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Comments on the Defect Structure in Wüstite

Several authors have shown experimentally that the defects in $Fe_{1-x}O$ consist of cation vacancy clusters and occluded interstitial cations. In fact, it has been shown that these clusters are based on attached groups of tetrahedra, each consisting of vacancies at the apices, with the interstitial ion in the center (*1*, *2*) and sharing corners. The ratio of vacancies to tetrahedrally coordinated cations (ρ) is ≈ 3.2 from these studies, and this ratio has been confirmed by neutron scattering studies on polycrystals at high temperatures in gaseous environments (*3*). The method employed was the least-squares refinement procedure for integrated intensities (P) typical for structural studies with a modest number of atoms per unit cell. [The arrangement can only be obtained experimentally from an analysis of diffuse scattering, as was done in Refs. (*1*, *2*). Integrated Bragg peaks as in Ref. (*3*) can only give the ratio of vacancies to tetrahedral ions.] The defect arrangement has been examined by theoretical methods (*4*), which showed that edge sharing was slightly favored over corner sharing.

Recently, in this journal, Gavarri *et al.* (*5*) published a study of this problem employing high-temperature powder diffraction which purports to show that the ratio, ρ, is less than 3, and thus that the corner-sharing cluster (described above) is unlikely. Their results were obtained by considering the ratio of two powder peaks, the 200 and 220. Whereas least-squares refinement of intensities at least partly includes the effect of thermal diffuse scattering (TDS) in the Debye–Waller factors (*3*, *6*), this is not the case when peak ratios are employed.

Accordingly, we have reexamined the data in Ref. (*5*). We chose their method I, which assumes a continuous flat background. (Their second method attempts to subtract the diffuse scattering from the vacancy clusters, but this is clearly difficult to estimate with any precision; see the dotted lines in their Fig. 2.) As Willis (*7*) has shown that the TDS correction is identical to that for X rays for the large contribution due to acoustic modes (except in special cases), we employed the correction formula in Ref. (*6*), for $\sigma = P(\mathrm{TDS})/P(hkl)$, the ratio of the two contributions. Then, P measured $= (1 + \sigma)P_{\mathrm{true}}$. To employ this correction, it is only necessary to know the 2θ scan ranges for the peak and background which were estimated from Fig. 2 in Ref. (*5*), the Debye–Waller factors which were taken from Ref. (*3*), and the lattice parameters which were taken from Ref. (*8*). The measurements in Ref. (*5*) were reported in sufficient detail to estimate the P's; see Tables 1 and 2. Integration ranges were taken to be 6°2θ and 9°2θ for the 200 and 220 reflections. If smaller ranges were employed by Gavarri *et al.*, shoulders of the peaks were excluded. TDS was then subtracted and the ratio of Eq. (3) in Ref. (*5*) for the two peaks was employed to obtain the ratio of cation vacancies to tetrahedral iron (ρ). The TDS correction was 21% for the 220 peak, 7.5% for the 200. The results are as follows:

$\rho = 3.3$ for $x = 0.0988$, 1075°C,

$\rho = 3.3$ for $x = 0.0907$, 985°C.

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These values are clearly in agreement with all previous studies. At the very least, this result indicates that there is some question concerning the conclusions in Ref. 5. Further work at high temperatures with single crystals would be useful.

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E. GARTSTEIN
J. B. COHEN

Department of Materials Science
and Engineering
The Technological Institute
Northwestern University
Evanston, Illinois 60201

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