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MÖSSBAUER SPECTROSCOPY OF STRONTIUM FERRITES RELATED TO PERMANENT MAGNET MATERIALS

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1. Introduction.- Current interests in the synthesis and magnetic properties of SrFe$_{12}$O$_{19}$ are directed toward (1) the reaction mechanism, which is known to be different from that for BaFe$_{12}$O$_{19}$, but is otherwise controversial and not well understood /1/, especially for the technically important non-stoichiometric compositions; and (2) the physical and chemical basis for the superior magnetic properties of the non-stoichiometric materials compared to those of stoichiometric SrFe$_{12}$O$_{19}$ /2/. The optimal compositions for non-stoichiometric hexaferrites correspond to SrO/Fe$_2$O$_3$ ratios in the reactants between 1/5 and 1/5.5.

We report here on our investigation of two aspects of the above concerns: First, we have sought to determine the existence of an intermediate phase, its crystal chemical characteristics and role in the formation of SrFe$_{12}$O$_{19}$; and secondly, we have attempted to establish the nature of the non-stoichiometry in the hexaferrites with excess strontium, i.e. whether single-phase or multi-phase and if multi-phase, the magnetic character of each phase.

2. Experimental.- Sample preparation and the acquisition of the Mössbauer spectra were as described previously /3/, except for the use of ultra-high purity (99.99 % pure) SrCO$_3$ and Fe$_2$O$_3$.

3. Results and discussion.- SrFe$_{12}$O$_{19}$ does not form directly from SrO and Fe$_2$O$_3$; SrFe$_2$O$_5$ and Sr$_2$Fe$_3$O$_7$ had been reported /4/ as the intermediate phases.

first appearing at 925 K and reacting at 1025 K and above with Fe$_2$O$_3$ to give SrFe$_{12}$O$_{19}$. This reaction scheme has been questioned recently /1/ and the following reaction sequence has been proposed for the formation of SrFe$_{12}$O$_{19}$ from SrCO$_3$ and Fe$_2$O$_3$.

$$
\text{SrCO}_3 + 6\text{Fe}_2\text{O}_3 = \text{SrFe}_{12}\text{O}_{19} + 5.5\text{Fe}_2\text{O}_3 + \text{CO}_2$$(1)

$$
\text{SrFe}_{12-x}\text{O}_{19} + 5.5\text{Fe}_2\text{O}_3 = \text{SrFe}_{12}\text{O}_{19} + (\frac{1 - 2x}{4})\text{O}_2 \quad (2)
$$

This reaction sequence is clearly confirmed by the $^{57}$Fe Mössbauer spectra in figure 1. Below 990 K, the reaction mixture consists of hematite, SrO and a small quantity of SrFe$_{3-x}$O$_{2-x}$, $x = 0.15$, as indicated by the weak absorption near -0.2 mm/s$^{-1}$. At 1073 K, the concentration of SrFe$_{3-x}$O$_{2-x}$ has increased substantially and SrFe$_{12}$O$_{19}$ is also present. At 1178 K, SrFe$_{3-x}$O$_{2-x}$ is no longer present and the resulting material is single phase SrFe$_{12}$O$_{19}$. No evidence exists for the presence of SrFe$_2$O$_4$ or Sr$_2$Fe$_2$O$_5$.

For reaction mixtures with excess strontium, the reaction mechanism is apparently more complicated than that given by equations (1) and (2). First, SrFe$_{3-x}$O$_{2-x}$ is not present among the reaction products as might be expected on the basis of equations (1) and (2) /1/. Before this investigation, it was not certain whether these two latter formulae represented two distinct phases; however, during the process of annealing SrFe$_{12}$O$_{19}$ at 1473 K, it was observed that the Mössbauer spectrum approached that of SrFe$_6$O$_{13}$, for long annealing times.
We, therefore, conclude that the correct composition for the phase in question is Sr$_4$Fe$_6$O$_{13}$ for which the $^{57}$Fe Mössbauer spectrum is shown in figure 2. The spectrum of this material is quite different from that of SrFe$_{12}$O$_{19}$ and it is therefore surprising that Sr$_4$Fe$_6$O$_{13}$ has not been observed in the Mössbauer spectra of non-stoichiometric Sr-hexaferrites /3/. To determine the detectability of Sr$_4$Fe$_6$O$_{13}$ in a mixture of SrFe$_{12}$O$_{19}$, a highly non-stoichiometric composition, i.e. SrO/Fe$_2$O$_3$ = 1/3, was fired to give a product in which the intensity of the X-ray diffraction lines of Sr$_4$Fe$_6$O$_{13}$ was comparable to that of SrFe$_{12}$O$_{19}$, and a mechanical mixture of 28 mole percent Sr$_4$Fe$_6$O$_{13}$ and 72 mole percent SrFe$_{12}$O$_{19}$ was also prepared. As seen from figure 2, the spectra of these two phase mixtures can be accounted for within the usual goodness-of-fit criterion on the assumption that SrFe$_{12}$O$_{19}$, alone, is present. $^{57}$Fe Mössbauer spectra of the sample with the 1/3 SrO/Fe$_2$O$_3$ ratio taken above the Néel temperature of Sr$_4$Fe$_6$O$_{13}$ clearly demonstrates the presence of this phase. Consequently, it is entirely possible that Sr$_4$Fe$_6$O$_{13}$ is present in non-stoichiometric Sr-hexaferrites but goes undetected in the Mössbauer spectra. Indeed a reconsideration of the spectra presented in an earlier study /3/ shows that the resolution of the spectra between 6.7 mm.s$^{-1}$ and 9.3 mm.s$^{-1}$ depends sensitively on the SrO:Fe$_2$O$_3$ stoichiometry. For highly stoichiometric materials all five magnetic sublattices can be observed in the 298 K spectrum in the absence of an applied magnetic field. As the SrO/Fe$_2$O$_3$ ratio varies from 1/6 to 1/5, the five, well-resolved lines between 6.7 mm.s$^{-1}$ and 9.3 mm.s$^{-1}$ degenerate into three, highly-broadened absorption lines. Thus, even though the presence of Sr$_4$Fe$_6$O$_{13}$ in non-stoichiometric hexaferrites is not obvious, there are some features which can be definitively associated with the existence of this phase and which can, in principle, be put on a quantitative basis.

It is noteworthy that strontium hexaferrites having unusually large values for the remanent magnetization and coercive force /3/ exhibit poorly-resolved
lines in the 6.7 mm.s$^{-1}$ to 9.3 mm.s$^{-1}$ region of their Mössbauer spectra. This result suggests that Sr$_4$Fe$_6$O$_{13}$ may have a significant beneficial effect on the bulk magnetic properties of ceramic compacts of nonstoichiometric Sr-hexaferrites. Whether this beneficial influence is effected through texture control or a direct superposition of the magnetic properties of the two phases must await further experimentation.

In summary, the present investigation has shown the following: (1) SrFe$_{1-x}$Fe$_x$ is an intermediate phase in the formation of SrFe$_{12}$O$_{19}$ from SrCO$_3$ and Fe$_2$O$_3$; (2) high purity, stoichiometric SrFe$_{12}$O$_{19}$ exhibits a 298 K Mössbauer spectrum in which all five magnetic sublattices are obvious; (3) nonstoichiometric Sr-hexaferrites contain Sr$_4$Fe$_6$O$_{13}$; and (4) Sr$_4$Fe$_6$O$_{13}$ among the final products of nonstoichiometric materials has a beneficial influence on the bulk magnetic properties compared to materials resulting from stoichiometric starting compositions.

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