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## MORIN TRANSITION IN $\alpha$-Fe₂O₃ MICROCYRSTALS*

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Surface effects depress the Morin transition in microcrystals of $\alpha$-Fe₂O₃ by increasing the lattice spacing homogeneously throughout the whole microcrystal volume.

We have investigated the Morin transition in microcrystals of $\alpha$-Fe₂O₃ (hematite). Due to surface effects the lattice spacing in these microcrystals is larger than in bulk crystals. The Morin transition temperature is found to be depressed under this negative "equivalent pressure" at a rate comparable with the increase observed in bulk under hydrostatic pressures. The sharpness of the transition indicates that the change in the lattice spacing is homogeneous throughout the whole volume of the microcrystals.

Changes in the lattice spacing as a function of particle size have been observed before, for example, in gold microcrystals,[1] where they have been related[2] to observed increases[3] in the Debye-Waller factor. We have investigated this relationship quantitatively for $\alpha$-Fe₂O₃ microcrystals. The microcrystals were produced either by the technique described by Kündig et al.[4] using silica gel, or by heating nitrate solutions at controlled temperatures for short periods. To measure at the same time both the particle size and the lattice parameter, the various-sized crystallites were used as targets in a Co x-ray spectrometer. The Bragg peaks broaden with decreasing particle size, and are displayed as the lattice spacing changes from the bulk value. The change of lattice spacing with microcrystalline size is shown in Fig. 1. These results were obtained by evaluating several Bragg lines for each sample following the analysis of King and Alexander.[5] The lattice

spacing increases with decreasing particle size, and this increase is inversely proportional to the particle diameter. This inverse proportionality is similar (but opposite) to that occurring in a liquid drop under surface tension; it can be expressed as a negative free surface energy and is related to the modification of covalent bonds.[6,7] Drickamer has studied the pressure dependence of the lattice spacing in hematite.[8] At +180 kbar the volume change is $dV/V = -6.4\%$, which is equivalent in magnitude to the lattice spacing change $da/a = +2.1\%$ which we observe in 50-Å-diam particles. So we might say that 50-Å particles are under a pressure equivalent to minus 180 kbar.

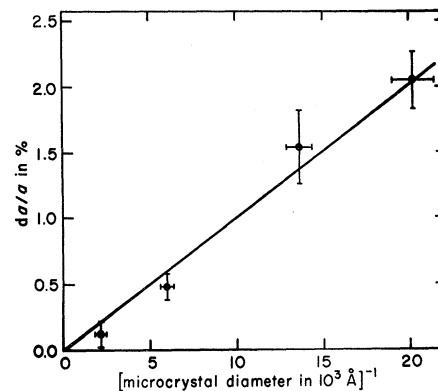Bulk $\alpha$-Fe₂O₃ undergoes a spin flip near 260°K,



FIG. 1. Particle size versus fractional lattice-spacing change $da/a$ for various-sized samples of hematite microcrystals.

the so-called Morin transition.[9,10] Above this transition the spins are almost perpendicular to the $z$ axis and the oxide is slightly ferromagnetic; below the transition the spins are along the $z$ axis and the oxide is antiferromagnetic. This transition is very pressure sensitive, with a pressure gradient of about 4°K/kbar.[11,12] By means of the Mössbauer effect we have measured the temperature at which this transition occurs both in bulk and in a sample with an average particle diameter of $525 \pm 100$ Å. Our experimental equipment was a Mössbauer spectrometer consisting of a TMC 305/306 electromechanical drive together with a TMC 404 multichannel analyzer operated in the multiscaling mode. The spectrum linearity was about 1% over the whole velocity range. The single-line source was $^{57}$Co diffused into Cu. The absorber was cooled in a liquid-nitrogen cryostat, in which the temperature could be controlled to within 2°K by means of a heating coil. The Mössbauer spectrum of $\alpha$-$Fe_2O_3$ below the Néel point (about 950°K) has six lines, corresponding to coupled magnetic and quadrupole interactions. The angle between the magnetization vector $\vec{H}$ and the electric field gradient $V_{zz}$ along the $z$ axis is $\theta(\vec{H}, z) = 90°$ above and $\theta(\vec{H}, z) = 0°$ below the Morin transition.[9,10] We label as 1 to 6 the resonance lines in the Mössbauer spectrum going from negative to positive velocities, and define $\Delta_{12}$ and $\Delta_{56}$, respectively, as the differences in velocity of the two outermost lines at negative and positive velocities. Then $\Delta = (\Delta_{12} - \Delta_{56})$ is proportional to $+\frac{1}{2}eQV_{zz}$ and $-eQV_{zz}$, respectively, above and below the Morin transition; i.e., the sign and magnitude of $\Delta$ change with the spin flip (cf. Ref. 4). As the criterion to evaluate the average transition temperature for our samples, we use the fact that $\Delta$ lies halfway between the two extreme values when half of a sample has undergone the transition.

Figure 2 shows the value of $\Delta$ as a function of temperature for bulk $\alpha$-$Fe_2O_3$ and for a sample of particles with an average diameter of $525 \pm 100$ Å. The Morin transition occurs at $258 \pm 2$°K for the bulk sample in agreement with the average value of 257°K of Umebayashi et al.[12] For the 525-Å sample, on the other hand, it has been suppressed to $166 \pm 10$°K. From this data we can calculate the pressure coefficient

$$K_P = \frac{dT}{(da/a)}$$

for the Morin transition. Here $dT$ is the change in the transition temperature for a fractional change $da/a$ in the lattice spacing. We do not want to use the coefficient expressed in terms of the pressure $P$, because at higher pressures $P$ is not proportional to $da/a$ (cf. Fig. 1 of Ref. 8). The lattice spacing for the 525-Å particles is larger by $da/a = +0.20 \pm 0.04\%$ than for bulk. According to Lewis et al.[8] this is equivalent to $-29 \pm 6$ kbar. The Morin transition has been depressed by $92 \pm 10$°K through this spacing change, corresponding to a coefficient $K_P = -(4.6 \pm 1.1) \times 10^4$ °K. This agrees within error with the experimental values for this coefficient obtained under hydrostatic pressure by nmr[11] and neutron-diffraction techniques,[12] namely $K_P(\sim 3.6 \pm 0.3°K/kbar) = -(5.8 \pm 0.8) \times 10^4$ °K and $K_P(\sim 3.7 \pm 0.2°K/kbar) = -(5.9 \pm 0.7) \times 10^4$ °K, respectively. It does disagree with an earlier value of $K_P(\sim +10°K/kbar) = 16 \times 10^4$ °K as determined by astatic magnetometer measurements.[13] So it appears to make sense to talk about negative "equivalent pressure" in microcrystals. Kündig et al.[4] find that the Morin transition does not take place in their sample with average particle size of 180 Å. This is easily explained on the basis of the above consideration: For 180-Å particles $da/a = 0.58\%$ from Fig. 1. If $K_P$ is independent of temperature, the Morin transition will be depressed by 290°K to below absolute zero; i.e., it will not be detectable.
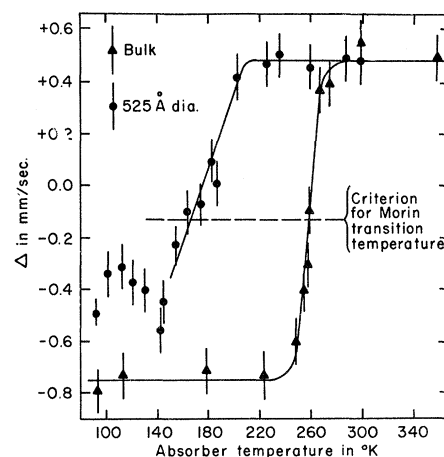
Even more significant than the determination



FIG. 2. $\Delta$ versus the temperature in hematite for a bulk sample and for a sample with an average microcrystal diameter of $525 \pm 100$ Å. $\Delta$ is a measure of the fraction of the sample which has undergone the Morin transition (spin-flip).

of the value of this coefficient at negative "equivalent pressures" is the fact that the coefficient can be so clearly fixed. The surprising thing is that such a sharp transition between a positive and a negative value for $\Delta$ occurs. This indicates that the particle size distribution in the sample is narrow—at least at the large-diameter end of the distribution. And even more important, we can conclude that the change in the lattice parameter is homogeneous throughout the whole microcrystal volume. In the past (cf. Maradudin,[14] Burton and Godwin,[15] and Kündig et al.[16]), surface effects have generally been viewed as distorting the first few surface atomic layers, while not significantly affecting the bulk below. The present experiments indicate otherwise. Since the 525-Å crystals are about 100 atomic layers thick, if the surface effects were restricted to the top few layers, a sizable portion of the sample would be under bulk conditions. Since bulk undergoes the transition at 258°K, we would then have the Morin transition spread all the way from 258°K on down. Instead, we see a very abrupt onset of the transition at about 200°K.

In Fig. 2 the magnitude of $\Delta$ for the bulk sample increases by a factor of about 1.5 in going through the Morin transition. This increase should actually be a factor of 2; however the linearity of our apparatus is not good enough to state whether this agreement is significant or not. For the 525-Å sample the transition is never completed. It is clear from the actual Mössbauer spectra that a fraction of the sample has not undergone the transition. Whether this fraction consists of very small particles, or whether the magnetization vector never flips for some of the sample, still has to be investigated.

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