

Magnetic Anomaly in FeTiO_3 - $\alpha\text{Fe}_2\text{O}_3$ System by Mössbauer Effect

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The solid solutions $(1-x)\text{FeTiO}_3$ - $x\text{Fe}_2\text{O}_3$ 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+} , although the quadrupole splitting of 0.62 mm/sec is smaller than that observed in other ferrous environments.

EXTENSIVE investigation has previously been carried out on the FeTiO_3 - $\alpha\text{Fe}_2\text{O}_3$ system by magnetic¹⁻³ and neutron-diffraction⁴ measurements. It was shown that the ordering of Fe and Ti, in compositions on the FeTiO_3 side, results in strong ferrimagnetic moments though both the end members are antiferromagnetic. These solid solutions were reexamined by Mössbauer effect⁵ in Fe^{57} , which gives new information concerning the magnetic as well as chemical environment.

Both ilmenite, FeTiO_3 , and hematite, $\alpha\text{Fe}_2\text{O}_3$, have the rhombohedral structure. $\alpha\text{Fe}_2\text{O}_3$ 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 $\alpha\text{Fe}_2\text{O}_3$ 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, Fe spins are parallel within a given (111) plane and antiparallel between adjacent planes.

The Néel temperature of the solid solution system, $(1-x)\text{FeTiO}_3$ - $x\text{Fe}_2\text{O}_3$, increases almost linearly from 68°K for FeTiO_3 to 950°K for Fe_2O_3 . 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 this present study are the same samples previously examined by neutron diffraction.⁴

The Mössbauer absorption of Fe^{57} in FeTiO_3 at room temperature is shown in Fig. 1. The data are obtained by using multichannel analyzer coupled with the instantaneous velocity measurement of the stainless steel source.⁷ The center shift δ and a quadrupole splitting

2ϵ as defined in Fig. 1 are

$$\delta = 1.20 \pm 0.05, \quad \epsilon = 0.31 \pm 0.05 \text{ (mm/sec)}.$$

Measurement at 80°K gives $\delta = 1.30$ and $\epsilon = 0.50$. Walker, Wertheim, and Jaccarino⁸ have recently utilized ion wave-function calculations by Watson⁹ to calibrate the isomer shift, which constitutes the main part of the observed center shift. According to their interpretation, the observed center shift indicates that the electronic configuration of the iron in FeTiO_3 is $3d^6 4s^{0.1}$, in agreement with the cruder chemical description of "ferrous."

In addition to the major peaks, two small satellites appear around 0.6 and 1.9 mm/sec. Though these are barely outside of the counting statistics, they were also observed in two other independent runs at approximately the same positions. They give $\delta' = 1.25$ and $\epsilon' = 0.65$ mm/sec. These peaks might come from Fe^{3+}

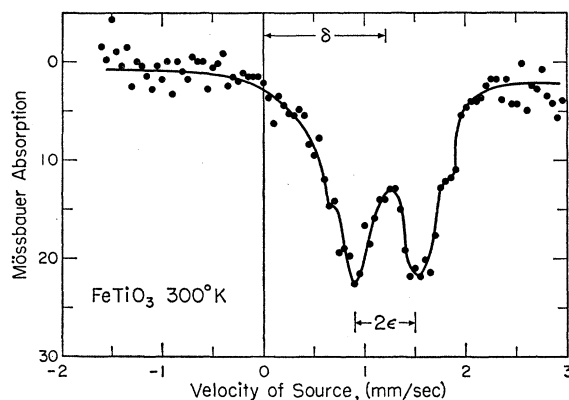


FIG. 1. Mössbauer absorption of FeTiO_3 . The source is 321 stainless steel and the areal density of the sample is 35 mg/cm². Positive velocity indicates a motion of source towards absorber. The ordinate represents additional Mössbauer absorption (in percent) after the background due to 120-kev γ rays is subtracted.

¹ T. Nagata, S. Akimoto, and S. Uyeda, *J. Geomag. Geoelec. (Kyoto)* **5**, 168 (1953); T. Nagata and S. Akimoto, *Geofis. pura e appl.* **34**, 36 (1956).

² Y. Ishikawa and S. Akimoto, *J. Phys. Soc. Japan* **12**, 834, 1081 (1957).

³ R. M. Bozorth, D. E. Walsh, and A. J. Williams, *Phys. Rev.* **108**, 157 (1957).

⁴ G. Shirane, S. J. Pickart, R. Nathans, and Y. Ishikawa, *J. Phys. Chem. Solids* **10**, 35 (1959).

⁵ R. L. Mössbauer, *Z. Physik* **151**, 124 (1958).

⁶ C. G. Shull, W. A. Strauser, and E. O. Wollan, *Phys. Rev.* **83**, 333 (1951).

⁷ S. L. Ruby and D. E. Bolef, *Phys. Rev. Letters* **5**, 5 (1960).

⁸ L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

⁹ R. E. Watson, Solid-State and Molecular Theory Group, Technical Report No. 12, Massachusetts Institute of Technology, June 15, 1959 (unpublished).

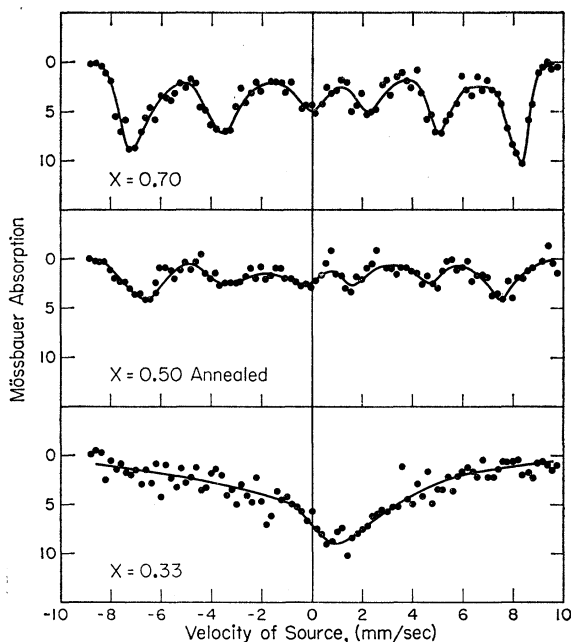


FIG. 2. Mössbauer absorption of $(1-x)\text{FeTiO}_3-x\text{Fe}_2\text{O}_3$. The corresponding Néel temperatures are 370°, 500°, and 670°K for $x=0.33$, 0.50, and 0.70, respectively.

ions which may exist in the sample because of slight nonstoichiometry ($\sim 1.5\%$ of Fe_2O_3 according to chemical analysis) or in the form of $\text{Fe}^{2+}\text{Ti}^{3+}\text{O}_3$. A more probable origin is Fe^{2+} in the Ti layers since the neutron diffraction measurements showed that approximately 5% of Fe^{2+} are located in the Ti layers. The latter assumption is supported by the fact that the center shift is like that of Fe^{2+} and not that of Fe^{3+} (usually ~ 0.5 mm/sec.). The difference in quadrupole splitting of the two kinds of Fe^{2+} , namely those in the Fe layers and those on the Ti layer, can be readily explained by different chemical environments in these two sites.⁴

Mössbauer spectra were taken, at room temperature, on compositions $x=0, 0.12, 0.33, 0.50, 0.70$, and 1.00. The results on Fe_2O_3 agree well with the work of Kistner and Sunyar.¹⁰ Figure 2 shows spectra for $x=0.50$ and 0.70. The Néel temperatures are 500° and 670°K, respectively, and hyperfine "6 finger" patterns are expected. This is observed, but they are noticeably blurred. Unique interpretations of the spectra from solid solutions are at best quite difficult because they are a superposition of contributions from at least two, and possibly four, Fe ions; namely, Fe^{2+} and Fe^{3+} on Fe or Ti layers.

¹⁰ O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

The observed absorption patterns are consistent with a model in which the center and quadrupole shifts of Fe^{2+} and Fe^{3+} found in the end members are retained approximately even in solid solutions and in which all iron atoms in a given sample see approximately the same internal field.

Surprising results are obtained, however, for $x=0.33$, in which the magnetic measurements indicated a Néel temperature of 370°K. The spectrum in Fig. 2 indicates that a fairly large fraction (about $\frac{1}{2}$) of the iron atoms remain paramagnetic even at 70°K below the Néel temperature. This fraction decreases at 80°K. This is in contradiction with the usual concept of a unique Néel temperature.

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. The best hypothesis at the moment is, however, that the clusters are created by incomplete chemical order and that their size decreases with increasing temperature or increasing local concentration of Ti. Under these circumstances, the Néel temperature is no longer well defined.¹¹ These ideas will be tested in the near future by Mössbauer and neutron diffraction measurements, both with low temperatures and with applied magnetic fields.

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¹¹ This model is quite similar to the one used by D. M. Grimes, S. Legvold, and E. F. Westrum, Jr. [Phys. Rev. 106, 866 (1957)] for mixed nickel-zinc ferrites.