The Anomalous Thermal Expansion of Hematite at a High Temperature

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It has long been known that magnetic and specific heat anomalies are shown by hematite, α-Fe_2O_3, in the 650—700°C region.

Néel[1] has suggested that this magnetic change comprises a transition from an antiferromagnetic state below 675°C to a paramagnetic one above this temperature.

However, when Willis and Rooksby[2] examined the crystal structure of hematite at elevated temperatures from 20°C to 950°C by means of a high temperature X-ray powder camera, they did not find any crystallographic phase transitions. However, at a temperature near 675°C the expansion coefficient of the c_h-axis in the hexagonal system showed a sudden increase. These results were interpreted in terms of the magnetic transition of pure hematite.

Finch and Sinha[3] observed the surface of a hematite single crystal by electron diffraction after heating it in air at 700°C; they concluded that γ-Fe_2O_3 was the stable form of Fe_2O_3 at high temperatures.

Blackman and Kaye[4] examined single crystals of hematite between 700°C and 1000°C by electron diffraction; they claimed that, in some cases, oriented layers of Fe_3O_4 occurred, but, in contrast to the results of Finch and Sinha, they found no evidence for the presence of γ-Fe_2O_3.

In view of these differences in the high temperature structural behavior of hematite, the present investigations were undertaken in order to determine the change in the unit cell of hematite precisely.

Experimental

The materials used in this experiment were specular hematite, obtained from the Quebec-Cartier Company of Canada, and reagent grade hematite, α-Fe_2O_3, obtained from the Fisher Scientific Company. The specular hematite, which was ground in a small tungsten carbide ball mill, contained about 2.5% Fe_3O_4 and a small percentage of SiO_2. This hematite ore powder was pre-heated at about 1000°C for 1 hr. because the original powder has lattice strains resulting from the grinding. Minus 325 mesh fractions of powder samples of both hematite ore and Fisher reagent were taken for X-ray measurements.

The equipment used was a Norelco X-ray difractometer, with, attached, a Materials Research Corporation Model X86-N furnace using a platinum ribbon heater.

The spacings of (10.4), (11.0) and (30.0) of hematite were measured at 50°C intervals, from room temperature to 1100°C, through the heating and cooling cycles. Both the heating and cooling rates of the furnace were 10°C per minute, and the specimens were kept at a constant temperature for 10 min. before performing the X-ray measurements.

The thermocouple measurements were calibrated by the data of the lattice parameter changes for magnesium oxide as a function of the temperature;[5] moreover, in this experiment the lattice strain of magnesium oxide due to the distorsion of the sample holder during heating was checked at each temperature by the above data of the lattice parameter for magnesium oxide.[5] The temperature control of the furnace was maintained within ±5°C.

The lattice parameters of the hexagonal cell, a_h and c_h, at each temperature were computed from the measured average reflection angles, without taking corrections by the extraporation method. The rhombohedral unit cell dimensions, the cell edge, a_R, and the angle, α, were computed from the hexagonal lattice parameters.

Results and Discussion

The lattice parameter values at each temperature during heating and cooling are plotted in Figs. 1 and 2 as functions of the temperature. Figure 1 compares the thermal expansions of both a_h- and c_h-axes with one together. The values shown are $\Delta a_{ht}/a_{h20}$ and $\Delta c_{ht}/c_{h20}$ in percent for a_h- and c_h-axes expansions respectively. a_{h20} or c_{h20} means the lattice parameter value at 20°C, while Δa_{ht} or Δc_{ht} means the difference between each parameter value at 20°C and at t°C. In this case, the lattice parameter values at each temperature in the cooling stage were slightly larger than those in the heating stage. Figure 2 shows the expansion of the rhombohedral cell edge, $\Delta a_{Rt}/a_{R20}$, in percent. a_{R20} is the value

1) L. Néel, *Ann. Phys., Paris*, **12**, 249 (1949).
2) B. T. M. Willis and H. P. Rooksby, *Proc. Phys. Soc.*, **65B**, 950 (1952).
3) G. I. Finch and K. P. Sinha, *Proc. Roy. Soc.*, **A241**, 1 (1957).
4) M. Blackman and G. Kaye, *Proc. Phys. Soc.*, **75**, 364 (1960).
5) W. J. Campbell, *U. S. Bureau of Mines, Reports of Investigation*, No. 6115 (1962).

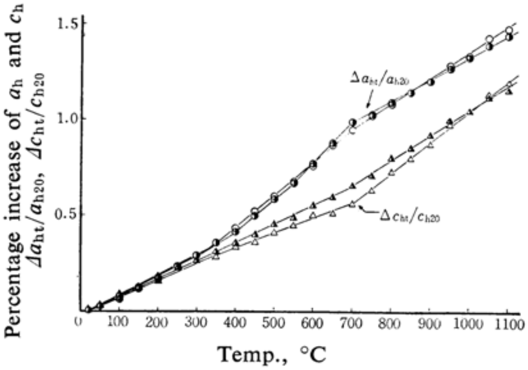

Fig. 1. Thermal expansion of hexagonal lattice parameters for hematite ore.

○—○ Heating stage
◑—◑ Cooling stage
△—△ Heating stage
▲—▲ Cooling stage

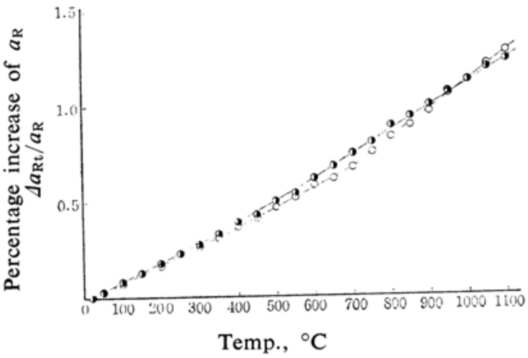

Fig. 2. Thermal expansion of rhombohedral lattice parameter for hematite ore.

○—○ Heating stage
◑—◑ Cooling stage

of the cell edge at 20°C. Δa_{Rt} is the difference between the cell edge values at 20°C and at t°C. Figure 3 shows the rhombohedral angle-temperature curve for the expansion of the rhombohedral unit cell.

As may be seen in these figures, two anomalies, at about 300°C and 700°C, are observed for the thermal expansion curve of hematite. The hexagonal lattice parameters increase uniformly from room temperature to about 300°C, and they also increase almost uniformly above about 700°C; however, in the temperature range from about 300°C to 700°C, the two axes show different expansion behavior. Similar behavior is also observed in the experiment with Fisher hematite.

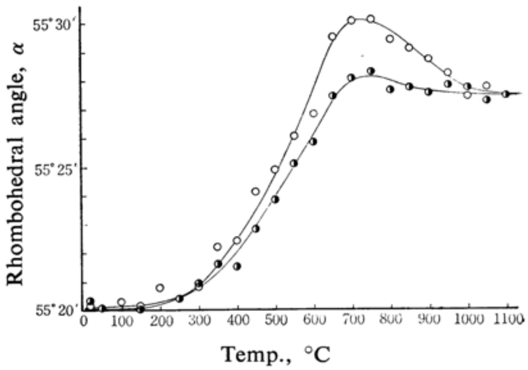

Fig. 3. Rhombohedral angle variation with temperature for hematite ore.

○—○ Heating stage
◑—◑ Cooling stage

It has, therefore, been found that the rhombohedral hematite has three stages of thermal expansion. Below about 300°C and above about 700°C the rhombohedral angle is almost constant, but in the temperature range from about 300°C to 700°C the rhombohedral angle increases. On the other hand, as may be seen in Fig. 3, the values of α in the 700—800°C range during heating are slightly larger than during cooling above 700°C. This irreversibility of the rhombohedral cell expansion at high temperatures during the heating and cooling cycles was also observed in the experiment with Fisher hematite. X-ray measurements were also performed in a nitrogen atmosphere, but no distinct differences were observed. On further heating above 1100°C, the rhombohedral unit cell of hematite underwent a complete deformation because of its dissociation to magnetite.

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