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Structural Realization of Oxygen Nonstoichiometry in Nickel–Zinc Ferrite*

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We have carried out a study of nickel–zinc ferrite of composition $Zn_{0.218}Ni_{0.752}Fe_{2.03}O_{4+\gamma}$ with varying oxygen nonstoichiometry γ. The method used was to measure the intensity of three groups of X-ray reflections on single crystal specimens with subsequent division of the amounts of mean-square dynamic and static displacement of the ions on the sublattices. From the amount of static displacement compared to two calculated models, one of which was based on an ionic approximation while the other was based on approximation of an elastically isotropic continuum, the character and distribution of point defects in the spinel structure was determined. It was established that in nickel–zinc ferrite with $\gamma < 0$ anion vacancies are formed whereas with $\gamma > 0$ vacancies appear in the octahedral cation sublattice.

Introduction

Examination of ferrites as phases of variable composition with deviations from stoichiometry in the oxygen and cation sublattices (*1*) requires rigorous care in their synthesis inasmuch as nonstoichiometry can exert a substantial influence on the various properties of the materials.

In accord with the present theory of disorder (*2*), nonstoichiometry of a crystal is related to formation of point defects of the vacancy type or to insertion of ions in interstitial structural positions. Considering that ferrites with spinel structure have two cationic and one anionic sublattice, it is difficult without direct experimentation to resolve the question of the nature of the predominant point defects. In a few cases, the necessary information can be obtained from thermodynamic investigations. Nevertheless, the nature of the defects and the character of their distribution over the sublattices of a complex crystal can be determined on the basis of structural investigations combined with measurement of the intensity of diffracted reflections in defect crystals. The presence of point defects in a crystal leads to a rise in static displacements of the ions from their equilibrium positions, contributing further to a weakening in the intensity of the X-ray reflection, dependent on thermal oscillation of the ions.

In this work we used the X-ray method for determining the full mean-square displacements of the ions in crystals with spinel structure with subsequent division of dynamic and static displacements in each of the three sublattices. To characterize the type of defects and their distribution, the experimental data were compared with values of $\bar{U}_{st}^2$ as calculated on an ionic model (I) and on an elastically isotropic continuum (II).

Objects and Methods of the Experiment

An X-ray study of nonstoichiometry defects was carried out on single crystals of nickel–zinc ferrite of composition $Zn_{0.218}Ni_{0.752}Fe_{2.03}O_{4+\gamma}$ pulled from the melt at $p_{O_2} = 12$ atm. On the basis of chemical analysis data, the initial monocrystals had a notable deficit of oxygen corresponding to degree of nonstoichiometry $\gamma = -0.022$. Samples with various values of γ were obtained by thermal treatment at differing partial pressures of oxygen. A composition corresponding to $\gamma = +0.004$ was obtained by quenching after annealing for 100 hr at 900°C and $p_{O_2} = 1$ atm; after annealing for 24 hr at a temperature of 1050°C and $p_{O_2} = 0.21$ atm, $\gamma = -0.025$.

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X-Ray measurements were made on spherical samples with a diameter of 0.4–0.6 mm, using incident radiation Mo*Kα* on a URS-50 IM diffractometer. Monochromatization was realized by reflection from the (200) plane of a LiF monocrystal or (002) of graphite.

We determined complete mean-square displacements $\bar{U}^2_{\mathrm{st+dyn}}$ at temperatures of 300 and 163 K by measuring the angular dependence of the integrated intensity of reflection of three groups of the spinel crystal lattice. We measured the intensity of reflections (800)–(12 12 0), (600)–(10 10 0), and (666)–(10 10 10). The choice of reflections with large values of the sum of the squares of the indices allowed us to eliminate the influence of primary extinction and to decrease the error due to uncertainty in the atom form factor of oxygen. Pairs of reflections were selected so that the intensity of the reflections for each of them was dependent on a different summary contribution from the cationic and anionic spinel sublattices (*3*).

The method of measurement was verified on a silicon monocrystal for which we obtained a value of the Debye characteristic temperature of 560 ± 5 K, which agrees with published data (*4*).

Structure amplitudes of the measured reflections were determined in the following fashion:

$$\begin{aligned} F_{880} &= 8f_T + 16f_O + 29.2f_K, \\ F_{12\,12\,0} &= 8f_T + 16f_O + 25.8f_K, \\ F_{660} &= -8f_T - 1.6f_K, \\ F_{10\,10\,0} &= -8f_T - 4.4f_K, \\ F_{666} &= 16f_O - 28.8f_K, \\ F_{10\,10\,10} &= 16f_O - 24.1f_K. \end{aligned} \tag{1}$$

Here f_T, f_O, and f_K are the mean atomic scattering functions of the tetrahedral, octahedral, and oxygen sublattices, respectively. The values for the coefficients for the oxygen sublattices in formulas (1) were determined by calculating the oxygen parameter, which, in agreement with Ref. (*5*), was found equal to 0.382. The cation distribution in a nickel–zinc ferrite of similar composition, as was shown in (*5*), does not change over a wide interval of temperature, in connection with which F_{hkl} was calculated for the cation distribution $\mathrm{Zn}^{2+}_{0.218}\mathrm{Fe}^{3+}_{0.782}[\mathrm{Ni}^{2+}_{0.752}\mathrm{Fe}^{3+}_{1.248}]$. Atomic scattering factors for the ions Fe^{3+}, Zn^{2+}, and Ni^{2+} were taken from tables (*6*) and corrected for anomalous dispersion and for O^{2-}, from Ref. (*7*). The mean atomic scattering factor for each cationic sublattice was obtained from

$$f_i = \frac{\sum \mu_j f_j}{\mu_j} \tag{2}$$

where μ_j is the number of cations j in the corresponding sublattice.

Separation of the values of the static, $\bar{U}^2_{\mathrm{st}}$, and dynamic, $\bar{U}^2_{\mathrm{dyn}}$, displacement of the ions in the sublattices was effected from the temperature dependence of the complete mean-square displacements $\bar{U}^2$. Independent of the form of the phonon spectrum

$$\bar{U}^2 = \bar{U}^2_{\mathrm{dyn}} + \bar{U}^2_{\mathrm{st}} = A\frac{kT}{m} + \frac{\hbar^2}{4mkT} + \bar{U}^2_{\mathrm{st}}, \tag{3}$$

where $A = \int_0^\infty [g(\omega)/\omega^2]\,d\omega$ and $g(\omega)$ is the number of vibrations in the frequency range ω and $\omega + d\omega$. Considering that, in the temperature interval used (300–163 K), the quantity A does not depend on temperature

$$\bar{U}^2 - \frac{\hbar^2}{4mkT} = A\frac{kT}{m} + \bar{U}^2_{\mathrm{st}},$$

there is a linear dependence on temperature. In such case, at $T = 0$ K the straight-line intersects the ordinate axis at the value $\bar{U}^2_{\mathrm{st}}$.

The error in measuring the integrated intensity of reflections was 1–2%. By taking account of the errors of the calculation method, the maximum error in determination of the values of $\bar{U}^2_{\mathrm{st}}$ came to about 14%.

Discussion

The values found for the mean-square static and dynamic displacements for the three sublattices of nickel–zinc ferrite and the lattice constants *a* are shown in Table I.

By correlation of the values $\bar{U}^2_{i\mathrm{st}}$ for the various sublattices and the summary values $\sum_i \bar{U}^2_{i\mathrm{st}}$, there is obtained an evaluation of the type and distribution of point defects in nickel–zinc ferrite crystals differing in oxygen nonstoichiometry.

In the first case the data of Ref. (*8*) were used, where, from an ionic approximation model with calculation of the strength of electrostatic interaction and Born repulsion, we determined the relative values of mean-square static distortions accompanying formation of various kinds of point defects in crystals with spinel structure. The behavior of the measured values $\bar{U}^2_{i\mathrm{st}}$

TABLE I

VALUES OF THE MEAN-SQUARE DYNAMIC AND STATIC DISPLACEMENTS AND LATTICE CONSTANTS OF NICKEL–ZINC FERRITES $Zn_{0.218}Ni_{0.752}Fe_{2.03}O_{4+\gamma}$

Non-stoichiometry Ni–Zn ferrite γ	$a \pm 0.002$ Å	$\bar{U}^2_{i\,\mathrm{dyn}} \times 10^2$ (Å^2) (300 K)			$\bar{U}^2_{i\,\mathrm{st}} \times 10^2$ (Å^2)			Ratio of $\bar{U}^2_{i\,\mathrm{st}}$ in sublattices and type of defects by Model I		$\sum \bar{U}^2_{i\,\mathrm{st}} \times 10^2$ (Å^2)	$\bar{U}^2_{\mathrm{st}} \times 10^2$ (Å^2) according to Model II	
		T	*O*	*K*	*T*	*O*	*K*	Measured	Calculated		Vacancies	Interstitials
+0.004	8.354	0.3	0.6	0.4	0.7	0.1	0.8	7:1:8	5:1:8 (octahedral vacancies)	1.6	1.65	3.48
−0.022	8.360	0.4	0.6	0.3	0.3	0.1	0.4	3:1:4	4:3:10 (anion vacancies)	0.8	0.97	2.05
−0.025	8.363									1.3	1.11	2.37

corresponding to this model (I) permits us to consider that in nickel–zinc ferrite nonstoichiometry corresponding to $\gamma < 0$ is realized in the form of anionic vacancies whereas for $\gamma > 0$ there appear cation vacancies in the octahedral sublattice.

According to Model (II) (*9*), one can judge the type and distribution of point defects by the quantity $\sum_i \bar{U}^2_{i\,\mathrm{st}}$. The calculation of $\bar{U}^2_{\mathrm{st}}$ is based on the harmonic approximation in the theory of crystals with a calculation of interaction between nearest neighbors. This calculation is valid when the lattice constant varies linearly with composition or when the concentration is small. Both these requirements are fulfilled in the case of the specimens investigated, inasmuch as the concentration of defects is not large, since it was dependent on deviation from stoichiometry, and the lattice constant changes linearly depending on excess or deficit of oxygen in the ferrites.

The value of the mean-square displacement $\bar{U}^2_{\mathrm{st}}$ is determined from the behavior of the elastic modulus and from the derivative of the volume of the unit cell with concentration in the case of substitution (vacancy formation) and insertion according to the following equations:

substitution

$$\bar{U}^2 = c(1-c)a^2(1+2V_1)^2\left(\frac{1}{v}\frac{\partial v}{\partial c}\right)^2 \times 10^{-2}\left[0.1424 + \frac{1.204}{(1+V_1+2V_2)^2} \times (1 - 1.055\alpha + 2.47\alpha^2 - 7.36\alpha^3 + 24.2\alpha^4) + \frac{1.011}{(1+2V_1+4V_2)^2}\right]. \quad (4)$$

insertion

$$\bar{U}^2 = c(1-c)a^2(1+2V_1)^2\left(\frac{1}{v}\frac{\partial v}{\partial c}\right)^2 \times 10^{-2}\left[0.1424 + \frac{3.464}{(1+V_1+2V_2)^2} \times (1 - 0.394\alpha + 3.24\alpha^2 + 8.06\alpha^3 + 24.0\alpha^4) + \frac{3.154}{(1+2V_1+4V_2)^2}\right]. \quad (5)$$

Here v is the unit cell volume and

$$V_1 = \frac{c_{12}}{c_{11}}; \quad V_2 = \frac{c_{44}}{c_{11}}; \quad \alpha = \frac{V_2}{1+V_1+2V_2}.$$

For the calculations we used the lattice constant (for the stoichiometric composition $a = 8.364$ Å), the value of the oxygen nonstoichiometry recounted in defect concentration from the formula Me_3O_4, and the values of the elastic moduli of nickel ferrite ($c_{11} = 22.0$; $c_{44} = 8.12$; $c_{12} = 10.94$ (*10*)).

As is seen from Table I, the mean-square static displacements calculated according to Model II are compared with the experimental data for the substitution case which corresponds to formation of anionic vacancies for compositions with $\gamma < 0$ and cationic vacancies for $\gamma > 0$. When point defects are formed by insertion, the calculated values of $\bar{U}^2_{\mathrm{st}}$ are approximately twice as large as the measured ones.

Hence it has been established that nonstoichiometry of nickel–zinc ferrite is realized in the form of anion vacancies for deficit of oxygen and octahedral vacancies when it is in excess.

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