Conduction in Ionic Materials

18.D6 This problem asks, for the nonstoichiometric $Fe_{(1-x)}O$, given the electrical conductivity [1200 (Ω -m)⁻¹] and hole mobility (1.0 x 10⁻⁵ m²/V-s) that we determine the value of *x*. It is first necessary to compute the number of holes per unit volume (*p*) using Equation 18.17. Thus

$$p = \frac{\sigma}{|e|\mu_h}$$

$$= \frac{1200 \ (\Omega - m)^{-1}}{(1.602 \ \times 10^{-19} \ C)(1.0 \ \times 10^{-5} \ m^2 / V - s)} = 7.49 \ \times \ 10^{26} \ holes/m^3$$

Inasmuch as it is assumed that the acceptor states are saturated, the number of vacancies is also $7.49 \times 10^{26} \text{ m}^{-3}$. Next, it is possible to compute the number of vacancies per unit cell by taking the product of the number of vacancies per cubic meter times the volume of a unit cell. This volume is just the unit cell edge length (0.437 nm) cubed:

$$\frac{\# \text{ vacancies}}{\text{unit cell}} = (7.49 \times 10^{26} \text{ m}^{-3})(0.437 \text{ x} 10^{-9} \text{ m})^3 = 0.0625$$

A unit cell for the sodium chloride structure contains the equivalence of four cations and four anions. Thus, if we take as a basis for this problem 10 unit cells, there will be 0.625 vacancies, 40 O^{2-} ions, and 39.375 iron ions (since 0.625 of the iron sites is vacant). (It should also be noted that since two Fe³⁺ ions are created for each vacancy, that of the 39.375 iron ions, 38.125 of them are Fe²⁺ and 1.25 of them are Fe³⁺). In order to find the value of (1 - x) in the chemical formula, we just take the ratio of the number of total Fe ions (39.375) and the number of total Fe ion sites (40). Thus

$$(1-x) = \frac{39.375}{40} = 0.984$$

Or the formula for this nonstoichiometric material is $Fe_{0.984}O$.

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