

Comment on "Electron Diffraction Superlattice Lines in Magnesium Ferrite"

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THE electron diffraction pattern of thin films of magnesium ferrite was investigated by Walters and Wirtz.¹ All lines of the pattern could be indexed as spinel lines except those labeled 002 and 402, which are forbidden for the spinel structure. To determine the origin of the forbidden lines, two possible explanations have to be taken into account, i.e. (1) double diffraction of the electron beam, which is often found in thin films, and (2) a superlattice structure caused by ordering of the cations on the octahedral sites in the spinel lattice. Walters and Wirtz chose the latter explanation because they did not find the forbidden lines in the electron diffraction pattern of $MgAl_2O_4$ films. The conclusion was based on the consideration that $MgAl_2O_4$ has the normal spinel structure, with only one type of cation on the octahedral sites, whereas $MgFe_2O_4$ is an inverse spinel having two types of cations on the octahedral sites which could order in a superlattice structure.

The same forbidden reflections* have been found² by electron diffraction in manganese ferrite films. The extra lines could not be attributed to a second phase. Manganese ferrite has largely the normal spinel structure, as represented by the formula $Mn_{0.8}Fe_{0.2}[Mn_{0.2}Fe_{0.8}]O_4$, in which the fraction of octahedral ions is written between the brackets. In fact, the fraction of Mn ions on the octahedral sites in the films of Ref. 2 is expected to be even smaller than that given in the formula because they were prepared at rather low temperatures. The films investigated also included specimens having Mn contents lower than $MnFe_2O_4$. Consequently, the Mn/Fe ratio on octahedral sites is estimated to be $\approx 1:20$. This structure would produce an ordering that is very weak, if it exists at all.

The possibility of ionic ordering should also be considered from the point of view of available energy. A kind of Madelung energy can be calculated for the ordered ions only, taking into consideration weakening of this effect by the dielectric constant. Such a calculation is rather complicated, but the ordering energy must be proportional to the square of the ordered charges. Long-range ordering in the inverse spinel structure has, for example, been established³ in ferrous ferrite, $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, at $\approx 120^\circ K$. In this ferrite, ordering involves rearrangement of electrons, which are sufficiently mobile at these low temperatures, and the ordering energy results from the difference of 1 electronic charge. An example of long-range ordering by rearrangement of ions has

been found⁴ in lithium ferrite, $Fe^{3+}[Li_{0.5}^{1+}Fe_{1.5}^{3+}]O_4$, at $\approx 1020^\circ K$. At this temperature the ionic mobility is sufficient, and in this case the ordering energy results from a difference of 2 electronic charges between the octahedral ions.

In the Mn ferrite, ordering should be ionic, but the difference in electronic charge is only 1. From the foregoing examples, it follows that the ordering temperature will be much too low to be realized by ionic diffusion. Even short-range ordering, as proposed by Romeijn⁵ for inverse spinels, would be very unlikely because of the small Mn/Fe ratio on the octahedral sites. It is not expected that such an effect would be clearly evident in the diffraction pattern. Moreover, an ordering effect would not be detectable because the diffracting capabilities of octahedral Mn and Fe ions are nearly equal because their atomic numbers differ by only 1. Therefore, a superlattice structure has to be excluded as the origin of the extra lines. Double diffraction remains the more probable explanation for the forbidden reflections in Mn ferrite. In our opinion, the same conclusion holds for inverse spinels such as Mg ferrite, in which the electronic charge difference between the ions is only 1. However, the conditions necessary for double diffraction in ferrite films have yet to be determined.

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*In Ref. 2 the 331 line was erroneously indicated as a forbidden reflection. This line is allowed for the spinel structure, although it is not indexed by the Joint Committee on Powder Diffraction Standards.

¹ D. S. Walters and G. P. Wirtz, "Electron Diffraction Superlattice Lines in Magnesium Ferrite," *J. Amer. Ceram. Soc.*, 55 [1] 59 (1972).

² W. S. Hulscher, K. G. van den Berg, and J. C. Lodder, "Manganese Ferrite Thin Films: I," *Thin Solid Films*, 9 [3] 363-75 (1972).

³ E. J. W. Verwey and P. W. Haayman, "Electronic Conductivity and Transition Point of Magnetite (Fe_3O_4)," *Physica*, 8 [9] 979-87 (1941).

⁴ P. B. Braun, "Superstructure in Spinel," *Nature (London)*, 170, 1123 (1952).

⁵ F. C. Romeijn, "Physical and Crystallographical Properties of Some Spinel: I and II," *Philips Res. Rep.*, 8 [4] 304-20 (1953).

Reply by G. P. Wirtz

IN COMMENTING on the note by Walters and Wirtz,¹ Hulscher and Jonker² have taken the subject of octahedral cation ordering in $MgFe_2O_4$ out of context. This ordering was proposed to explain the kinetics of cation redistribution between octahedral and tetrahedral sites.³ The superlattice lines, observed later, were offered as supporting evidence for the proposed mechanism. The suggestion of alternative mechanisms yielding the observed kinetic behavior would be gratefully received. The observation of superlattice lines in $MnFe_2O_4$ is noteworthy but scarcely refutes our attribution of the superlattice lines in $MgFe_2O_4$ to octahedral sublattice ordering. Hulscher and Jonker attempt to establish 4 main points, which will be discussed in turn.

Hulscher and Jonker state that Mn ferrite is largely a normal spinel, as expressed by the formula $(Mn_{0.8}Fe_{0.2})[Mn_{0.2}Fe_{0.8}]O_4$. The fact that this determination seems to have been made nearly 20 years ago,⁴ on totally different samples, may or may not be pertinent. Without firm evidence to the contrary, the present worker will continue to suspect that the equilibrium cation distribution in $MnFe_2O_4$ is also temperature-dependent. However, even if only 10% of the octahedral

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