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Characterization of CoO–ZnO Solid Solutions

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Lattice parameters, magnetic susceptibilities (over the temperature range 98–298°K) and reflectance spectra (uv and visible) of solid solutions of CoO–ZnO up to 10% *M* CoO have been studied. It is shown that true solid solution is achieved and that Co^{2+} ions substitute the Zn^{2+} ions in tetrahedral positions. The effect of addition of Co^{2+} is to increase the *a* parameter and decrease the *c*/*a* ratio. The magnetic moment of Co^{2+} has been found to be $4.54 \pm 0.05\ \mu_B$ by extrapolation. A discussion of the structural and magnetic data in terms of the presence of a C_{3v} effective symmetry is given.

Introduction

Solid solutions of transition metal ions in oxide matrices are receiving attention in catalysis; accordingly a complete characterization of the system and a comparison with single crystal results become necessary. In particular, the chemical nature of the surface complexes involved in catalytic reactions may be more easily understood if overall electronic structural information, such as magnetic data, is available.

In the present paper we report a study of the solid state chemistry of Co^{2+} tetrahedrally coordinated in polycrystalline zinc oxide.

It is known (*1–5*) that CoO dissolves in ZnO up to a content dependent upon temperature and also the ZnO dissolves in CoO. The state diagram permits the evaluation of the solubility limits by X-ray methods (*4*), which confirm that at ca. 1000°C the solubility of CoO in ZnO is about 20% *M*. This result confirms that both size considerations [ionic radii of Co^{2+} and $Zn^{2+} = 0.83$ Å (*6*)] and symmetry factors are favorable for tetrahedral coordination of Co^{2+} (*7*, *8*).

Samples of ZnO containing cobalt have been investigated by magnetic methods and optical spectroscopy. The theory proposed by several authors (*7–12*) fits the experimental optical spectra satisfactorily, and the agreement in the energy levels is fairly good. Less magnetic data are available and some uncertainty exists about the magnetic moment value of Co^{2+}_{tet} in oxide matrices. Hence, the purpose of the present paper is to characterize carefully solid solutions of CoO in ZnO (0.05–10% by atoms) by means of precise lattice parameter determination, reflectance spectroscopy and magnetic susceptibilities.

Since Co^{2+} in tetrahedral sites has a magnetic moment different from that in octahedral sites (*13*) the study of magnetic susceptibilities of the solid solutions offers a means of characterizing the solids by independent methods.

In addition, we discuss discrepancies arising between the present and previous magnetic data.

Experimental Procedure and Results

Sample Preparation and Chemical Analysis

The ZnO used as a matrix for the solid solutions was obtained by heating $ZnCO_3$ (Erba R.P.) for 1 hr at 600°C. Samples were then impregnated with a comparable volume of titrated solutions of $Co(NO_3)_2 \cdot 6H_2O$ (J.M. specpure). The soaked mass was dried at 120°C for 24 hr, ground, and then heated at

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TABLE I

ANALYTICAL AND MAGNETIC DATA FOR ZCo SAMPLES

Nominal content[a]	Experimental content[a]	μ_B	θ (°K)
ZCo 0.05	0.055	—	—
ZCo 0.1	0.109	—	—
ZCo 0.5	0.522	4.59	−14
ZCo 1	1.09	4.49	−2
ZCo 5	5.28	4.52	−15
ZCo 10	9.46	4.57	−60

[a] Co atoms/100 Zn atoms.

TABLE II

X-RAY DATA FOR ZCo SAMPLES

Sample	$a_{21°C}$ (Å)	$C = c/a$
ZnO	3.24964	1.6020
ZCo 0.05	3.24961	1.6017
ZCo 0.1	3.24960	1.6016
ZCo 0.5	3.24981	1.6015
ZCo 1	3.25000	1.6015
ZCo 5	3.25084	1.6005
ZCo 10	3.25148	1.6005

600°C for 1 hr. The samples were reground, heated in air at 1200°C for 5 hr, and finally quenched in air. The same procedure was adopted for the pure matrix.

The color of the samples ranged from very pale green to very intense green.

The specimens, hereinafter called ZCo, are designated by means of a figure after ZCo giving the nominal concentration of Co atoms per 100 Zn atoms.

Atomic absorption spectrophotometry was employed to evaluate the effective Co content present. The standards for the calibration curve were obtained by dissolving stoichiometric titrated Co_3O_4 J.M. in diluted H_2SO_4 (as for ZCo samples) with the appropriate amount of Zn^{2+}. The analytic results are reported in Table I.

X-Ray Analysis

A cylindrical Debye–Scherrer camera (11.46 cm i.d.) was used to identify phases other than pure ZnO. All the samples studied were found to be monophasic, i.e., solid solutions, since only the ZnO phase was detected. Lattice parameters were measured following the procedure adopted previously (*14*) and using CuK_α (Ni-filtered) radiation (which did not produce disturbing fluorescence effects for the more concentrated samples). Lattice parameters and C ($=c/a$) values are reported in Table II.

The graphical extrapolation method (a against $\varphi tg\varphi$, where $\varphi = 90° - \theta$), has been adopted, leading to a standard deviation on a values of about $\pm 5 \times 10^{-5}$ Å. The axial ratio C was determined according to Archard (*15*), with a SD of $\pm 1 \times 10^{-4}$. All values are corrected to a temperature of 21°C using the factors $(\Delta a/a) = 5.85 \times 10^{-6}/°C$ and $(\Delta c/c) = 5.25 \times 10^{-6}/°C$ (*16*).

Magnetic Susceptibilities

Measurements were carried out on a Gouy balance in the range 98–298°K. The instrument was first calibrated with $Co[Hg(CNS)_4]$. The magnetic susceptibilities/g of sample, χ, were corrected for the diamagnetism of the matrix, taken as -0.3×10^{-6} erg G^{-2} g^{-1}.

The moments were derived for all samples from χ_{Co}^{-1} vs T plots between 98 and 298°K. Values are reported in Table I. For samples with a Co^{2+} content less than 0.5% the diamagnetism of the matrix leads to a very large error in the determination of the weight variation. The magnetic susceptibility was found to be field independent within experimental error, by measuring it at 4000 and 8000 G in the range 98–298°K.

Figure 1 shows a $\chi_{Co}^{-1} \rightarrow T$ plot illustrating the field independence and the extrapolation carried out.

Reflectance Spectroscopy

Optical reflectance spectra (r.t.) were obtained with a Beckman DK 1 A spectrophotometer in the range 2500–350 nm. Pure ZnO (1200°C) was used as the reference in order to eliminate background effects. There is, however, a shift of the charge transfer absorption edge, as discussed below. For the more concentrated samples ZCo 5 and ZCo 10 the signal was too strong and was therefore reduced by addition of pure ZnO to the original specimens in the weight ratio 1:1.

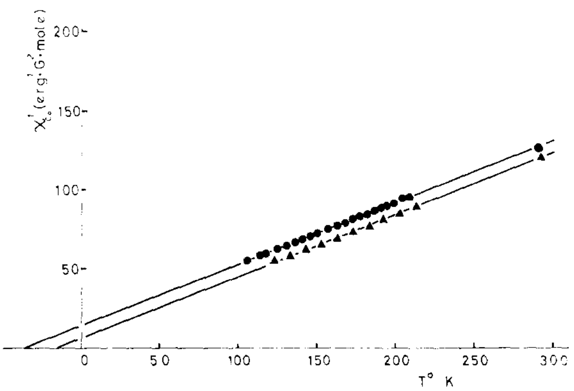

FIG. 1. χ_{Co}^{-1} vs T plot for ZCo 5 sample tested at 2 different fields: ▲ 4000 G; ● 8000 G.

The optical spectra of all samples show 4 absorption bands (see Fig. 2). The first at about 2400 nm is presumably due to the $^4A_2 \rightarrow {}^4T_2(F)$ transition. The second extends from 1200 to 1700 nm and is composed of 3 components; the third band, lying between 550 and 650 nm, is narrower than the second (although better resolved) and again split into 3 peaks. The fourth band is a sharp single peak at 420–450 nm.

In agreement with the results of previous studies on tetrahedrally coordinated Co^{2+} in ZnO (*9–10*), we attribute the 3 peaks of the second band to the $^4A_2 \rightarrow {}^4T_1(F)$ transition and those of the third one to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition (see Table III). With regard to the sharp peak at 420 nm, this probably arises from a shift of the electronic transition from the valence band to the conduction band of the pure matrix, brought about by the presence of the guest ions.

Discussion

X Rays and Reflectance Spectra

Table II and Figs 3 and 4 show graphs of the lattice parameter *a* vs [Co], and *C* vs [Co],

TABLE III

OPTICAL SPECTRA DATA FOR ZCo SYSTEMS

Upper level designation	$^4T_1(F)$	$^4T_1(P)$
	6000	15400
Our band maxima[a] (cm^{-1})	7000	16400
	7600	17700
	6170	15310
Ref. (*1*)[a]	7150	16360
	7690	
	6000	15400
Ref. (*2*)[a]	7000	16400
	7600	17600
	6009; 6097.5; 6195.8	15408; 15650; 15961
Ref. (*3*)[b]	6649; 6798; 6944	16268; 16666
	7189; 7518.8; 7698	17652

[a] Spectra obtained at room temperature.

[b] Spectrum obtained at 78°K.

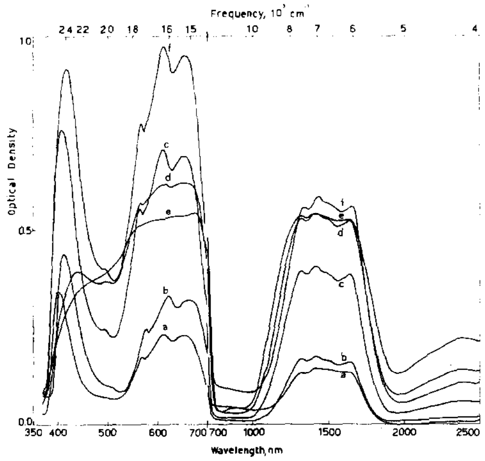

FIG. 2. Optical spectra of ZCo samples. Reference: pure ZnO (1200°C). (a) ZCo 0.05; (b) ZCo 0.1; (e) ZCo 0.5; (d) ZCo 5; (e) ZCo 10; (f) ZCo 1. ZCo 5 and ZCo 10 diluted with pure matrix 1:1 by weight.

respectively. The *a* values increase continuously with cobalt content, showing that no saturation effect is present in cobalt concentration range explored (i.e., $\leqslant 10\%$). This is in agreement with earlier findings (*1–5*). The *C* ratios decrease with increasing Co content. This decrease, and the increase in the *a* values with Co content, indicate that on substituting Zn^{2+} by Co^{2+} ions, the ZnO unit cell tends to contract along the *c* axis.

Recalling that the ionic radii of Zn^{2+} and Co^{2+} are 0.83 and 0.82 Å, respectively, and that Co^{2+} and Zn^{2+} are in ground electronic states of symmetry $^4A_2$ and $^1A_1$, respectively, one would expect an isotropic influence of cobalt addition on the ZnO structure. The wurtzite structure is known to be distorted with respect to the regular hexagonal close packed lattice (*C* value is 1.6020 (*14*) against a *C* value of 1.633 for the regular packing). Hence the addition of Co^{2+} ions to ZnO results in a slightly anisotropic perturbation of the host lattice. A tentative explanation will be given after discussing the optical spectra.

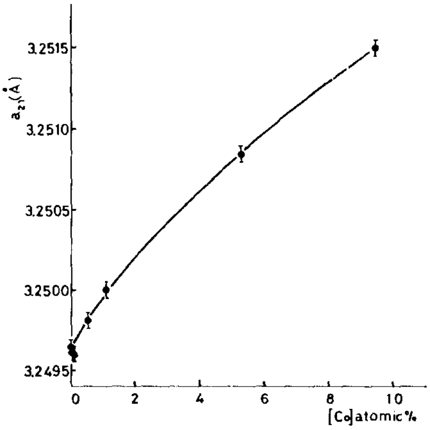

FIG. 3. Lattice parameter $a_{21^\circ C}$ vs cobalt content for ZnO and ZCo samples.

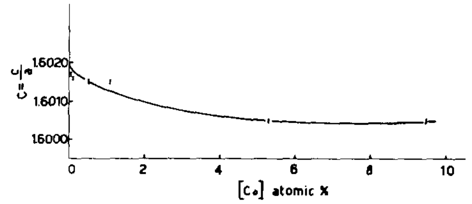

FIG. 4. $C = c/a$ ratios vs cobalt content for ZnO and ZCo samples.

The reflectance spectra are in agreement with a simple crystal field model and suggest that the Co^{2+} ions substitute Zn^{2+} ions in tetrahedral positions. The absence of symmetries other than tetrahedral, such as octahedrally coordinated Co^{2+}, present in CoO if incompletely dissolved in ZnO, can be demonstrated within experimental error. Thus, although the position and the intensity of spectra of tetrahedral Co^{2+} are reported to be superimposible on those of octahedral Co^{2+} (*10*), it has been shown that in oxide systems with a preponderant amount of tetrahedral Co^{2+} the presence of octahedral Co^{2+} may be detected via a shoulder at 1100 nm (*17*).

Turning now to the problem of the contraction along the *c* axis of the ZnO unit cell when Co^{2+} ion is added, as mentioned above the observed anisotropy cannot be accounted for on the basis of group symmetry considerations; however, an explanation based on the Co^{2+}_{tet} absorption spectra interpretation can be proposed. As suggested by Weakliem for the ZCo system (*9*), a C_{3v} component of the crystal field potential exists, which leads to a lower symmetry than the pure tetrahedral one. This lowering of symmetry would have as a consequence a rearrangement of *d* levels with a participation of excited configurations $^4T_1$ (e^3t^4 and e^2t^5) to the ground state $^4A_2$ (e^4t^3). A possible suggestion may be that the presence of these 2 excited states is the result of a transfer of *d* electrons from a nonbonding to an antibonding orbital. It can be shown that the tetrahedron would then be distorted by the Jahn–Teller effect and in order to remove the degeneracy, the tetrahedron would flatten.

Magnetic Measurement

The spin-only value $2[S(S+1)]^{1/2} = 3.88$ μ_B, attributable to a pure *A* ground state, has never been observed for tetrahedrally coordinated Co^{2+}, and on an orbital contribution to the magnetic moment (the magnitude of which depends on the nature of the ligands) has been found (*12*). The higher magnetic moments are explained in terms of mixing of $^4T_2$ and $^4T_2$ states into the $^4A_2$ ground state (*13*, *18*).

Our experimental results confirm values well above the spin-only one and show that, in the temperature range explored, the Curie–Weiss law $\chi = C/(T-\theta)$ is obeyed. No temperature independent paramagnetism (TIP) contribution has been taken into account in evaluating the μ values, because of the linearity of χ_{Co}^{-1} vs *T* plots. Indeed, the TIP value of 0.58×10^{-3} erg G^{-2} mole $^{-1}$ quoted by Cossee (*11*) is in excellent agreement with our value 0.5×10^{-3} erg G^{-2} mole $^{-1}$ calculated from the χ_{Co} vs $1/T$ plot for the ZCo 1 specimen, where the low θ value permits a good evaluation of TIP value by extrapolation. Thus, the contribution of the TIP on our magnetic moments is well within the experimental error, and only if a large temperature range is explored (*11*) does the inclusion of the TIP term become experimentally meaningful.

The μ values reported in Table II give an average value of 4.54 ± 0.05 μ_B, whereas values of 4.07 (*11*) and 4.26 μ_B (*19*) were previously reported. In order to support such a μ value attributed to tetrahedral cobalt in ZnO, EPR measurements have been performed on ZCo 1 at L.N. (Liquid nitrogen) temperature (*20*). Now, $\mu = g[S(S+1)]^{1/2}$ and $g = 2(1 - 4\lambda/\Delta)$, hence is it possible to calculate the ratio $(4\lambda/\Delta)$, and the spin-orbit coupling constant λ from the measured *g* value. Values of 0.15 $\pm$0.01 and -166 cm^{-1}, respectively, taking Δ as 3900 cm^{-1} (*10*), are obtained, whereas λ for the free ion is -180 cm^{-1}. The μ values so calculated (4.46 ± 0.04 μ_B) agree within experimental error with the μ values determined by magnetic measurements and with that calculated theoretically by Cossee (*11*). The discrepancy between our and previous results may be not surprising if we take into account the distortion existing in the solid solution lattice. A change in geometry could in fact, as Ferguson suggested (*21*), be responsible for an orbital contribution that is not purely spin-orbit in origin.

We conclude that the distortion is important in determining the magnetic properties, and different mixing of the excited states into the ground state can occur according to the preparation methods. This discrepancy did not exist for single crystals, and powder, crystallised from solution. Thus, for example, for Cl^- ligands the agreement between various authors is excellent (*22*, *23*).

Finally, it may be noted that, if $\Delta\lambda(\lambda_{\text{free ion}} - \lambda_{\text{coord. ion}})$ is a measure of the covalency in the M—O bond, the $\Delta\lambda$ values for Ni–O (about -170 cm^{-1}) (*24*) and for Co–O (about -14 cm^{-1}) (this work) seem to indicate a more pronounced ionicity for the Co–O bond with respect to Ni–O bond, when both are dissolved in ZnO.

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