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Neutron Diffraction Study of the Cation Ordering in $Cu_{1.5}Mn_{1.5}O_4$ and $CuMg_{0.5}Mn_{1.5}O_4$

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A structure refinement of the compounds $Cu_{1.5}Mn_{1.5}O_4$ and $CuMg_{0.5}Mn_{1.5}O_4$, based on neutron powder diffraction data, has been carried out; the degree of ordering, the cation distribution and the displacements of the ions from the ideal spinel positions are determined.

Introduction

Blasse (1966) has shown that the spinels $CuMg_{0.5}Mn_{1.5}O_4$ and $Cu_{1.5}Mn_{1.5}O_4$ have interesting magnetic properties which are related to the ionic ordering of the cations on the octahedral sublattice. He reported weak superstructure reflexions in the X-ray diffraction pattern of $CuMg_{0.5}Mn_{1.5}O_4$ indicating a 1:3 octahedral ordering and suggested a similar ordering for the other compound, but no direct proof could be obtained from X-ray diffraction because of the small differences between the scattering powers of Cu and Mn. Brabers & Vandenberghe (1973) reinvestigated these materials with IR spectroscopy and, from the appearance of fine structure in the spectra, the existence of a 1:3 ordering in this compound could be proved. Moreover, from thermal expansion measurements it was deduced that the cation distribution in these compounds is temperature dependent; in particular the Cu and Mn ions follow the equilibrium Cu^+(tetr.) + Mn^{4+}(oct.) $\rightleftarrows$ Cu^{2+}(oct.) + Mn^{3+} (tetr.) (Vandenberghe, Robbrecht & Brabers, 1973). At higher temperatures this equilibrium shifts to the right, consequently the order–disorder transition temperatures (410 and 450 °C respectively) are rather low compared with those of similar ordered Li-spinels (Vandenberghe, Brabers & Robbrecht, 1974).

Neutron powder diffraction measurements were carried out on these compounds in order to refine the structure parameters, *i.e.* the cation distribution, the degree of ordering on octahedral sites and the displacements of the ions from the ideal spinel positions. The neutron diffraction technique is very well suited to studying the structure of these compounds since Cu and Mn have neutron scattering lengths of opposite sign [$b(Cu) = 0.76 \times 10^{-12}$, $b(Mn) = -0.36 \times 10^{-12}$ cm].

Experimental

Polycrystalline samples of $CuMg_{0.5}Mn_{1.5}O_4$ and $Cu_{1.5}Mn_{1.5}O_4$ were prepared from co-precipitated hydroxides. The co-precipitated mixture of the magnesium compound was presintered for 24 h at 675°C in 1 atm O_2, ground, pressed into bars and sintered again at 600°C in O_2 for another 24 h. $Cu_{1.5}Mn_{1.5}O_4$ was prepared by sintering the co-precipitated hydroxides for 10 d at 530°C in 1 atm O_2 (Vandenberghe *et al.*, 1973). The sintered products were slowly cooled at a rate of 7°C h^{-1} in order to establish the cation ordering. The compound $Cu_{1.5}Mn_{1.5}O_4$ was also prepared in a disordered state by quenching from 500°C.

Neutron diffraction data were collected at room temperature on the powder diffractometer installed at the BR2 reactor of the S.C.K.–C.E.N. at Mol. The powders were enclosed in a cylindrical vanadium sample holder of diameter 1·5 cm. The neutron wavelength used in this experiment was 1·261 Å.

Structure refinement

The neutron diffraction diagrams of slowly cooled $CuMg_{0.5}Mn_{1.5}O_4$ and $Cu_{1.5}Mn_{1.5}O_4$ (Fig. 1) show, in addition to the reflexions of the f.c.c. lattices of the spinel structure, many reflexions which are forbidden in this structure. These lines fulfil the conditions of the space group $P4_332$ (or $P4_132$) and are a direct proof of the 1:3 crystallographic order. The atomic positions of a 1:3 octahedral ordered spinel with formula $A(B1)_{0.5}(B2)_{1.5}O_4$ are given by (Braun, 1952):

8A at 8(*c*) with $x=\Delta_1$ $\quad P4_332$
4B1 at 4(*b*)
12B2 at 12(*d*) with $x=\frac{5}{8}+\Delta_2$
24O at 24(*e*) with $x=\frac{1}{8}+\Delta_3$, $y=\frac{7}{8}-\Delta_4$, $z=\frac{1}{8}+\Delta_5$
8O at 8(*c*) with $x=\frac{3}{8}+\Delta_6$.

Table 1. *Refined parameters of the three compounds*

	Slowly cooled samples		Quenched from 500°C
	$Cu_{1.5}Mn_{1.5}O_4$	$CuMg_{0.5}Mn_{1.5}O_4$	$Cu_{1.5}Mn_{1.5}O_4$
a (Å)	8·28	8·29	8·29
Cation distribution	$\delta=1$ ($\pm$0·01)	$\delta=1$ (assumed) $\delta'=0.99$ ($\pm$0·01)	$\delta=0.97$ ($\pm$0·02)
S	0·99 ($\pm$0·01)	0·99 ($\pm$0·01)	—
B ($Å^2$)	1·5 ($\pm$0·3)	1·1 ($\pm$0·3)	1·5 ($\pm$0·4)
Δ_1 ($\pm$0·002)	0·007	0·008	—
Δ_2 ($\pm$0·001)	0·004	0·005	—
Δ_3 ($\pm$0·001)	0·027	0·027	0·012 (u=0·387)
Δ_4 ($\pm$0·001)	0·017	0·017	
Δ_5 ($\pm$0·001)	0·001	0·001	
Δ_6 ($\pm$0·002)	0·008	0·007	
R	0·06	0·04	0·05

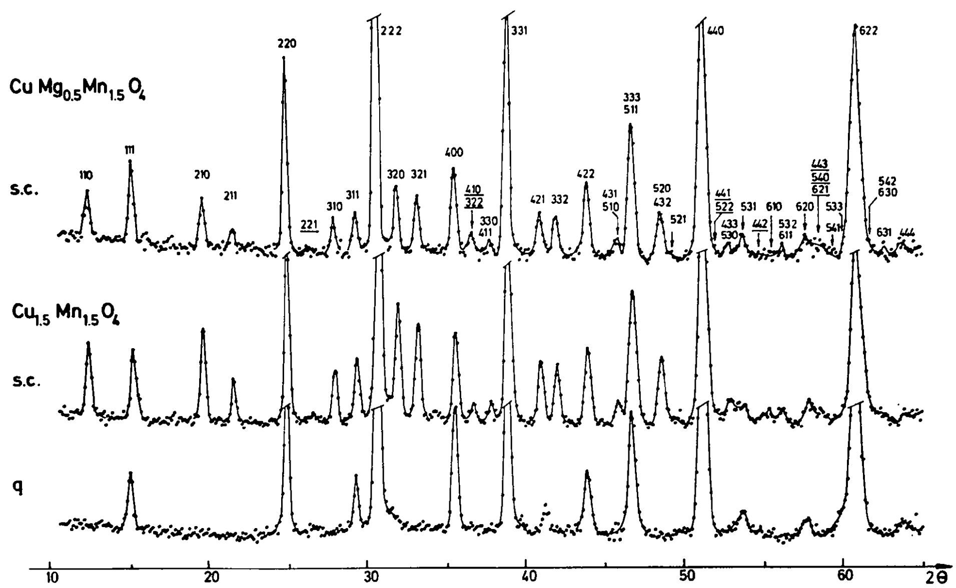

Fig. 1. Neutron diffraction patterns of the slowly cooled (s.c.) and quenched (q) compounds. The reflexions with underscored indices arise solely from ion displacements.

In addition to the six parameters Δ_i, the diffraction intensities are dependent on three other factors, *i.e.* the cation distribution among the octahedral and tetrahedral sites, the degree of ordering on the octahedral sublattice and the Debye–Waller factor. For the compound $Cu_{1.5}Mn_{1.5}O_4$ the cation distribution can be characterized by a distribution parameter δ according to the formula $Cu_{\delta}Mn_{1-\delta}[Cu_{1.5-\delta}Mn_{0.5+\delta}]O_4$. The average scattering lengths of the atoms at the tetrahedral (A) and octahedral sites (B1 and B2) may then be written as

$$b(A)=\delta b(Cu)+(1-\delta)b(Mn)$$
$$b(B1)=pb(Cu)+(1-p)b(Mn)$$
$$b(B2)=qb(Mn)+(1-q)b(Cu)\,,$$

in which

$$p=\tfrac{1}{4}(3-2\delta)[1+(1+2\delta)S]$$
$$q=\tfrac{1}{4}(1+2\delta)[1+(1-2\delta/3)S]$$

and S stands for the usual long-range ordering parameter (Cowley, 1950), with the condition $S(\max)=1(3-2\delta)$.

In the case of $CuMg_{0.5}Mn_{1.5}O_4$ we cannot exclude the possibility of the presence of a small amount of Mg^{2+} ions on the tetrahedral sites. Therefore the cation distribution must be characterized by two parameters δ and δ' according to the formula

$$Cu_{\delta+\delta'-1}Mg_{1-\delta'}Mn_{1-\delta}[Mg_{\delta'-0.5}Cu_{2-\delta-\delta'}Mn_{0.5+\delta}]O_4\,.$$

However, in order to restrict the number of parameters, it was assumed that $\delta=1$, which is permitted in view of the results obtained from $Cu_{1.5}Mn_{1.5}O_4$. In this case the average scattering lengths are given by

$$b(A)=\delta' b(Cu)+(1-\delta')b(Mg)$$
$$b(B1)=2p[(\delta'-0.5)b(Mg)+(1-\delta')b(Cu)]+(1-p)b(Mn)$$
$$b(B2)=2(1-q)[(\delta'-0.5)b(Mg)+(1-\delta')b(Cu)]+qb(Mn)\,,$$

with $p=\tfrac{1}{4}(1+3S)$ and $q=\tfrac{1}{4}(3+S)$. The Debye–Waller factor B is taken into account with the temperature factor $\exp[-2B(\sin\theta/\lambda)^2]$.

The structure parameters Δ_i, the ordering parameter S, the cation distribution (δ or δ') and the B factor are determined by fitting calculated to observed integrated intensities for about 25 peaks. The last three parameters are obtained in an iterative way in which at each turn the structure parameters Δ_i are simultaneously refined by application of the simplex algorithm (Dauwe, Dorikens & Dorikens-Vanpraet, 1974). The optimization function (reliability) is defined by

$$R=\sum_{hkl}|\sqrt{I_c}-\sqrt{I_o}|/\sum_{hkl}\sqrt{I_o}.$$

The neutron diffraction diagram of quenched $Cu_{1.5}Mn_{1.5}O_4$ (Fig. 1) showed no superstructure lines, which confirms the disordered state at 500 °C [the small extra peak at 41·4°(2θ) could not be identified and is probably caused by internal scattering of the apparatus]. The crystal structure now belongs to the space group $Fd3m$ in which only one structure parameter $u=\tfrac{3}{8}+\Delta$ of the O atoms has to be determined.

The different refined parameters of the three compounds are presented in Table 1.

Discussion

From the neutron diffraction results it is clear that in the compounds $CuMg_{0.5}Mn_{1.5}O_4$ and $Cu_{1.5}Mn_{1.5}O_4$ the tetrahedral sites contain only copper ions. On the octahedral sites the ordering is complete at low temperature. At 500 °C the compound $Cu_{1.5}Mn_{1.5}O_4$ shows a small inversion in accordance with the cation exchange Cu(tetr.) + Mn(oct.) $\rightleftarrows$ Mn(tetr.) + Cu(oct.). The ions in the compounds investigated are repelled by large amounts from the ideal spinel positions, which is conceivable in view of the large differences in atomic radii. Also the B factor is remarkably larger than usually expected in spinels (~0·5). However, in view of the low melting point of copper oxide it is plausible that in our materials the Debye temperature will be low and the B factor high.

Moreover, there will be an additional contribution to the B factor for $Cu_{1.5}Mn_{1.5}O_4$ due to the presence of Jahn–Teller active cations, namely Cu^{2+}. The distortions of the octahedra caused by these cations are not strongly coupled to each other because the octahedral Cu^{2+} concentration is relatively low and besides, these cations never are nearest neighbours due to the Coulomb interactions (Anderson, 1956). The distortions of the octahedra will in this case rather be coupled to the lattice vibrations (dynamic Jahn–Teller effect) which in turn enhances the B factor.

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