BRIEF COMMUNICATION

Preparation of Trigonal and Hexagonal Cuprous Chromite and Phase Transition Study Based on Single Crystal Structure Data

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Single crystals of trigonal $3R$-$CuCrO_2$ were grown by a flux decomposition method. A new metastable hexagonal phase of $2H$-$CuCrO_2$ was prepared by quenching the trigonal crystals from 1100°C to room temperature. A model of the atom shifts occurring during the $3R$–$2H$ structural phase transition is presented. During the transformation parts of the layered structure do not change. In other regions atom displacements up to 1.72(1) Å occur. The phase transition unites a first-coordination reconstructive transformation and a second-coordination distortional transformation. © 1996 Academic Press, Inc.

INTRODUCTION

Numerous $A^{1+}B^{3+}O_2$ compounds crystallize isotypically with trigonal delafossite ($CuFeO_2$) and different stacking variants have been reported (1–3). The trigonal $3R$ variant (space group $R\bar{3}m$) is the most common one with an AABBCC stacking of the oxygen layers. The $2H$ variant has a hexagonal structure (space group $P6_3/mmc$) with AABB stacking of the oxygen layers. Some ABO_2 compounds are known to crystallize both in the $3R$ and $2H$ structures (2–8).

With a view to study the relation between both structures we report a method suitable for the preparation of single crystals of $3R$-$CuCrO_2$ and a procedure for preparing single crystals of the $2H$ modification. A model of the atom shifts between the $3R$ and the $2H$ phase is presented.

EXPERIMENTAL

Plate shaped single crystals of $3R$-$CuCrO_2$ were grown by a flux decomposition method (see Ref. 9). $K_2Cr_2O_7$ (80 wt%) and CuO (20 wt%) were introduced into a 20 ml

platinum crucible and heated up to 860°C for 18 hr (heating/cooling rates were 100°C/hr). Black platelets with hexagonal morphology and a maximum size of $7 \times 5 \times 1$ mm³ are obtained. Guinier diagrams of these crystals proved the presence of the $3R$ phase. The structure of this phase has been determined by single crystal X-ray diffraction (see Ref. 10). Cell parameters were found to be $a = 2.9734(3)$ Å and $c = 17.100(4)$ Å. The atomic positions are given in Table 1. These results are in agreement with those reported by Dannhauser and Vanghan (11).

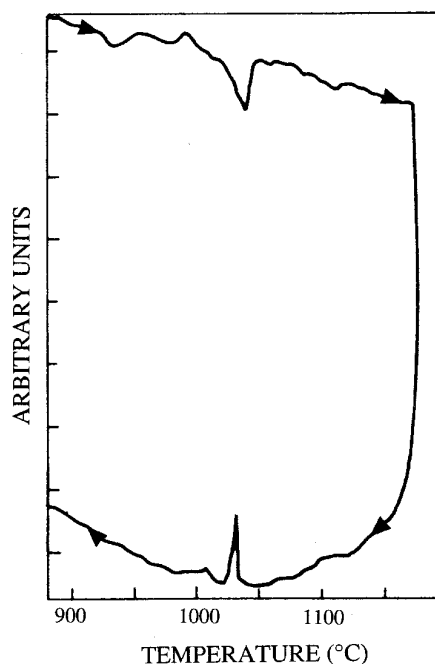Metastable single crystals of $2H$-$CuCrO_2$ can be pepared

FIG. 1. DTA curve of unquenched $CuCrO_2$ crystals (45.3 mg). Heating/cooling rate = 10°C/min.

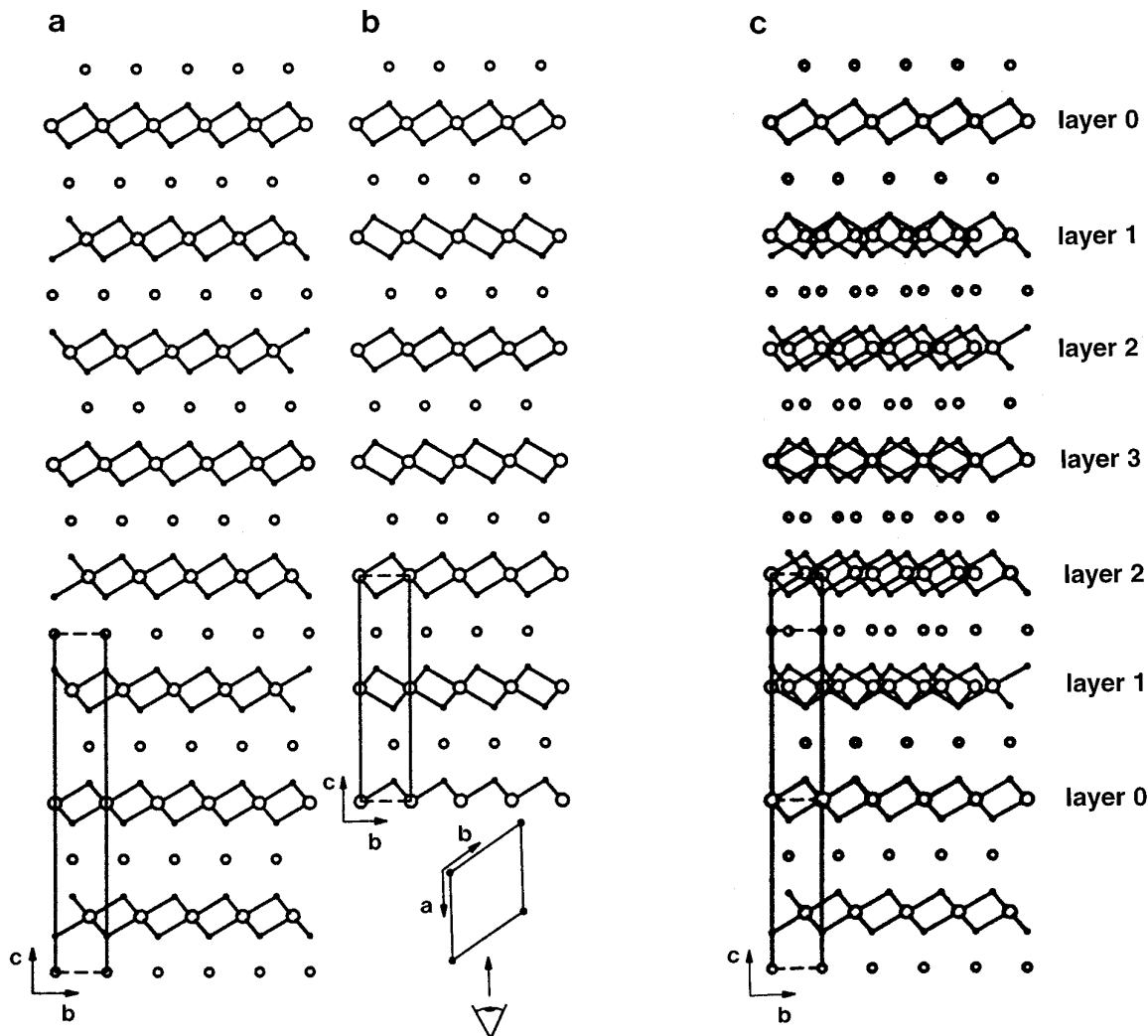[1] To whom correspondence should be addressed.

FIG. 2. Projections of the 3R and 2H structures of CuCrO$_2$ and their superposition. The lines link the chromium and oxygen atoms in the octahedra. The direction of observation is also shown.

from 3R crystals. The latter are rapidly heated to 1100°C in a 2 ml platinum crucible and then quenched into water. The structure of the 2H phase has been determined on a thin (0.025 mm), plate shaped single crystal by X-ray diffraction (see Ref. 12). Cell parameters were found to be $a = 2.970(1)$ Å and $c = 11.400(1)$ Å. The atomic positions are given in Table 1. It should be noted that it was not possible to obtain a powder with a pure 2H phase, probably because of the insufficient quenching speed. The Guinier diagrams show 10.0(5)% of the 2H phase and 90.0(5)% of the 3R phase.

It can be assumed that the metastable 2H phase is stabilized by quenching of the high-temperature 2H phase because: (i) The DTA of unquenched CuCrO$_2$ crystals (Fig. 1) shows a signal which can be attributed to a first order

phase transition from the 3R to the 2H phase, at 1040°C on heating and 1034°C on cooling. (ii) No X-ray reflections of the 2H phase were found from samples heated to 1100°C and cooled slowly. (iii) The reflections of the 2H phase present in quenched powder samples disappear when the samples are reheated above 1040°C, followed by slow cooling.

DISCUSSION

The possibility of comparing the 3R and 2H structures, one of which represents a high temperature structure, at room temperature may make it possible to understand the atom shifts occurring during the phase transition. In the
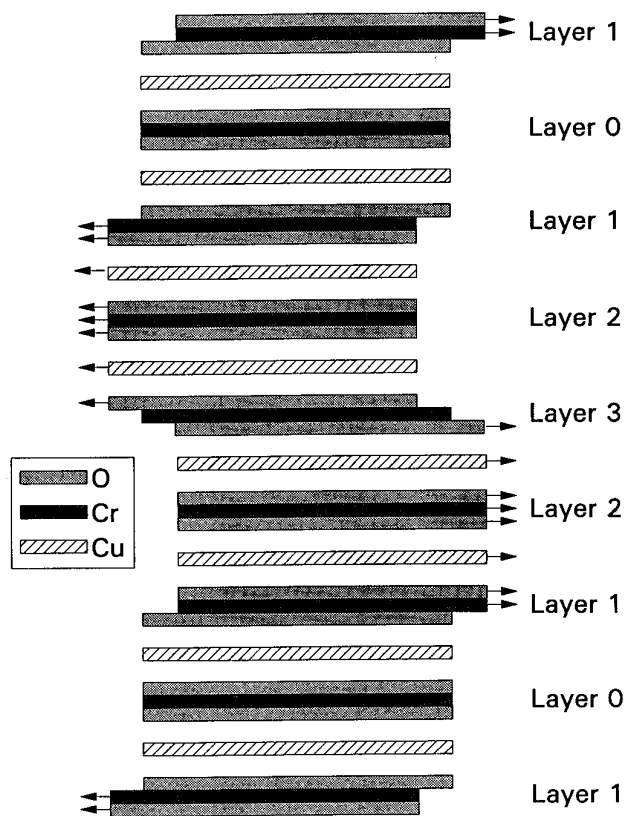
FIG. 3. Schematic representation of the atom shifts in the different layers during the 3R–2H phase transition.

types of layer with an atom displacement of 1.72(1) Å are involved in the phase transition (see Fig. 2c, a superposition of Figs. 2a and 2b).

Layer 0: No atoms of this layer are displaced during the phase transition.

Layer 1. separates into an immobile and a mobile part. Copper and oxygen atoms close to layer 0 show no displacement. The chromium and oxygen atoms close to layer 2 are displaced by 1.72(1) Å in different directions. The copper atoms follow the oxygen displacement. The direction of displacement of the chromium atoms is not the same as that of the oxygen atoms since this would oblige them to come too close to an immobile oxygen atom. This is avoided by deflecting the direction of displacement by 60°. So a change in the coordination sphere of the chromium atoms is implied. It should be noted that the atoms of the 2H phase have two equidistant possibilities to move to their new positions in the 3R phase. The apparent difference on Fig. 2c is due to the projection.

Layer 2. All atoms, in the chromium–oxygen octahedra or in the copper plane, move with the same displacement and in the same direction. Consequently, no bonds are broken or created within this layer.

Layer 3. Displacements of the oxygen/copper atoms are observed while the chromium atoms remain immobile. The lower oxygen/copper atoms are moving along $[11\bar{2}0]$, while the upper oxygen/copper atoms are moving in the opposite direction.

The next two layers are simply the centrosymmetric repetitions of the layers 1 and 2, with the centre of inversion lying in layer 3.

All atoms are displaced by ~1.72(1) Å. In fact, the chromium octahedra are mutually linked by the copper–oxygen bonds. This creates a three dimensional connection between the layers which gives atomic displacements of equal magnitude. Some layers (the type 0 layers) are acting like nodes since the atoms in these layers remain immobile

model of the 3R–2H phase transition presented below it is assumed that a minimum of atom shifts and of changes in the atomic coordination sphere occur during the phase transition.

In Figs. 2a and 2b the 3R and 2H structures are shown, viewed parallel to the *a* direction. It can be seen that four

TABLE 1
Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters
($\text{Å}^2 \times 10^4$) of Trigonal and Hexagonal Cuprous Chromite

Atom	Wyckoff notation	x	y	z	$U_{eq}{}^a$
Trigonal 3R-CuCrO$_2$ (space group $R\bar{3}m$ − 166) with a = 2.9734(3) Å and c = 17.100(4) Å					
Cu	3(a)	0	0	0	120(1)
Cr	3(b)	0	0	$\frac{1}{2}$	62(1)
O	6(c)	0	0	0.10792(8)	79(3)
Hexagonal 2H-CuCrO$_2$ (space group $P6_3/mmc$ − 194) with a = 2.970(1) Å and c = 11.400(1) Å					
Cu	2(c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	97(1)
Cr	2(a)	0	0	0	44(1)
O	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.0881(2)	58(3)

[a] $U_{eq} = \frac{1}{3}$ trace U, e.s.d.'s in parentheses.

while the directions of displacement of the atoms in the other layers (type 1, 2, or 3) are periodically alternated (see Fig. 3).

CONCLUSIONS

Single crystals of stable 3R trigonal and metastable 2H hexagonal cuprous chromite have been prepared. A model of the 3R–2H phase transition is presented. According to Buerger's phase transition classification (13) this transition unites a first-coordination reconstructive transformation (in the layer 1) and a second-coordination distortional transformation (in the layer 3).

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