JOURNAL OF SOLID STATE CHEMISTRY 36, 255–256 (1981)

NOTE

Letter to the Editor about "Comments on the Defect Structure in Wüstite"

In paper (*1*), concerning the defect structure of wüstite $Fe_{1-z}O$, a mean value $\rho = (z + t)/t = 2.4$ was determined with a small statistical scatter such that $\pm\Delta\rho = 0.03$ but with each value being known with an evaluated absolute uncertainty ± 0.4. Contesting a note (*2*) which discussed this uncertainty, it is important to point out that, of course, a small variation of ρ cannot be excluded within the range [2.0–2.8]. In addition, good agreement with most of the results in the literature is observed.

The results (*1*) were obtained without making the classical correction for thermal diffuse scattering (TDS) which can be evaluated, for example, from Chipman and Paskin's model (*3, 4*). For this reason, Gartstein and Cohen (*4*) have discussed the procedure chosen in (*1*) leading to the mean value of ρ. According to them, the TDS correction would modify the final results in a large way.

The purpose of this note is to rebut this affirmation and to justify the experimental procedure selected in (*1*).

1. The major part of the results published by Cheetham *et al.* (*5*) is not modified in a large manner by TDS corrections. The authors (*5*) clearly explain why these corrections are not useful.

2. In the least-squares procedure, it is well known that the largest intensities are predominant in the calculation. So the most accurate intensities $I(hkl)$, i.e., those measured for the peaks (200), (220), and (222) for the smallest θ angles, were selected to determine the two parameters B and ρ. For higher-angle peaks the background is too complicated to be evaluated because of the overlapping of several undulations.

3. To make a correct TDS calculation, it is necessary to estimate the experimental factor $(\Delta \cdot \cos\,\theta)$ from the diffraction profiles. In the so-called second method of (*1*) considered alone as physically significant the Bragg peaks have been exploited taking into account their profiles, the diffuse scattering varying with z and with the temperature, and the errors involved when drawing the various profiles. Such a variable background includes the TDS contribution. In other words, the TDS correction is only valid when a flat background is involved without any defect structure, which is not the case in wüstite $Fe_{1-z}O$.

However, an overestimation of the true TDS influence on the final results may be given. Let us choose a sample with a small value of z in order to minimize the defect structure influence: $n°$ 3 with $z = 0.058$ at $\Theta = 1075°C$ (1). According to the model (*3*) and using the intensities measured by the second method (*1*):

$$I_{hkl}^{\text{obs}} = I_{hkl}^{\text{true}} + \sigma_{hkl} \cdot I_{hkl}^{\text{true}},$$

$$\sigma_{hkl} = (\pi/3)^{1/3} \cdot \frac{h^2 + k^2 + l^2}{a} \cdot \frac{\Delta\cos\theta}{\lambda} \cdot \frac{B_{\text{Th}}^{\text{true}}}{4}.$$

According to the law [9] from (*1*):

$$B(z,\Theta) = B_{\text{St}}(z) + B_{\text{Th}}(\Theta).$$

At $\Theta = 1075°C$, $B_{\text{Th}}(1075) = 2.7$ Å^2, $B_{\text{St}}(0.058) = 0.20$ Å^2, $\lambda = 1.0$ Å, $a = 4.37$

0022-4596/81/020255-02$02.00/0

Å, $\Delta \cdot \cos\theta = 0.061$. The values found for σ are $\sigma_{200} = 3.8\%$, $\sigma_{220} = 7.7\%$, $\sigma_{222} = 11.5\%$.

We may calculate B_{Th}^{true}, assuming that the σ values are small, that is to say: $I^{obs} \simeq I^{true} \cdot \exp(+\sigma_{hkl})$. So we find:

$$B_{Th}^{true} = 2.7 + 0.36 = 3.06\ \text{Å}^2.$$

And thence the value

$$B^{true} = B_{St} + B_{Th}^{true} = 3.26\ \text{Å}^2$$

allows us to calculate the ratio ρ from $I(200)$ and $I(220)$. In place of $\rho = 2.30$ (*1*), we obtain the overestimated value $\rho = 2.35$. As it has already been pointed out in (*5*), the TDS correction modifies significantly only the temperature factor B_{Th} but not the ratio ρ.

For small values of z, the defect structure is negligible. However, there is an important undulation with a gaussian-like profile under the (220) Bragg peak. It corresponds to the TDS contribution. Since this profile of diffusion is drawn, it is possible to deduct the TDS contribution under the Bragg peaks. Calculated (*3*) and measured TDS contributions have neighboring values.

This remark seems to validate again our experimental procedure which allows us to deduce the values of ρ without making any TDS corrections.

On the other hand, verifications have been obtained from structural models which were partly described in (*6, 7*) and which will be published shortly (*8*).

References

1. J. R. Gavarri, C. Carel, and D. Weigel, *J. Solid State Chem.* **29**, 81 (1979).
2. P. Vallet, *J. Solid State Chem.* **29**, 299 (1979).
3. D. R. Chipman and A. Paskin, *J. Appl. Phys.* **30**, 1998 (1959).
4. E. Gartstein and J. B. Cohen, *J. Solid State Chem.* **33**, 271 (1980).
5. A. K. Cheetham, B. E. F. Fender, and R. I. Taylor, *J. Phys. C* **4**, 2160 (1971).
6. J. R. Gavarri, Thèse de Doctorat ès Sciences, Paris, 23 Sept. 1978.
7. J. R. Gavarri and C. Carel, Poster session, 6th European Crystallographic Meeting, Barcelona, Spain, July 1980.
8. J. R. Gavarri and C. Carel, Evolution structurale de monoxydes nonstoechiométriques du type wüstite. Simulations et relations entre paramètres structuraux. To be published.

J. R. Gavarri
D. Weigel

ERA au CNRS n° 456
Ecole Centrale des Arts et Manufactures
92290 Chatenay-Malabry, France

C. Carel

Laboratoire de Cristallochimie
L.A. au CNRS n° 254
35042 Rennes Cédex, France

Received June 25, 1980, in revised form September 30, 1980