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Neutron Diffraction Study on the Spinel $Cu_{0.72}Co_{2.28}O_4$

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A neutron powder diffraction refinement of the positional and thermal structure parameters of $Cu_{0.72}Co_{2.28}O_4$ spinel has been carried out. It has been found that the spinel is inverse, with inversion parameter approximately equal to one half of the copper content value.

Introduction

The existence of spinel type copper-cobaltite oxides with a common formula $Cu_xCo_{3-x}O_4$ presents a number of interesting questions from both preparative and crystallochemical points of view. The problems connected with the thermodynamics, kinetics, and mechanism of their formation remain unclarified. The fact of their existence, having been in doubt for many years (*1–3*), can now be considered to be convincingly established (*4*). Accordingly, the interest in these materials shifts from purely preparative studies to crystallochemical ones.

The first attempt to determine the cation distribution in $Cu_xCo_{3-x}O_4$ spinels was performed in (*5*) by means of X-ray powder diffraction. Two compositions were investigated, one with $x = 0.76$ and the other with $x = 0.92$. The refinement of the site occupancies and the positional and thermal parameters verified the hypothesis favoring inverse type spinels, as suggested in (*4*). It is well known, however, that the precision which can be achieved in the case of cations with close atomic X-ray scattering factors is rather low (*6*). In a number of cases, the results cannot be interpreted even qualitatively (*7, 8*). This disadvantage can be compensated for to a certain extent if very accurately measured integrated intensities are used (*9*), a requirement connected with tedious, labor-consuming experimental work.

In particular, copper-cobaltite spinels are more suitable objects for neutron diffraction studies. The coherent scattering amplitudes of copper, cobalt, and oxygen are considerably different in magnitude, which permits the precise determination of the oxygen positional parameter as well as the

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quantitative distribution of the cations over the lattice sites.

In this work we report the results of the crystal structure refinement of the spinel $Cu_{0.72}Co_{2.28}O_4$ on the basis of neutron elastic scattering data.

Experimental

Sample Preparation

The copper cobaltite was prepared by thermal decomposition of a mixture of nitrates of both metals, taken in appropriate proportions, as described in (*4*). Starting materials were of ultrapure grade. The content of copper and cobalt in the final product was determined by the atomic absorption spectrophotometry technique and was found to be 0.721 ± 0.005 Cu and 2.279 ± 0.005 Co for a formula unit.

X-ray Diffraction Analyses

X-ray diffraction experiments were carried out with a powder diffractometer using Co$K\alpha$ filtered radiation and a scintillation counter. The sample was found to be monophase. Careful analyses of the line profiles near (311) and (222) peaks of the spinel did not give any grounds to suppose that any detectable quantities of CuO are present. The detectable minimum of CuO for the given geometry was 1–2 wt%. The profiles of the high-angle diffraction lines were symmetrically broadened with respect to those of the Co_3O_4 reference sample, but no asymmetric broadening due to phase inhomogeneity was observed. The lattice parameter was determined from the angle positions of several diffraction lines in the range 110–150° (2θ), using 99.99% pure silicon as an internal standard. The results from the chemical and X-ray analyses are shown in Table I.

Neutron Diffraction

Neutron powder diffraction data were collected at room temperature on the two-

TABLE I

SUMMARY OF X-RAY AND NEUTRON DIFFRACTION DATA ON Co_3O_4 AND $Cu_xCo_{3-x}O_4$[a]

				Occupancies *A*			Occupancies *B*			
Sample	a_0(Å)	*B*(Å²)	*u*	Cu^{2+}	Co^{3+}	Co^{2+}	Cu^{2+}	Co^{3+}	*R*%	Reference
Co_3O_4	8.0835 ± 6	1.02 ± 6	0.3892 ± 10			1.00		2.00	2.37	(*7*)
	8.065	0.214	0.388			1.00		2.00	4.70	(*16*)
	8.0819 ± 3	0.51 ± 5	0.388 ± 1			1.00		2.00	3.10	(*5*)
$Cu_{0.92}Co_{2.08}O_4$	8.105 ± 1	1.39 ± 9	0.384 ± 1	0.25 ± 4	0.67 ± 4	0.08 ± 4	0.67 ± 4	1.33 ± 4	5.06	(*5*)
$Cu_{0.76}Co_{2.24}O_4$	8.098 ± 1	1.22 ± 7	0.384 ± 1	0.21 ± 5	0.55 ± 3	0.24 ± 3	0.55 ± 3	1.45 ± 3	3.36	(*5*)
$Cu_{0.72}Co_{2.28}O_4$	8.0978 ± 5	1.15 ± 9	0.3878 ± 1	0.36 ± 2	0.64 ± 2 total		0.36 ± 2	1.64 ± 2	3.40	this work

[a] Site occupancies normalized against one formula unit AB_2O_4.

axis neutron diffractometer at the Research Reactor IRT in Sofia. A monochromated neutron beam with wavelength of 1.061(2) Å was used. The samples were in a form of fine powder loosely packed into a thin-walled vanadium cylinder, 16 mm in diameter. The integrated intensities were evaluated from the diffraction spectra fitting Gaussian functions to peaks and second- or first-order polynomials to the background.

Crystal Structure Refinement Procedures

For the structure factor calculations, the origin of the unit cell was chosen at the center $\bar{3}m$, the tetrahedral, octahedral, and oxygen sites being, correspondingly, in 8(*a*), 16(*d*), and 32(*e*) positions of the space group *Fd*3*m*. The neutron scattering data were analyzed assuming random distribution of copper and cobalt cations among the tetrahedral and octahedral sites. Refinement was based on the observed integrated intensities $I_i^0 \equiv I_{hkl}^0$, with scale factor K, oxygen parameter u, average scattering amplitudes at tetrahedral A and octahedral B sites corresponding to b_A and b_B, and overall temperature factor B taken as free variable parameters.

Two different computer programs, POWLS and INVPAR, were used for the calculations. Both programs utilize the same powder patch for overlapping intensities data and the functional χ^2 is treated in its usual form

$$\chi^2 = \sum_{i=1}^{m} \frac{1}{(\Delta I_i)^2} (I_i^0 - \sum_{j=1}^{r_i} I_{i,j}^c)^2 \qquad 1 \leq r_i \qquad (1)$$

where i numbers the independent observed total intensities $-I_i^0$, ΔI_i^0 is the estimated standard deviation of I_i^0, $w_i = 1/(\Delta I_i^0)^2$ is the weight factor and $I_{i,j}^c$ is the calculated contribution to I_i^0 of an individual reflection j. In some of the calculations a constraint function

$$b_A + 2b_B = xb_{Cu} + (3 - x)b_{Co} \qquad (2)$$

binding b_A and b_B was applied. As an auxiliary criterion for the divergence of the experimental intensities from the theoretically calculated ones, the conventional reliability factor was used

$$R = \Sigma|I^0 - I^c|/\Sigma I^0. \qquad (3)$$

The program POWLS (*10*) uses the least-squares method for the minimization of the functional χ^2, the usual Gauss–Newton reiterative scheme being realized.

The program INVPAR was developed by one of the authors (K. K.). It is based on the program system REGN (*11*) involving an algorithm for solving nonlinear systems of equations on computers by means of autoregularized iteration processes of the Gauss–Newton type (*12*).

The unknown structure parameters were determined by solving the overdetermined system of nonlinear equations, written in a vector form

$$fX = Y \qquad (4)$$

where

$$X = (K, u, b_A, b_B, B)^T \in R^n \qquad n \leq 5$$

$$Y = (I_1^0, I_2^0, \ldots, I_m^0)^T \in R^m \qquad 1 \leq n \leq m$$

$$fX = (f_1(X), \ldots, f_p(X))^T \in R^p \qquad p = r_1 + r_2 + \cdots + r_m.$$

The R^n, R^m, and R^p are real coordinate spaces with dimensions n, m, and p. The T denotes a transposition of a vector or matrix, and $f_k(X) = I_{k,j}^c$. Any relation between the intensities or the unknowns, i.e., the constraint in Eq. (2), may be introduced by enlarging the system Eq. (4).

The second Gauss transformation is applied to Eq. (4) and the quadratic system

$$FX = (f'(X))^T W(fX - Y) = 0 \qquad (5)$$

is solved, where $f'(X)$ denotes the Jacoby matrix of the operator fX and W is the given diagonal weighting matrix. Eq. (5) is solved using the autoregularized iteration process (*12*)

$$x_n = x_{n-1} - ((f'(X))^{\mathrm{T}} W f'(X) + \varepsilon_n I_{Rp})^{-1} FX \quad (6)$$

where I_{Rp} is unit matrix. The autoregularizer is in the form

$$\varepsilon_n = ((\tau_n^2 + 4C\rho_n)^{1/2} - \tau_n)/2$$

and is used with the notation

$$\tau_n = \|(f'(X_n))^{\mathrm{T}} W f'(X_n)\|_\infty$$

$$\rho_n = \|FX_n\|_\infty$$

$$C = \varepsilon_0(\varepsilon_0 + \tau_0)/\rho_0$$

$$\varepsilon_0 = \text{const.} > 0$$

The iteration process is cut off at a number $\bar{n}$, for which the inequality $\rho_{\bar{n}} \leq 10^{-9}$ is satisfied. This makes plausible the application of the linear theory of errors to the best iteration in the nonlinear problem under consideration. The uncertainties of the unknowns x_i are then estimated according to the formula

$$\Delta x_i = \pm \left(\frac{2}{m - n + q} ((f'(X_n))^{\mathrm{T}} W f(X_n))_{ii}^{-1} \right)^{1/2} \qquad I = 1, 2, \ldots, n \quad (7)$$

where q is the number of eventually fixed unknowns. It is used so that the covariant matrix appears to be properly conditioned.

The calculation can be carried out in two steps: the system is (a) solved once with a weighting matrix determined from the variances of the observations, and then (b) solved repeatedly with a weighting matrix whose elements are the reciprocal values of the differences between the measured quantities and the calculated ones obtained in the preliminary solution (procedure LCH). If the latter is influenced to a certain extent by potentially unreliable estimates of the variances of the measured quantities, the process will converge further with an additional improvement of the reliability factor. The method has the advantage of converging quickly even for a rather rough initial approximation to the unknowns. The pseudosolutions so obtained are stable with respect to small deviations in input data and to the rounding errors.

Distribution of Cations

The distribution of cations among the spinel lattice sites can be described by the general formula

$$\mathrm{Cu}_{x-\alpha}^{2+}\mathrm{Co}_{1-x-t}^{2+}\mathrm{Co}_{\alpha+t}^{3+}[\mathrm{Co}_{2-\alpha-t}^{3+}\mathrm{Co}_t^{2+}\mathrm{Cu}_\alpha^{2+}]\mathrm{O}_4^{2-}. \quad (8)$$

A modified formula, based on general considerations concerning the limited possibility of Co^{2+} ions occupying octahedral positions, was proposed in (*4*)

$$\mathrm{Cu}_{x-y}^{2x}\mathrm{Co}_{1-x}^{2x}\mathrm{Co}_\gamma^{3+}[\mathrm{Co}_{2-y}^{3+}\mathrm{Cu}_\gamma^{2+}]\mathrm{O}_4^{2-}. \quad (9)$$

To the extent to which the coherent neutron scattering amplitude does not depend on the atomic valency state, the scatterer should be regarded as containing two cationic components, so that the formula (8) may be rewritten

$$\mathrm{Cu}_{x-\alpha}\mathrm{Co}_{1-x+\alpha}[\mathrm{Co}_{2-\alpha}\mathrm{Cu}_\alpha]\mathrm{O}_4 \quad (10)$$

where α is the inversion parameter.

Results

The neutron diffraction pattern recorded at room temperature is shown in Fig. 1. The results from the refinement procedures are shown in Table I. For comparison, the X-ray diffraction results reported in (*5*) on $\mathrm{Cu}_x\mathrm{Co}_{3-x}\mathrm{O}_4$ with $x = 0.76$ and $x = 0.92$ are summarized and presented in the same table.

In Table II are shown the observed integrated intensities I^0 and the calculated ones I_1^c and I_2^c found by the iteration process in steps (a) and (b), correspondingly. Satisfactory agreement of the data was observed when the scattering length of cobalt was taken as $b_{\mathrm{Co}} = 0.25.10^{-12}$ cm (*13, 14*) and

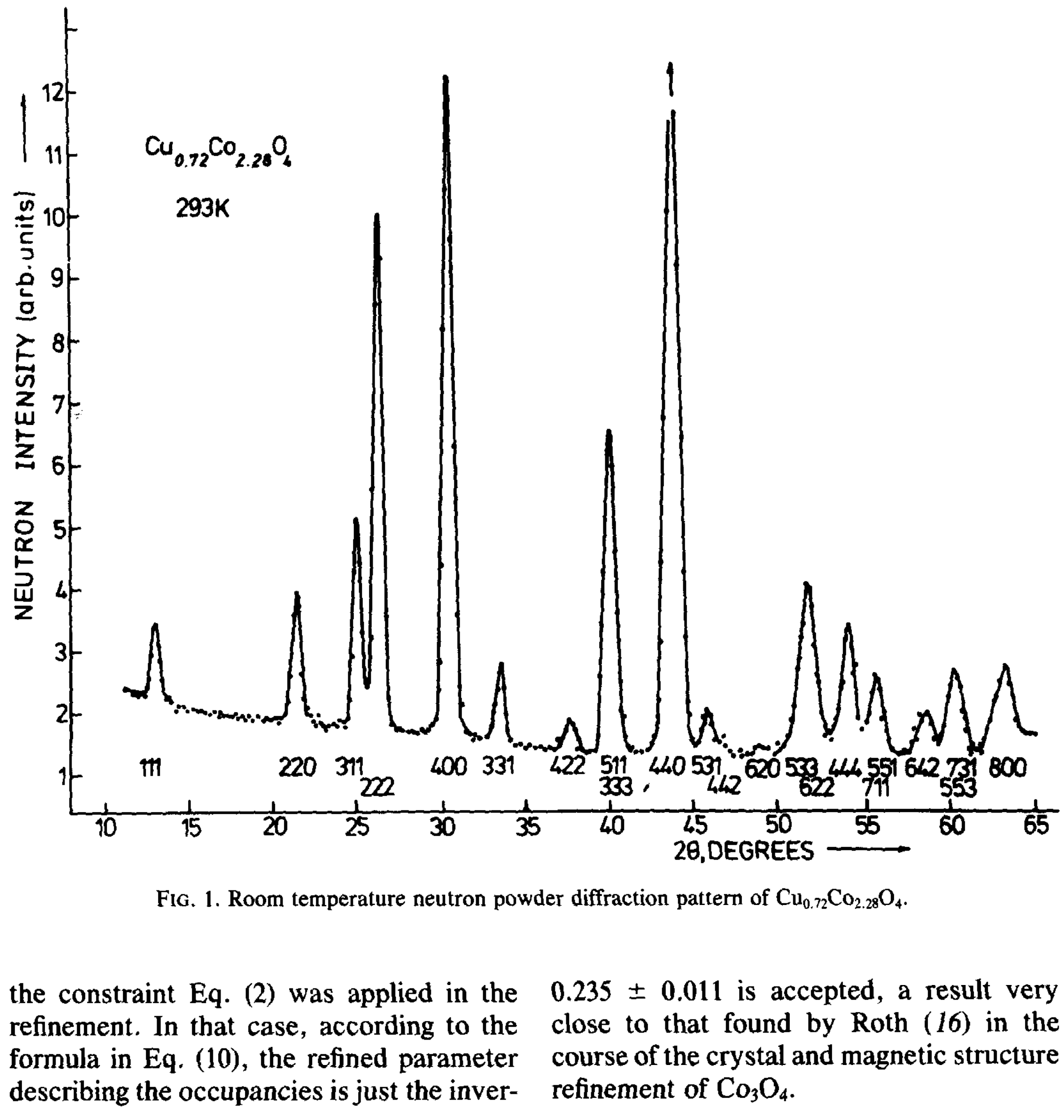

FIG. 1. Room temperature neutron powder diffraction pattern of $Cu_{0.72}Co_{2.28}O_4$.

the constraint Eq. (2) was applied in the refinement. In that case, according to the formula in Eq. (10), the refined parameter describing the occupancies is just the inversion parameter. When the recently tabulated (*15*) values $b_{Co} = 0.278.10^{-12}$ cm, $b_{Cu} = 0.7689.10^{-12}$ cm, and $b_O = 0.583.10^{-12}$ cm were used in the constraint function, a higher value $R = 6.5\%$ of the reliability factor was obtained.

The solution to the problem, when all structure parameters were allowed to be refined freely as independent unknowns, yielded the lowest value $R = 2.5\%$. In this case, however, an agreement with the chemical analyses for Cu and Co content can be achieved only if the value $b_{Co} = 0.235 \pm 0.011$ is accepted, a result very close to that found by Roth (*16*) in the course of the crystal and magnetic structure refinement of Co_3O_4.

The final estimates of the refined parameters, as well as the values of the degree of inversion α, are given in Table III. Both computer programs POWLS and INVPAR yielded very similar values of the refined parameters, the R factor being 1% lower than the R value for the case where the INVPAR program was used.

Discussion

The results of the structure parameters refinement by neutron powder diffraction

TABLE II

OBSERVED AND CALCULATED POWDER DIFFRACTION PATTERN OF $Cu_{0.72}Co_{2.28}O_4$ AT ROOM TEMPERATURE[a]

hkl	I^0	I_1^c	I_2^c
111	4972	6096	5748
220	7517	7539	7518
311	12802	13729	13579
222	34691	32680	32387
400	44115	45755	44880
331	4220	3989	4000
(333 511)	28058	26973	26656
440	68900	69380	69032
(531 442)	2754	2850	2738
(533 622)	19435	19022	19176
444	14669	13598	13547
(551 711)	8204	8366	8280
(731 553)	7698	8699	8732
R%		4.00	3.40

[a] I_1^c and I_2^c are integrated intensities calculated in steps (a) and (b) of the program INVPAR, correspondingly (see text); $b_{Co} = 0.25.10^{-12}$ cm.

data are in qualitative agreement with the X-ray powder diffraction refinement (*5*). The copper-cobaltite oxide spinel is partially inverted, its oxygen parameter is smaller, and the isotropic temperature factor is higher than the corresponding parameters of Co_3O_4. In principle, the values of the oxygen parameter and the degree of inversion determined by X-ray diffraction technique in the case $x = 0.76$ are expected to be close to those determined by neutron diffraction for composition $x = 0.72$. The observed differences are probably due to the stronger correlation between these two parameters and to the other drawbacks associated with the X-ray diffraction, as was pointed out in the Introduction. An additional argument in favor of the reliability of the neutron diffraction refinement could also be the much smaller errors of the unknowns.

The experimental value of the degree of inversion explains in a better way the lack of macroscopic Jahn–Teller lattice distortions. It is known that the critical concentrations of Jahn–Teller ions at which a cooperative distortion appears is relatively low for systems containing Cu^{2+} ions (*17, 18*). In the system studied, the retention of the cubic macrosymmetry can find its most likely explanation in the assumption that the static deformations associated with Cu^{2+} ions, situated in approximately equal quantities in both *A* and *B* sites, have opposite directions (*19, 20*). The question whether the local symmetry of the anion environment around the Cu^{2+} ions remains undistorted is still open. The character of the changes in the temperature factor, as well as the X-ray diffraction line broadening, suggest that such a distortion can be expected. The straightforward solution of the problem requires careful investigations at low and high temperatures of samples whose copper content varies extensively.

TABLE III

FINAL ESTIMATES OF THE PARAMETERS VALUES

R%	b_A (10^{-12} cm)	b_B (10^{-12} cm)	*u*	*B* (Å^2)	α	b_{Co} (10^{-12} cm)
6.5	0.440 ± 14	0.374 ± 7	0.3877 ± 1	1.14 ± 20	0.380 ± 30	0.278
4.0	0.427 ± 13	0.345 ± 6	0.3878 ± 3	1.20 ± 19	0.366 ± 20	0.25
3.4	0.430 ± 5	0.343 ± 2	0.3878 ± 1	1.15 ± 9	0.362 ± 20	0.25
2.5	0.428 ± 4	0.328 ± 3	0.3877 ± 1	1.17 ± 6	0.353 ± 20	0.235

References

1. T. V. Andrushkevich, G. K. Boreskov, V. V. Popovskii, L. M. Pljasova, L. G. Karakchiev, and A. A. Ostankovich, *Kinet. Katal.* **9**, 1224 (1968).
2. F. C. M. Driessens, G. D. Rieck, and H. H. Coenen, *J. Inorg. Nucl. Chem.* **30**, 747 (1968).
3. I. Rasines, *J. Appl. Crystallogr.* **5**, 11 (1972).
4. S. Angelov, E. Zhecheva, K. Petrov, and D. Mehandjiev, *Mater. Res. Bull.* **17**, 235 (1982).
5. K. Petrov, T. Karamaneva, S. Angelov, and D. Mehandjiev, *Mater. Res. Bull.*, to be published.
6. E. F. Bertaut, *J. Phys. Rad.* **12**, 252 (1951).
7. O. Knop, K. I. G. Reid, Sutarno, and Y. Nakagava, *Canad. J. Chem.* **46**, 3463 (1968).
8. G. Fagherazzi and F. Garbassi, *J. Appl. Crystallogr.* **5**, 18 (1972).
9. R. I. Anishchenko, E. G. Bogacheva, and A. H. Men', *Dokl. Akad. Nauk SSSR* **171** 535 (1966).
10. G. Will, *J. Appl. Crystallogr.* **12**, 483 (1979).
11. L. Aleksandrov, M. Drenska, and D. Karadjov, ORNL-RSIC-31, PSR-165/REGN (1981).
12. L. Aleksandrov, USSR Comm. JINR B 1-5-9869, Dubna (1976).
13. W. L. Roth, *Phys. Rev.* **110**, 1333 (1958).
14. R. M. Moon, *Phys. Rev.* **136**, A195 (1964).
15. C. W. Windsor, "Pulsed Neutron Scattering," Taylor & Francis, London (1981).
16. W. L. Roth, *J. Phys. Chem. Solids* **25**, 1 (1964).
17. P. J. Wojtovicz, *J. Appl. Phys.* **30**, 30 S (1959).
18. P. J. Wojtovicz, *J. Appl. Phys.* **116**, 32 (1959).
19. P. K. Baltzer and E. Lopatin, Proceedings, International Conference on Magnetism, Nottingam, (1964), p. 564.
20. M. Robbins and P. K. Baltzer, *J. Appl. Phys.* **36**, 1039 (1965).