

DISCUSSION

W. MARSHALL: At Harwell, C. Johnson and G. Perlow have observed the quadrupole effect in $FeSiF_6 \cdot 6H_2O$ following a suggestion by B. Bleaney that the electronic structure of this compound is simple enough for the quadrupole moment to be deduced unambiguously. In this compound the orbital triplet is split by a large amount so that only the lowest state, an orbital singlet, is occupied. We deduce $(1-\gamma)Q=0.12$ barns, so if we accept your value for γ we deduce $Q \simeq 0.2$ barns in excellent agreement with your value of $Q=0.18$ barns.

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Mössbauer Study of $FeTiO_3$ and Its Solid Solutions with αFe_2O_3

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The solid solutions $(1-x)FeTiO_3 \cdot xFe_2O_3$ exhibit strong ferrimagnetic moments for the compositions $x < 0.6$, where the Fe and Ti ions are ordered in the alternate (111) layers. The anomaly revealed by the Mössbauer measurements is that the ferrimagnetic phase consists of ferrimagnetic clusters surrounded by paramagnetic media. The size of these clusters decreases with increasing temperature or increasing local concentration of Ti. The isomer shift of $FeTiO_3$ is 1.2 mm/sec at room temperature as expected for Fe^{2+} . At 20°K, the hyperfine field was found to be 70 koe, considerably smaller than the expected value for Fe^{2+} .

Extensive investigation has previously been carried out on the $FeTiO_3$ - αFe_2O_3 system by magnetic¹⁻³⁾ and neutron diffraction⁴⁾ measurements. It was shown that the ordering of Fe and Ti, in composition on the $FeTiO_3$ side, results in strong ferrimagnetic moments though both the end members are antiferromagnetic. (See Fig. 1.) These solid solutions were re-examined by Mössbauer effect⁵⁾ in Fe^{57} , which gives new information concerning the magnetic as well as chemical environment.

Both ilmenite, $FeTiO_3$, and hematite, αFe_2O_3 , have the rhombohedral structure. αFe_2O_3 can be visualized as consisting of layers of Fe ions in the (111) planes with oxygen layers between them. The structure of $FeTiO_3$ can be derived from that of αFe_2O_3 by replacing every other layer of Fe ions by a layer of Ti ions. The neutron diffraction studies^{6), 4)} have shown that in both compounds the Fe spins are parallel within a given (111) plane and antiparallel between adjacent planes.

The Néel temperature of the solid solution system, $(1-x)FeTiO_3 \cdot xFe_2O_3$, increases almost

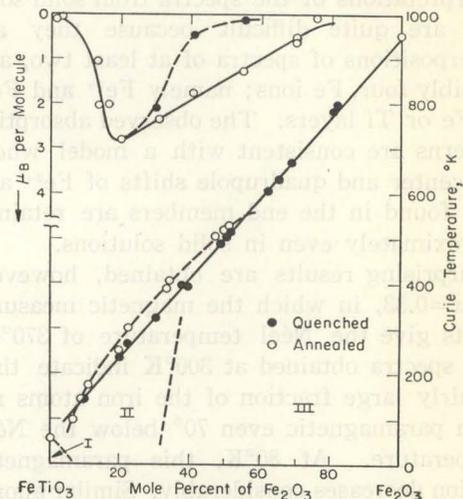


Fig. 1. Magnetic properties of $(1-x)FeTiO_3 \cdot xFe_2O_3$. According to Ishikawa and Akimoto²⁾ and Bozorth, Walsh, and Williams³⁾.

linearly from 55°K for FeTiO₃ to 950°K for Fe₂O₃. The large magnetic moments observed in compositions with $x \leq 0.6$ depend strongly on the heat treatment, especially near the composition $x=0.5$. The powder samples used in the present study are the same samples previously examined by neutron diffraction⁴.

The Mössbauer absorption of Fe⁵⁷ in FeTiO₃ was studied at 300°K, 80°K, and 20°K. The data are obtained by using a multi-channel analyser coupled with the instantaneous velocity measurement of the stainless steel source⁷. The center shift δ and a quadrupole splitting 2ϵ are, at 300°K, $\delta=1.20$, $\epsilon=0.31$ (mm/sec). This center shift is a typical value for Fe²⁺⁸. The measurement at 80°K gives $\delta=1.30$ and $\epsilon=0.50$.

The Mössbauer spectra obtained at 20°K, which is well below the Néel temperature of 55°K, can be explained by the assumption of $\delta=1.30$, $\epsilon=0.57$ (mm/sec) and $H_i=70$ koe. This hyperfine field is considerably lower than the expected values of 300–400 koe for Fe²⁺.

The Mössbauer spectra were taken, at room temperature, on compositions $x=0.12$, 0.33, 0.50, 0.70 and 1.00. The results on Fe₂O₃ ($x=1$) give $\delta=0.47$, $\epsilon=0.10$ (mm/sec) and $H_i=520$ koe and agree well with the work of Kistner and Sunyar⁹. Hyperfine "6 finger" patterns are observed for $x=0.50$ and 0.70, though they are noticeably blurred. Unique interpretations of the spectra from solid solution are quite difficult because they are superpositions of spectra of at least two, and possibly four, Fe ions; namely Fe²⁺ and Fe³⁺ on Fe or Ti layers. The observed absorption patterns are consistent with a model where the center and quadrupole shifts of Fe²⁺ and Fe³⁺ found in the end members are retained approximately even in solid solutions.

Surprising results are obtained, however, for $x=0.33$, in which the magnetic measurements give the Néel temperature of 370°K. The spectra obtained at 300°K indicate that a fairly large fraction of the iron atoms remain paramagnetic even 70° below the Néel temperature. At 80°K, this paramagnetic portion decreases considerably. Similar anomalies are not observed in the temperature dependence of the composition with $x=0.50$.

At $x=0.12$, an anomaly had been noted before in that, despite an observed magnetic

moment per molecule of one Bohr magneton, neutron diffraction had been unable to detect any long range order below the Néel point of 170°K. This suggested small ferrimagnetic clusters which are not sufficient in extent to produce coherent diffraction peaks. A Mössbauer spectrum at 80°K, however, shows a pattern typical of paramagnetic absorption, indicating that only a minority of the iron atoms are involved in these clusters. It must be emphasized that the Mössbauer pattern is contributed by all of the Fe atoms in the sample while the neutron diffraction is seeing only the magnetically ordered Fe atoms.

These results shed new light on the magnetic structure of the entire ferrimagnetic region. It appears that some kind of ferrimagnetic clusters, surrounded by paramagnetic media, must be assumed not only for $x=0.12$ but also for $x=0.33$. In the latter, it is not impossible that the observed paramagnetic characteristic may come from highly disordered magnetic sublattices or a small hyperfine field at Fe²⁺. The best hypothesis at the moment is, however, that the clusters are created by incomplete chemical order and their size decreases with increasing temperature or increasing local concentration of Ti.

Because of these anomalous results of Mössbauer absorption, the magnetic structure of the ferrimagnetic phase has recently been re-examined by neutron diffraction techniques¹⁰. The magnetic intensities of the (111) and (100) reflections, which are proportional to the total moment of the two sublattices, were investigated as a function of temperature. Intensities from $x=0.50$ follow closely the expected trend of the Brillouin function and no anomalies were observed. The composition $x=0.33$, on the other hand, exhibits a considerable amount of short range scattering in the temperature range where the Mössbauer absorption was found to be anomalous.

A part of the results of present investigation has been published lately¹¹ and the detailed account of the Mössbauer measurements, together with the neutron diffraction results, will be reported shortly.

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The antiferromagnetic phase of the system iron-palladium shows a small thermal expansion (negative behavior) at 30 At. % and larger, low temperature expansion at higher iron content. The behavior here is the opposite of the behavior of a magnetic sublattice which expands nearly up to pure iron. Due to the nature of a magnetic sublattice the expansion anomaly can be hardly explained here by a temperature dependent volume effect of ferro- and antiferromagnetic iron ions.

The iron property, i.e., anomalous thermal expansion, has been found especially in the cubic face centered phase of iron-nickel and non-platinum. It exists in the limited ranges of concentration around 35% Ni and 35% Pt, respectively. Besides the iron property these alloys have the following common characteristics which can be seen in Figs. 1 and 2.

(a) Relatively low Curie temperature in comparison with comparatively high magnetic and extremely high volume magnetostriction.

(b) Neighborhood to the region in which the phase becomes unstable and changes into the phase with a cubic body centered lattice by a dilatometer, martensitic type retraction.

(c) Neighborhood to the region in which the phase becomes unstable and changes into the phase with a cubic body centered lattice by a dilatometer, martensitic type retraction.

Further attempts of an investigation of the characteristic (b) by means of the partial overlapping of the x-ray transmission and its corresponding volume expansion in the iron region have been taken up by them. In order to circumvent the contradictions which result from the missing of expansion in the X-ray pattern and the instability of a phase at low temperatures, in 2-3 particles is highly dispersed and the particles are so small that they are nonmagnetic and can not be detected in the X-ray pattern. Another, these interpretations are difficult to prove experimentally, but could not be disproved as well.

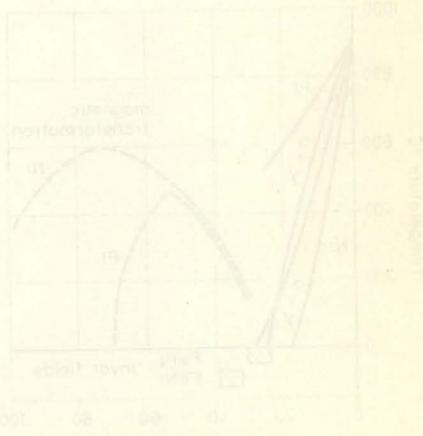


Fig. 1. Phase diagram of Fe-Ni and Fe-Pt alloys without ordered structures.