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Magnetic Properties of Ilmenite-Hematite System at Low Temperature

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The magnetic properties of $FeTiO_3$ containing 8, 12, 17 and 21 mole per cent Fe_2O_3 have been investigated between 2°K and room temperature using a Cioffi-type automatic fluxmeter. It was confirmed that each specimen has a transition point at low temperature, which decreases in temperature with increasing content of Fe_2O_3. This transition point was found to be the temperature where the antiferromagnetic interaction between the second nearest neighbour Fe layers becomes effective over long distances in the crystal. Above the critical temperature, the specimens with 8 and 12 mole % Fe_2O_3 show superparamagnetic behavior. Through analysis of the superparamagnetic magnetization curves, the sizes of the superparamgnetic clusters and the temperature dependence of magnetization inside the clusters were determined. The average sizes of clusters in these crystals are found to be explained by a simple assumption that one Fe^{+3} ion which enters into the Ti layers of ilmenite aligns the spins of 9 nearest-neighbour Fe ions parallel through a superexchange interaction.

Introduction

There have been extensive investigations of the ilmenite hematite system, $(1-x)FeTiO_3$-xFe_2O_3.[1),2),3),4)] The most interesting feature of this system is the appearance of strong ferrimagnetism in a limited range of composition ($0.1 \leqq x \leqq 0.6$), which is considered to be a result of the ordering of Fe and Ti ions along the C-axis of the rhombohedral structure and of the antiparallel coupling between the spins on adjacent (111) layers. The existence of such a ferrimagnetic order was confirmed by neutron diffraction for the specimens with $0.2 \leqq x \leqq 0.6$, but no coherent magnetic pattern was observed for $x=0.12$ even at 4°K, despite the fact that a sample of this composition has a rather large magnetic moment at low temperature. This fact suggests that the ferrimagnetic order exists only in clusters in this crystal. In the present work, we have paid particular attention to such an unusual property on the ilmenite side of the composition range. Magnetic properties of ilmenites containing 8, 12, 17 and 21 mole % of Fe_2O_3 were investigated carefully to determine the size and the magnetic properties of clusters as well as the mechanism of their formation. The results obtained are presented in this paper.

Experimental Procedure

All specimens used in this experiment were prepared by the method described in a previous paper[1)]. They were found by X-ray analysis to be single phase and the compositions were determined by both X-ray and chemical analysis. The results are presented in Table I, which shows that the compositions determined by the two methods agree very well.

Table I. Composition determined by X-ray and chemical analysis.

No.	X-ray analysis		chemical analysis	
	$FeTiO_3$	Fe_2O_3	$FeTiO_3$	Fe_2O_3
1	92	8	91.07	8.93
2	88	12	88.34	11.66
3	83	17	83.06	16.94
4	79	21	79.64	20.36

The hysteresis loops of these specimens were measured between 2°K and room temperature using a Cioffi-type automatic fluxmeter. Both magnetization and magnetic field were detected by coils placed in the gap of an electromagnet, so that the hysteresis loop could be measured in either high fields (±20000 Oe) or a low fields (±100 Oe). The temperature of specimens was detected by a Cu *vs.* 2% Co-Au thermocouple and was controled automatically to an accuracy of ±0.5 °K.

Experimental Results

The magnetization-temperature curves of these specimens measured in a magnetic field of 20000 Oe are shown in Fig. 1. A marked maximum is observed in each curve which is in agreement with the results of Bozorth *et al*[3]. The hysteresis loops of the ilmenite sample containing 8 mole % Fe_2O_3 are presented in Fig. 2. As is seen in the figure, this composition exhibits hysteresis only below the critical temperature T_c=45°K. This temperature corresponds to the maximum of the magnetization *vs.* temperature curve. Above the critical temperature, the sample has no hysteresis and we consider it to be superparamagnetic. Such a transition from ferromagnetism to superparamagnetism is more clearly observed for the specimen containing 12 mole % Fe_2O_3, as shown in Fig. 3. In this case, the transition temperature is found to be about 25°K and typical superparamagnetic behavior is observed above 39°K. The absence of hysteresis in the superparamagnetic region was confirmed by measuring the magnetization in very weak fields (±100 Oe) with increased sensitivity in

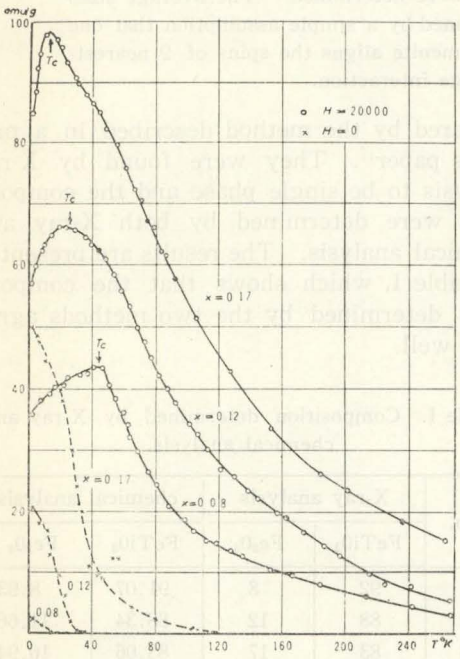

Fig. 1. Magnetization *vs.* temperature curves of specimens measured in a magnetic field of 20000 Oe.

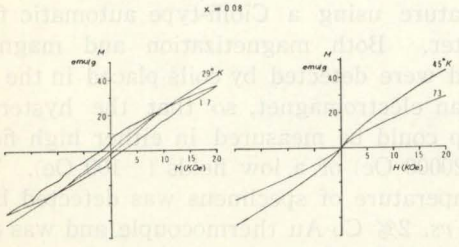

Fig. 2. Hysteresis loops of a specimen containing 8 mole%Fe_2O_3.

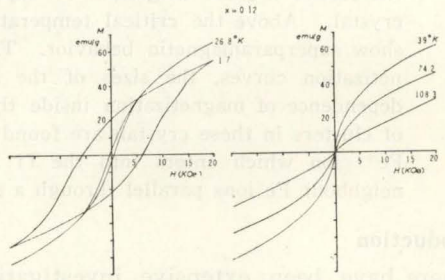

Fig. 3. Hysteresis loops of a specimen containing 12 mole%Fe_2O_3.

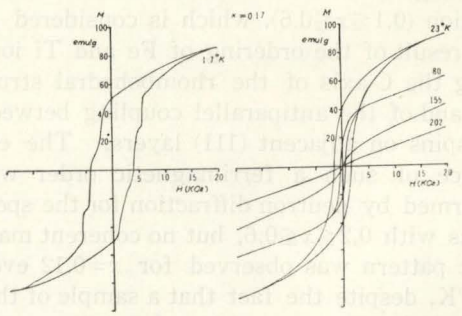

Fig. 4. Hysteresis loops of a specimen containing 17 mole%Fe_2O_3.

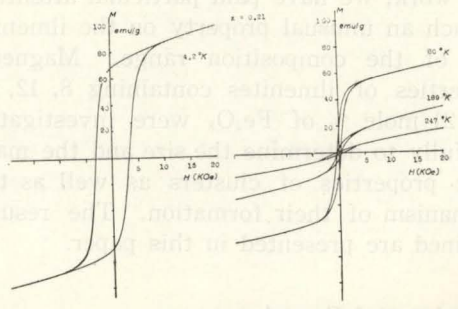

Fig. 5. Hysteresis loops of a specimen containing 21 mole%Fe_2O_3.

the measurement of magnetization. In contrast to this, the specimen with $x=0.17$ does not show superparamagnetic behavior even above the critical temperature $T_c=15°K$, and remanent magnetization is detected up to 100°K. The transition from ferromagnetism to antiferromagnetism, however, is not very sharp, as shown in Fig. 4. Consequently the determination of the Curie point is very difficult for this specimen. If the content of Fe_2O_3 exceeds 20 mole %, which corresponds to the composition range where long range magnetic order exists, the sample has, contrary to the former case, a definite Curie point near room temperature. The results obtained for $x=0.21$ is presented in Fig. 5.

Discussion

We have described in the previous section that specimens with $x=0.08$ and 0.12 show typical superparamagnetic behavior above the critical temperature. Therefore the size as well as the magnetic properties of the superparamagnetic cluster can be determined by analyzing the superparamagnetic magnetization curves. The analysis is rather difficult, because the initial susceptilities obey, in our case, not the Curie law but rather the Curie-Weiss law at low temperatures, so we must treat the superparamagnetism by assuming the presence of interactions between the clusters. The average sizes of the clusters, however, can be estimated from the Curie constant C_{mol} of the initial susceptibility.

$$\chi_{mol}=C_{mol}/(T-\theta)=MI_0/3k(T-\theta) \qquad (1)$$

where I_0 is the saturation magnetization of the crystal and M is that of the cluster, since

$$M=\tilde{v}I_s=(\sum_i n_i v_i)I_s \qquad (2)$$

where I_s is saturation magnetization of the substance of which the cluster is made and n_i is the fraction of the i-th cluster having a size v_i. The saturation magnetization I_s is not known for this composition range, so we

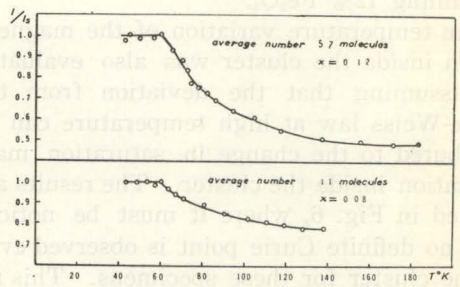

Fig. 6. Temperature dependence of magnetization inside the clusters of specimens containing 8 mole and 12 mole%Fe_2O_3.

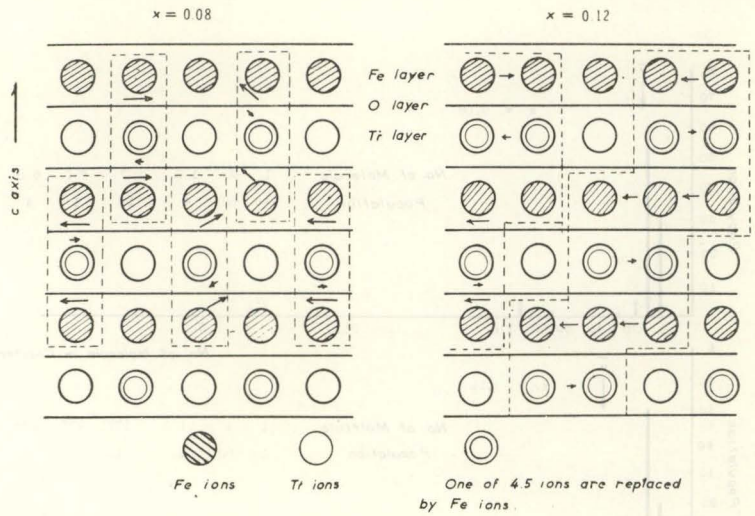

Fig. 7. Schematic representation of ilmenite containing a small amount of Fe_2O_3. Each circle represents 4.5 metal ions. A double circle indicates that one of 4.5 Ti ions is replaced by a ferric ion. The contour indicated by the broken line shows the cluster in which the magnetic moments are coupled in ferrimagnetic order.

have assumed that it varies as

$$I_s=4(1-x)\mu_B \qquad (3)$$

which is correct if the ferrimagnetic order which exists in the composition range $0.2 \leqq x \leqq 0.5$ is also established inside the cluster for x less than 0.2. Through an analysis of the initial susceptibilities, the clusters were determined to contain an average of 11 and 57 molecules for 8% and 12% Fe_2O_3, respectively. (By a molecule we mean one $FeTiO_3$ unit) The frequency of the thermal fluctuation of spins in such a small cluster should be very large, so that it is not surprising that Ruby and Shirane observed only a pattern typical of paramagnetic absorption at 80°K for the Mössbauer spectrum of ilmenite containing 12% Fe_2O_3.[5]

The temperature variation of the magnetization inside the cluster was also evaluated by assuming that the deviation from the Curie-Weiss law at high temperature can be attributed to the change in saturation magnetization inside the cluster. The results are plotted in Fig. 6, where it must be noticed that no definite Curie point is observed even in the cluster for these specimens. This result seems reasonable, because the short range order of spins in groups as large as the present clusters may remain coupled up to about 100°C above the Curie point even in an ordinary ferromagnet[6),7)].

Next we consider the mechanism of formation of the cluster. Fig. 7 is a schematic representations of ilmenite containing a small amount of Fe_2O_3. Each circle in the figure represents 4.5 metal ions. Such a division of metal sites is very convenient for understanding our problem, because each ion has a total of 9 nearest-neighbour metal ions with the most favourable interaction angle (~130°) in the two adjacent layers. Only this nearest neighbour interaction is important in the consideration of the superparamagnetism of this system, although the antiferromagnetic interaction which is the origin of the antiferromagnetism in pure ilmenite is found to act between the second nearest neighbour Fe layers below the critical temperature T_c. When one of the 4.5 Ti ions is replaced by an Fe^{3+} ion, as indicated by a double circle in the figure, this ions aligns the spins of the 9 neighbouring magnetic ions in adjacent layers through a superexchange interaction. Long range magnetic order can be developed throughout the whole crystal, if all Ti circles are replaced by "double circles," which should occur at 22 mole % Fe_2O_3. This is actually observed for the specimen containing more than 20 mole % Fe_2O_3. In the case of 8 mole %, only half of the Ti circles are replaced by "double circles" and the clusters of 9 molecules are isolated from each other as is shown in the left hand side of figure

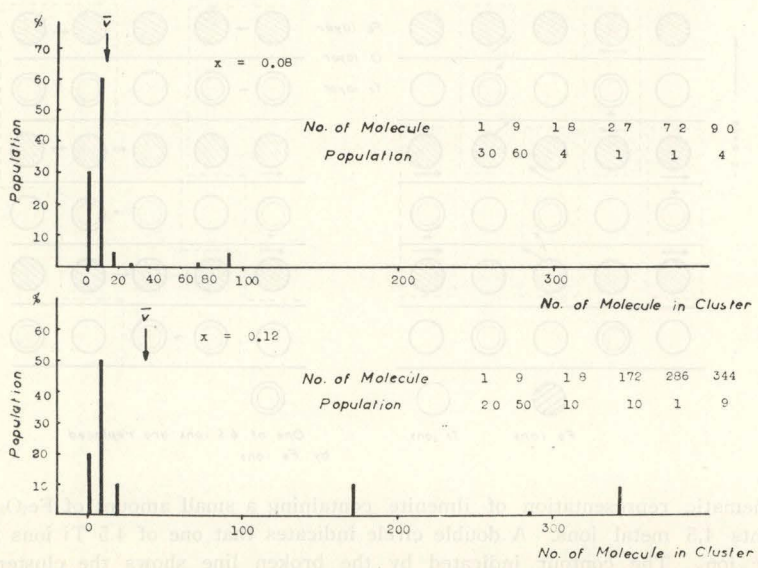

Fig. 8. Dispersion spectra of cluster size in the specimens containing 8 and 12 mole% Fe_2O_3.

by broken lines. On the other hand, if two thirds of Ti circles become "double circles" which would occur for 12 mole % Fe_2O_3, the right hand side of Fig. 7 suggests that clusters of 20 to 80 molecules can be expected. This size range is in good agreement with the experimental results. In order to fit the actual form of the superparamagnetic magnetization curves and their temperature dependences, a dispersion of the cluster sizes must be assumed. It was, however, found that no type of the analytical distribution function could explain the experimental curves. The best fit is achieved by assuming the distributions shown in Fig. 8. The dispersion spectra obtained suggest that about 20 to 30% of the magnetic ions are left uncoupled and at the same time some clusters with rather large sizes exist, which means that the Ti ions have some tendency to aggregate in this crystal.

The magnetic structure below the critical temperature is presumably very complicated, because not only are clusters with different sizes coupled antiferromagnetically with each other, but also the magnetic structure inside each cluster may become complicated. The fact that no long range magnetic order was detected by neutron diffraction for 12 mole % Fe_2O_3 is, therefore, attributed to such a complexity in the spin structure.

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