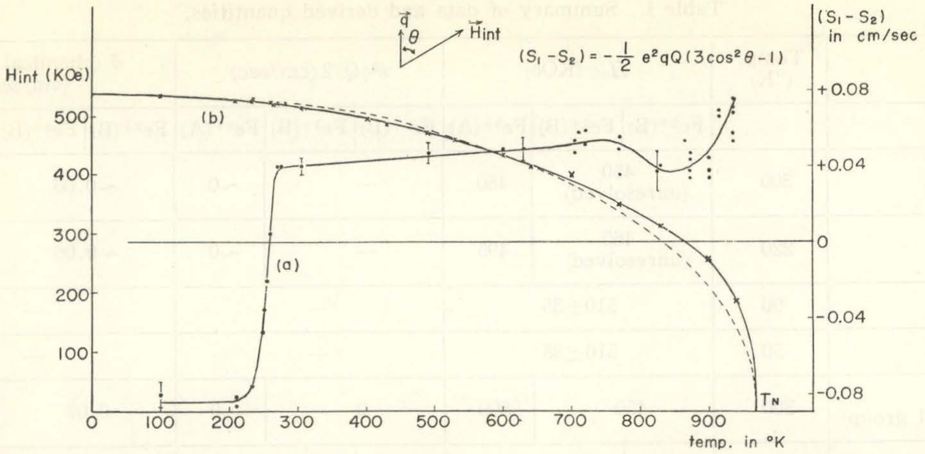

Fig. 4. a) Temperature dependence of $S_1-S_2=-(1/2)e^2qQ(3\cos^2\theta-1)$ in α-Fe_2O_3.
b) Temperature dependence of the internal magnetic field at the iron nucleus in α-Fe_2O_3. Dotted curve is the theoretical one for $S=5/2$ on the Weiss theory.

only one broad peak, indicating $e^2qQ/2<0.06$ cm/sec at 1000°K.

The curve (b) in Fig. 4 shows the internal magnetic field *vs* temperature. Dotted curve is the theoretical one for $S=5/2$ on the Weiss theory. The magnitude of the internal magnetic field is also found not to change at the transition temperature.

$FeS_{1.00}$ and $FeS_{1.05}$

The direction of spin in $FeS_{1.00}$ at 300°K and $FeS_{1.05}$ at 100°K are both along the *c* axis. The hyperfine spectra of them were very similar. Preliminary results obtained in $FeS_{1.00}$ are listed in Table 1. The values of the internal magnetic field is 320 KOe. $e^2qQ/2$ is small and it is about 0.02 cm/sec. (S_1-S_2) in $FeS_{1.05}$ at room temperature has opposite sign to that in $FeS_{1.00}$ at room temperature. This indicates that the direction of spin in $FeS_{1.05}$ at room temperature is perpendicular to the *c* axis.

Fe_3Al

The ordered Fe_3Al has two inequivalent iron ions. The hyperfine spectrum of Fe^{57} in the ordered Fe_3Al is shown in Fig. 5. Two hyperfine spectra are apparently resolved. The preliminary results show that the internal fields are 295 KOe and 230 KOe corresponding to the two inequivalent ions respectively. The intensities of the second and fourth lines of each spectra are abnormally large compared with the others. This is due to the fact that Fe_3Al is spontaneously magnetized in the plane of the foil and was verified by the measurements with an applied magnetic field parallel to the direction of the γ-ray.

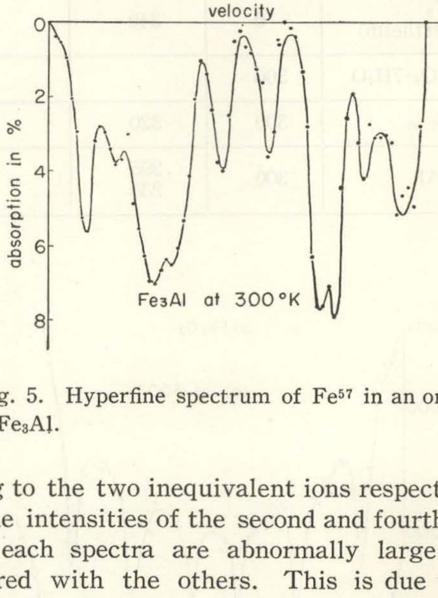

Fig. 5. Hyperfine spectrum of Fe^{57} in an ordered Fe_3Al.

References

1 R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer and E. Segal: Phys. Rev. **122** (1961) 1447.

2 O. C. Kistner and A. W. Sunyar: Phys. Rev. Letters **4** (1960) 412.

DISCUSSION

W. MARSHALL: It is very interesting that you find the quadrupole effect too small to be observable above T_N because we would not *a priori* expect *q* to vanish. However Burns and Wickner have pointed out that q is very sensitive to an internal cell structure parameter and that at a value quite close to the observed value, and within the experimental error of the X-ray experiments, q actually goes through zero. It seems possible therefore that the temperature dependence of the quadrupole effect is a consequence of a temperature dependence in this internal cell structure parameter.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Knight Shifts in the Intermetallic Compound $PtSn_2$*

S. S. DHARMATTI, V. UDAYA SHANKAR RAO
AND R. VIJAYARAGHAVAN
Tata Institute of Fundamental Research
Bombay, India

Introduction

It has been found by Rowland[1] that the Knight shift of Pt^{195} resonance in platinum metal is rather unusual in that it shows a large negative shift (−3.52%) with respect to its resonance in 1 molar chloroplatinic acid whereas normally in metals the shift is positive. Some light is thrown on its possible origin when one notes that a negative hyperfine interaction has been observed in the paramagnetic resonance spectra of Mn^{++} ion, which has a half-filled $3d$ electron shell with a net spin of 5/2. The theory of Abragam and Pryce[2] to explain this, by a mechanism in which one of the $3s$ electrons is promoted to a higher s state, has not been very successful to account for the magnitude of the interaction, though qualitatively it explained the origin of the negative interaction. On the other hand, Heine[3], and Wood and Pratt[4] have independently shown that the negative hyperfine interaction arises as a result of the inner s-shell electrons becoming unpaired due to exchange interaction with the $3d$ electrons. This mechanism could quantitatively account for the observed interaction in Mn^{++}. Goodings and Heine[5] have shown that the above explanation can also account for the fact that the effective magnetic field at the iron nucleus is directed oppositely to the electron magnetization. Therefore, in principle, there is no difficulty of understanding the occurrence of the negative Knight shift in platinum metal which has an unfilled $5d$ electron band. We wanted to study the effect of alloying on the Knight shift of Pt^{195} as there is a possibility of filling up of the d electron band with the electrons given by the guest metal, with which platinum is alloyed. A filling of the d electron band, would be expected to decrease its contribution to the magnetic susceptibility and thus give rise to a reduction in the exchange polarization. Hence the magnitude of the negative Knight shift should decrease or even assume a positive value. We studied the Pt^{195} and Sn^{119} resonances in the intermetallic compound $PtSn_2$, having a cubic structure, isotypic with CaF_2.

Experimental Results and Discussion

It is observed, that the Knight shift of Pt^{195} in $PtSn_2$ is −0.16% with respect to 1 molar chloroplatinic acid solution. Thus there is a large reduction in the magnitude of the negative Knight shift of this isotope from that of pure platinum metal. Pure platinum metal is paramagnetic with $\chi=1\times10^{-6}$ e.m.u./gm. A measurement of the susceptibility of the alloy showed that it has been reduced by a factor of four. This fall in the susceptibility is an indirect evidence

---

* Submitted for publication, in a condensed form, in "Il Nuovo Cimento".