JOURNAL OF SOLID STATE CHEMISTRY 3, 501–504 (1971)

An X-Ray and Magnetic Investigation of Solubility of NiO in ZnO

M. LO JACONO, P. PORTA AND A. CIMINO

Centro di Studio (C.N.R.) su Struttura ed Attività Catalitica di Sistemi di Ossidi, Istituto Chimico, Università di Roma, Roma, Italy

Received February 23, 1971

The limits of solubility of NiO in ZnO at different temperatures of calcination have been determined by means of lattice parameter and magnetic measurements. The limits have been estimated as less than 0.5, from 0.5 to 1.0, and from 1.0 to 1.5 Ni atoms per 100 Zn atoms for the firing temperatures of 1000, 1200, and 1300°C, respectively.

It is well known that the electronic configuration of transition metal ions influences their coordination number and symmetry. The difference of solubility of transition metal oxides in oxide matrices of different structure has accordingly been ascribed in some cases to a *symmetry* factor rather than to a *size* factor. An example is offered by the Ni^{2+} ion (d^8) which prefers octahedral symmetry. NiO is soluble in MgO (where Ni^{2+} ions occupy octahedral sites) forming continuous solid solutions, whereas its solubility in ZnO (where Ni^{2+} ions occupy tetrahedral sites) is very limited. Indeed, by means of optical measurements on the series $Ni_xZn_{1-x}O$ ($x = 10^{-3}$, 10^{-2}, 10^{-1}, 2.10^{-1} *M*), the solubility has been estimated by Schmitz-DuMont, Gössling and Brokopf to be about 10^{-2} *M* (*1*), and the same order of magnitude (0.9 mole % at 800°C) has been determined by Bates, White and Roy by means of Electron Micropobe Analyzer technique (*2*). It may be recalled that the ionic radii (Goldschmidt) of Ni^{2+}, Mg^{2+} and Zn^{2+} are not widely different, being 0.78, 0.78 and 0.83 Å, respectively.

The solid solutions of transition metal ions in oxide matrices have, in fact, acquired considerable interest in catalytic research (*3*) and, accordingly, a definite characterization of different systems is necessary. Since the limits of solubility of NiO in ZnO have not been precisely determined nor temperature effects checked, it was thought of interest to follow the formation of solid solutions by precise determination of the lattice parameters of ZnO. Furthermore, since Ni^{2+} ions in tetrahedral sites have a different magnetic moment from that found in octahedral sites (*4*), it was interesting to study the magnetic susceptibility of solid solutions, in order to characterize the solids by independent means.

Experimental Procedure

Specimen Preparation. $ZnCO_3$ (Erba RP, stated impurities: Pb, 0.001%; Cd, 0.001%; Fe, 0.002%; Ni, 0.001%; alkaline ions, 0.4%) was treated at 600°C for 5 hr in order to obtain ZnO. The oxide was impregnated with a titrated solution of $Ni(NO_3)_2$ (Erba RP, stated impurities: Pb, 0.003%; Fe, 0.003%; Cu, 0.005%; Zn, 0.02%; Co, 0.10%; alkaline ions, 0.25%) of a volume comparable to the solid, dried at 120°C for 24 hr and heated to 600°C for 1 hr. The samples were then divided into three portions, each of which was finally heated for 5 hr at 1000°, 1200° and 1300°C, respectively. The colour of the samples ranged from pale-green to green with increasing nickel concentration and firing temperature. The specimens are designated as follows: ZO, pure zinc oxide; ZN, nickel-doped zinc oxide, followed by a figure giving the nominal concentration of Ni (in atoms per 100 Zn atoms), and by the firing temperature in °C (in brackets).

Chemical Analysis. Gravimetric analyses (dimethylglyoxime) were performed on some samples to determine the nickel content, and the results are summarised in Table I.

X-Ray Analysis. Lattice parameters were measured by means of a back-reflection symmetrical focusing camera (Charles-Supper), 12 cm in diameter, using CuK_α (Ni-filtered) radiation. The following reflections, which gave well resolved α_1–α_2 doublets,

TABLE I

X-RAY DATA FOR NiO-ZnO SPECIMENS PREPARED AT DIFFERENT TEMPERATURES

Samples	x_{exp}[a]	1000°C			1200°C			1300°C		
		a	c/a	NiO[b]	a	c/a	NiO	a	c/a	NiO
ZO		3.24971	1.6020		3.24968	1.6019		3.24970	1.6019	
ZN-0.5	0.56				3.25016	1.6005		3.25012	1.6012	
ZN-1	1.10	3.25006	1.6011	+	3.25036	1.6002	+	3.25040	1.6006	
ZN-1.5	1.57				3.25042	1.6001	+	3.25054	1.6003	+
ZN-2	2.35				3.25056	1.6000	+	3.25072	1.5997	+
ZN-3		3.25016	1.6011	+	3.25052	1.6000	+	3.25074	1.5997	+
ZN-5		3.25022	1.6009	+	3.25052	1.6000	+	3.25070	1.5998	+

[a] experimental Ni content: atoms per 100 of Zn atoms.
[b] + = extra lines of the NiO phase present in the sample, as observed by X-ray spectra.

were utilized for the measurements (the second figure is the θ angle): (311)(86.2°), (222)(83.3°), (310)(80.7°), (220)(71.4°), (214)(69.2°), (106)(68.2°), (205)(66.9°). The positions of the lines were read visually to an accuracy of 0.005 cm with a Norelco measuring device. The graphical extrapolation method against $\varphi \tan \varphi$ has been adopted. It should be noted that the occurrence of three reflections at very high angles, one of which (310) is insensitive to the c/a ratio, leads to very accurate determination of a. The standard deviation on a was evaluated to be not larger than $\pm 5 \times 10^{-5}$ Å. The axial ratio c/a was determined by minimizing the deviations of a values, and its error (dependent on the scatter of points) was observed to be about $+1 \times 10^{-4}$ Å. All lattice parameters were reduced to 21°C by means of the linear thermal expansion coefficients quoted by Beals and Cook (*5*). The majority of determinations were made within ±4°C from 21°C. In order to observe all phases present other than ZnO, a cylindrical Debye–Scherrer camera (11.46 cm in diameter) was used.

Magnetic Measurements. Magnetic measurements were performed using the Gouy method in the range of temperature 98–298°K. A Mettler semimicro balance reading to ±0.01 mg has been employed and the instrument was first calibrated with $Co[Hg(CNS)_4]$. The molar magnetic susceptibilities χ_m were corrected for the diamagnetism of the sample. A plot of χ_m^{-1} *vs.* T (Fig. 1) shows a slight curvature, thus indicating that the Curie–Weiss law $\chi_m = C/T - \theta$ is only approximately obeyed. The values of the effective magnetic moment μ were derived for each sample from the χ_m values at room temperature. The magnetic moments of the samples were found to be field independent.

Experimental Results and Discussion

As shown in Table I, a few samples [namely, ZN-0.5 (1200) and (1300), and ZN-1 (1300)] were observed by X-ray examination to contain a single NiO-ZnO solid solution phase. The X-ray spectra of all other specimens revealed the presence of the cubic NiO phase as well. This indicates that the incorporation of Ni^{2+} ions into the ZnO lattice can be complete only at higher temperatures and small nickel concentrations.

The lattice parameters are reported in Table I; the variation of a against the total nickel content for all firing temperatures is shown in Fig. 2. It can be seen that for each temperature the lattice parameter a increases up to a certain percentage of nickel. The trend exhibited by the a *vs.* $[Ni^{2+}]$ curves in Fig. 2 indicates that the limits of solubility of Ni^{2+} ions in ZnO does increase with increasing temperature, but the solubility is rather low. Its value may be estimated as less than 0.5, from 0.5 to 1.0, and from 1.0 to 1.5 Ni atoms per 100 Zn atoms for the series 1000°, 1200°, and 1300°C, respectively, thus increasing temperature, as expected.

The specimens ZN-0.5 (1200), ZN-0.5 (1300), and ZN-1.0 (1300), which failed to show extra NiO lines in the X-ray spectra, and which, therefore, have Ni^{2+} ions in tetrahedral sites, have values of the magnetic moments equal to 4.14, 4.17, and 4.09 BM, respectively, in agreement with the values expected for tetrahedral Ni^{2+} which range from 4.0 to 4.2 BM (*4*). All other samples have values of the

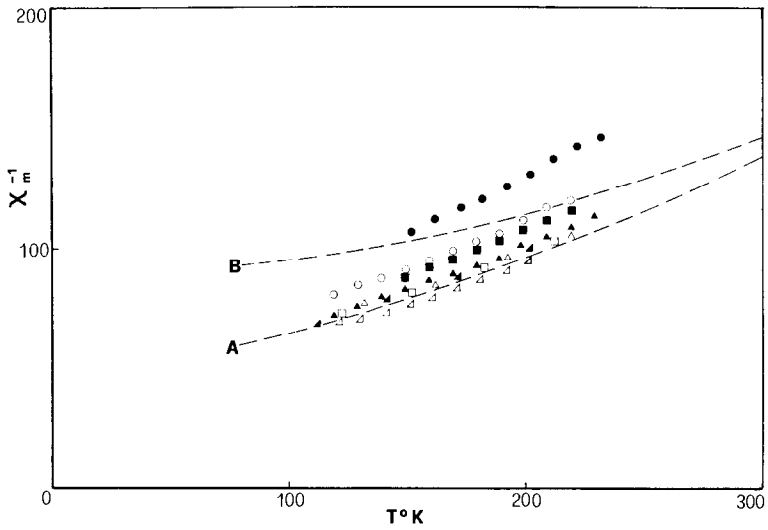

FIG. 1. χ_m^{-1} *vs* T plots for NiO-ZnO specimens prepared at different temperatures:
◢ = ZN-0.5 (1200); ■ = ZN-1.0 (1200); ▲ = ZN-1.5 (1200); ● = ZN-2.0 (1200); ◿ = ZN-0.5 (1300); □ = ZN-1.0 (1300); △ = ZN-1.5 (1300); ○ = ZN-2.0 (1300); not all experimental points are shown for the sake of clarity;
Curve A = calculated from the formula given by Figgis for tetrahedral Ni^{2+} (*4*) and assuming the values of Dq, B and λ as 415 800, and -175 cm^{-1}, respectively; *Curve B* = calculated from the same formula and assuming the values of Dq, B and λ as 415, 800, and -275 cm^{-1}, respectively.

apparent magnetic moment less than 4.0 BM and show an increase of the Weiss temperature θ with increase of nickel content, thus indicating an increase of the antiferromagnetic NiO phase.

It should also be noted that the experimental magnetic susceptibilities of the same specimens were found to be in good agreement (as shown in Fig. 1) with the values of χ_m calculated from the formula given by Figgis (*4*) for tetrahedral Ni^{2+}, assuming the values of the parameters Dq, B and λ as 415, 800, and -175 cm^{-1}, respectively (curve A). The χ_m value is not very sensitive to variation of either Dq or B.

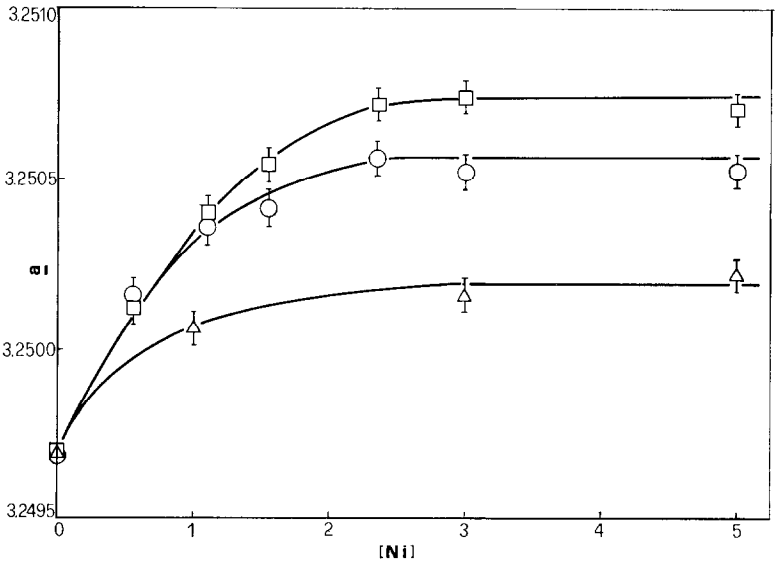

FIG. 2. Lattice parameters *a vs* [Ni] (in atoms per 100 Zn atoms) for NiO-ZnO specimens prepared at different temperatures: △ = 1000°C; ○ = 1200°C; □ = 1300°C.

On the contrary, as shown in Fig. 1, the dependence of χ_m on T is sensitive to variation of λ. It may be noted that the best fit is given by taking $\lambda = -175$ cm^{-1} (curve A), in accordance with Brumage and Lin (*6*), rather than $\lambda = -275$ cm^{-1} (curve B) as formerly suggested by Schmitz-DuMont *et al.* (*1*). The decrease of the λ value with respect to that of the free-ion ($\lambda = -340$ cm^{-1}) has been explained in terms of a larger electronic delocalization from the metal, which results in the formation of a strong covalent Ni-O bonding when present in the ZnO structure.

Acknowledgments

The authors wish to thank Dr. J. M. Criado for assistance in the preparation of some specimens, and Mr. G. Minelli for his help in the analysis of the samples. The financial support of the NATO Research Grants Programme is also acknowledged.

References

1. O. SCHMITZ-DUMONT, H. GÖSSLING AND H. BROKOPF, *Z. Anorg. Allg. Chem.* **300**, 159 (1959).
2. C. H. BATES, W. B. WHITE, AND R. ROY, *J. Inorg. Nucl. Chem.* **28**, 397 (1966).
3. A. CIMINO AND M. SCHIAVELLO, *J. Catalysis*, to appear.
4. B. N. FIGGIS, "*Introduction to Ligand Fields*", p. 248–292, Interscience, New York, 1967.
5. R. J. BEALS AND R. L. COOK, *J. Amer. Ceram. Soc.* **40**, 279 (1957).
6. W. H. BRUMAGE AND C. C. LIN, *Phys. Rev.* **134** (4A), 950 (1964).