Temperature dependence of the cation distribution in CuAl₂O₄ spinel

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Abstract

The temperature dependence of the cation distribution in $CuAl_2O_4$ spinel has been determined from 600 to 1100°C on quenched specimens by powder X-ray diffraction, and from room temperature to 1000°C by in-situ high-temperature powder neutron diffraction. The results, in agreement with earlier work, show that $CuAl_2O_4$ is a largely normal spinel, which is already highly disordered at 600°C, the lowest temperature at which the cation distribution is inferred to be in equilibrium, with an inversion parameter, x, at this temperature of 0.35 ± 0.005 from the neutron diffraction experiments. Increasing temperature to 1000°C only causes a modest increase in x, to 0.40 ± 0.005 . This somewhat unusual behaviour may be ascribed to the electronic contribution to the entropy of disorder of Cu^{2+} (electronic configuration 3d⁹) from electron degeneracy in the regularly coordinated tetrahedral site, or alternatively, to a large and positive quadratic term in the enthalpy of disordering. There is no sign of a Jahn-Teller distortion in the structure, which has cubic symmetry (space group Fd $\overline{3}m$) under all investigated conditions.

Introduction

The distribution of cations in a simple end-member oxide spinel may be written $(A_{(1-x)}B_x)^{tet}[A_xB_{(2-x)}B_x]^{tet}[A_xB_x]^$ $_{x}$)^{oct}O₄, where x is the inversion parameter. If x is 0, the cations are completely ordered onto the two cation sites, the structural formula is $(A)^{tet}[B_2]^{oct}O_4$, and the spinel is said to have the "normal" cation distribution. The opposite extreme occurs if x is 1, corresponding to $(B)^{tet}[AB]^{oct}O_4$, in which case the spinel is said to have the "inverse" cation arrangement. With increasing temperature there will be a tendency for both normal and inverse spinels to disorder towards the random, maximum entropy, cation arrangement, at x = 2/3. Spinels that trend towards x = 2/3 from the low x side of this divide are known as "largely normal" while those whose cation distribution is at x>2/3 are "largely inverse" (terminology of O'Neill and Navrotsky, 1984). Although many of the factors controlling the cation distribution in oxide spinels are reasonably well understood (O'Neill and Navrotsky, 1983, 1984), recent work, both experimental and theoretical, has emphasised that there remains much to be learnt. The temperature dependence of the cation distribution in CuAl₂O₄ spinel is of particular interest as the presently available measurements ((Cooley and Reid, 1972) suggest that it may be among the most disordered of any largely normal spinel, if an arbitrary temperature of equilibration is chosen to make a comparison. The measurements of Cooley and Reed (1972), which used powder XRD on quenched samples annealed at 613°C to 1195°C, found that x changed from 0.32 at the former temperature, which is a very high degree of disorder for this temperature, but only increased to 0.36 at the highest temperature. The smallness of the change in x over this temperature range is quite surprising, since, given the comparatively disordered state of the spinel at the lowest temperature, one might expect from simple thermodynamic considerations (reviewed below) that the cation

distribution would approach more closely to the random state (x = 2/3) at the high temperature end of the range studied.

There are two possible reasons to do with the kinetics of cation distribution that could explain the Cooley and Reid results. If cation redistribution is rapid, the almost constant degree of inversion could correspond to the temperature at which x freezes in during quenching, i.e., somewhere below 600°C. In this case the equilibrium degree of disorder in $CuAl_2O_4$ would be even greater at higher temperatures. Alternatively, if cation redistribution is sluggish, the lack of change between the high and low temperature results could be due to not annealing the low temperature samples for long enough. It is thus not clear if the Cooley and Reid results refer to the equilibrium cation distribution. Furthermore, O'Neill and Navrotsky (1984) noted that the cation distribution in $CuAl_2O_4$ as reported by Cooley and Reid (1972) could not be accounted for by their attempt at systemising cation distributions in end-member oxide spinels.

In order to characterise the equilibrium cation distribution in $CuAl_2O_4$ more certainly as a function of temperature, we first revisited the approach of Cooley and Reid with a powder XRD study on quenched specimens, but using modern refinement methods, and ensuring that the samples were annealed for long periods of time. These results support the early work, but of course still leave open some of the kinetic questions. We therefore also did an in-situ study using neutron diffraction at temperatures to 1000°C.

Experimental

Sample preparation.

The Al_2O_3 -Cu-O phase diagram shows that $CuAl_2O_4$ is stable only to ~1170 °C in air, decomposing to $CuAlO_2 + Al_2O_3$ at higher temperatures (Gadalla and White, 1964; Jacob and Alcock, 1975). For our first attempt at sample preparation, Al(OH)₃ + CuO were mixed, pelleted and heated in a muffle furnace at 900°C in air, with four intermediate regrinding and repelletizing steps for a total run time of 132 hours (SM1). Small amounts of the oxide components $(7\%CuO+4\%Al_2O_3)$ persisted despite the long run time and the multiple regrinding steps, probably indicating that alumina once formed is unreactive under these conditions. Accordingly, a different synthesis route was tried. A solution of the required stoichiometry was prepared by dissolving nitrates (Al(NO₃)₃.9H₂O and $Cu(NO_3)_2 \cdot 2.5H_2O$ in water in a Teflon beaker, reducing the solution by evaporation, and coprecipitating the Al and Cu, presumably as hydroxides, with ammonia. Since ammonia in excess redissolves Cu, the whole slurry was evaporated to dryness in situ with occasional stirring, then transferred to a Pt crucible and heated progressively to 1000°C, first over a Bunsen burner, then in an oven. The resulting powder was reground under acetone, pelletised and fired in flowing O2 at 1200°C for 70 hours (SM2). The nitrates were calibrated for their Al and Cu contents by slowly decomposing ~3 g aliquots by progressive heating in a box furnace to 1500°C and 1000°C respectively, and weighing as Al₂O₃ and CuO. Five replications indicated that the reproducibility was within 0.3%. The subsequent XRD experiments on this material showed it to be single-phase spinel, with no extra phases detectable. For the neutron diffraction experiments this process was repeated to produce ~18 g of material, except that the final firing was at 1100°C in air, and the material was then annealed at 600°C for 26 hours in air (SM3).

For the room-temperature X-ray diffraction experiments, aliquots of SM2 were annealed at 600 to 1100°C for times shown in Table 1 as powders in loosely crimped Pt capsules, then quenched as rapidly as possible by dropping into water (see O'Neill et al., 1991, 1993). The times selected were based on experience with other spinels, but the kinetics of cation order-disorder in oxide spinels varies enormously, and anyway depends on the exact stoichiometry of the sample (O'Neill, 199*).

Powder XRD

The room-temperature powder XRD investigation of the quenched specimens was carried out at UCLA. Digital data were collected by step-scanning using a CuKα-target sealed X-ray tube, Phillips goniometer operating in reflection mode, with continuously variable slit widths to give a constant 12x15 mm illuminated area, a graphite exit-beam monochromator and scintillation detector. Samples were mounted as flat specimens on glass plates, not spun. Data were measured in 15 second incremental steps of 0.025° 20 from 18 to to 144°. Structure refinement was carried out as described in O'Neill et al. (1991) and O'Neill and Dollase (1994). Briefly, reflection intensities were determined using an in-house least-squares peak-fitting program, FITX, which fits an asymmetric peak profile of variable peak location, area, and two widths (width of leading edge, width of trailing edge), peak shape and background height. Peak shape (Lorenzian/Gaussian proportions) and width functions of weak peaks were interpolated from trends revealed from fitting the strong reflections. Reflection intensities were corrected for LP, monochromator and multiplicity factors to produce squared structure factors, which were used to refine structure parameters with the in-house program, SIMU. Neutral atom scattering curves, taken from the International Tables, were corrected for real and imaginary components of anomalous dispersion. All structural refinements, both XRD and neutron diffraction, were carried out in the usual space group for spinels, Fd3m, with cubic symmetry. The results are given in Table 1.

The material used for the neutron diffraction experiments (SM3) was characterised at RSES, ANU by powder XRD using a Siemens D-5000, Co K α radiation, and adding an internal standard of NIST Si (a_o= 5.431195 Å). Data were collected from 15 to 135° 2 θ with stepsize 0.02, 9 sec/step, on a zero-background quartz plate, rotated 20 times a minute. The data were refined by the Rietveld

method using DBW2 (Table 1). The sample was confirmed to be single-phase spinel, with a lattice parameter of 8.0812 Å (probable uncertainty about ± 0.0002 Å).

Neutron Diffraction

Powder neutron diffraction measurements were made on the Medium Resolution Powder Diffractometer using thermal neutrons ($\lambda = 1.6652$ Å) from the HIFAR nuclear reactor at ANSTO (Kennedy, 1995). Data were collected using a bank of 32 ³He detectors over the range $-4^{\circ} < 2\theta <$ 138°, in 0.1° steps. The sample was heated in air and data collected at room temperature, 100 °C and then in 100 °C steps to 1000 °C. Structural refinements were carried out by the Rietveld method using the RIETICA program (Hunter, 1998) with pseudo-Voigt peak shapes and refined backgrounds. In light of the results from the XRD study, the thermal parameters for the octahedral and tetrahedral sites were constrained to be the same, but different for the oxygen site. Very good fits to the data were obtained (R_p : ~4.1% - 4.9 %) over the entire temperature range. A typical set of observed, calculated and difference neutron diffraction profiles (collected at 1000 °C) are shown in Figure 1. The diffraction peak labelled with "*" at $2\theta \sim 27.15^\circ$ is due to the furnace as opposed to the sample. Because the lattice parameters in high-temperature neutron diffraction experiments may be systematically in error due to sample displacement, the recorded lattice parameter at 20°C (8.0778 Å) was normalised to the value obtained by powder XRD with the internal standard of NIST Si (8.08123 Å), and the higher temperature values adjusted accordingly.

Results

Both the room-temperature XRD measurements and the high temperature neutron diffraction measurements confirm that the cation distribution in $CuAl_2O_4$ is highly disordered. The values of x

are plotted against presumed equilibration temperature in Fig. 2. The overall agreement with the study of Cooley and Reed (1972) is quite good, the latter being displaced to ~ 0.03 lower x, consistent with the loss of accuracy expected in their study since only a few diffraction peaks were used in their refinement; this loss of accuracy can be demonstrated empirically by a comparison of their results on NiAl₂O₄ with more recent work using full pattern refinements (O'Neill et al., 1991). Nevertheless, our results essentially confirm their surprising findings that despite the high degree of disorder at c. 600°C, there is very little further increase in disorder on heating to higher temperatures.

The value of x from the XRD experiments on the quenched samples are in good agreement with the in-situ neutron diffraction experiment at 600°C, but fall at slightly lower values of x at higher temperatures. The two data at 800 and 900°C show no increase in x over that at 600°C, indicating that their cation distribution may have reset during quenching. Because of this uncertainty we adopt the in-situ neutron diffraction results as being the more reliable. For all samples the oxygen positional parameter u is ~0.261, typical for "largely normal" 2-3 spinels (O'Neill and Navrotsky, 1983).

O'Neill and Navrotsky (1983) showed from lattice energy arguments that the change in enthalpy with x in a spinel was expected to have a quadratic form, i.e., $\Delta H(x) = \alpha x + \beta x^2$. The entropy accompanying cation disorder can be divided into two parts, the ideal configurational entropy, and the rest or nonconfigurational entropy, which might arise from changing vibrational entropy with x, short-range order, or for transition metal cations, electronic contributions (O'Neill and Navrotsky, 1983, 1984). The electronic entropy is of particular significance for CuAl₂O₄ as Cu²⁺ is a d⁹ cation. The ideal configurational entropy is:

$$S_{cf} = -\left(\sum_{M,b} n_b X_M^b \ln X_M^b\right) \tag{1}$$

where X_M^b is the fraction of cations of type M in site b. The non-configurational entropy is assumed to be a linear function of x, i.e., $S_{ncf} = \sigma x$. The free energy of the spinel relative to a standard state of the perfectly normal spinel (x=0) is therefore:

$$\Delta G(\mathbf{x}) = \alpha \mathbf{x} + 2\beta \mathbf{x}^2 - T\sigma \mathbf{x} + RT(\sum_{\mathbf{M},\mathbf{b}} n_{\mathbf{b}} \mathbf{X}_{\mathbf{M}}^{\mathbf{b}} \ln \mathbf{X}_{\mathbf{M}}^{\mathbf{b}})$$
(2)

At equilibrium, the free energy is at a minimum $(\partial \Delta G(x) / \partial x = 0)$, hence:

$$\operatorname{RT}\ln\left(\frac{x^2}{(1-x)(2-x)}\right) = -\alpha - 2\beta x + T\sigma$$
(3)

The small range of x causes two problems in fitting the present data to Eq. 3. Firstly, the terms in β and σ are so closely correlated that they cannot both be determined simultaneously. We therefore initially present two provisional models, one with σ set at zero, the other with β at zero. Secondly, previous experience studying the cation distribution in spinels with in-situ high-temperature methods has shown that when a sample is heated up, at some temperature the cation distribution that is frozen into the starting material begins to relax towards the equilibrium distribution at the temperature of the measurement (Redfern et al., 1996; Harrison et al., 1997). But for CuAl₂O₄, because of the small change in x with temperature, it is difficult to decide where this relaxation occurs. Accordingly, in fitting our data for CuAl₂O₄ we first used only the three highest-temperature data (800, 900 and 1000°C). We then successively added data until the quality of the fit, as measured by the reduced chisquared statistic (χ^2_v) deteriorated. We found that for both models, there was a sharp upturn in χ^2_v when the 500°C datum was included, hence we take 600°C as the lowest temperature at which equilibrium was reached. This conclusion seems reasonable in light of the kinetics of cation distributions in other spinels, and with the results from the quenched samples in the XRD part of the study. We emphasise, however, that we cannot rigorously exclude that equilibrium was not achieved

down to lower temperatures, particularly considering the fit to the $\sigma = 0$ model (Fig. 3). Including lower temperature data alters the best fit parameters somewhat, but this makes little difference to the arguments that follow. From 600 to 1000°C inclusive, these best fit parameters for the two provisional models are:

1)
$$\sigma = 0$$
 model: $\alpha = -18.3 \pm 9.6$, $\beta = +45.0 \pm 12.4$ kJ/mol; $\chi_v^2 = 0.49$

2)
$$\beta = 0$$
 model: $\alpha = 6.6 \pm 1.1$ kJ/mol, $\sigma = -9.3 \pm 1.0$ J/K.mol; $\chi_v^2 = 0.47$

These fits and their extrapolation to lower temperatures are compared to the data in Fig. 3. The peculiar reluctance of $CuAl_2O_4$ to disorder much further above 600°C may thus be ascribed either to a large positive β term, or to a large σ term.

Discussion

The Cu^{2+} cation has the 3d⁹ electronic configuration, and consequently is potentially subject to a strong Jahn-Teller effect. In $CuCr_2O_4$ and $CuRh_2O_4$, in which all the Cu^{2+} is in tetrahedral coordination due to the very high crystal-field stabilization energies of Cr^{3+} and Rh^{3+} in octahedral coordination, this manifests itself in a reduction of symmetry from $Fd\overline{3}m$ to a tetragonal derivative of the spinel structure (I4₁/amd), in which there is a considerable flattening of the Cu^{2+} coordination tetrahedron along the c axis (Dollase and O'Neill, 1997). Although this is accompanied by some distortion of the Cr^{3+} and Rh^{3+} coordination octahedra, it is clear from the fact that other Cr^{3+} and Rh^{3+} spinels are cubic (apart from the Ni²⁺ examples, which is expected because Ni²⁺ is also a Jahn-Teller ion in tetrahedral coordination) that the driving force for the distortion comes from the stereochemistry of the Cu^{2+} cation. $CuFe_2O_4$ does not show this structural distortion, consistent with it being a largely inverse spinel in which most of the Cu^{2+} is in octahedral coordination (Ohnishi and

Teranishi, 1961). Our results confirm that there is no structural distortion in $CuAl_2O_4$ either, despite approximately 2/3 of the Cu^{2+} being in the tetrahedral sites.

The tetrahedral site in cubic spinels with space group $Fd\overline{3}m$ is perfectly symmetrical, such that the Cu²⁺ cation with its d⁹ configuration will be associated with an entropy of Rln3 or 9.13 J/K.mol, due to the degeneracy of its electron orbitals (the Schottky effect). The corresponding electronic entropy in perfectly symmetrical octahedral coordination is Rln2 or 5.76 J/K.mol. The net electronic entropy of disordering, σ_{el} , would therefore be -3.37 J/K.mol (O'Neill and Navrotsky, 1983, Table 4). This is much less than the entropy of disordering deduced from the $\beta = 0$ model, which is -9.3 ± 1.0 J/K.mol. However, the octahedral site is in general somewhat distorted from the symmetrical in Fd $\overline{3}m$ spinels, potentially removing the orbital degeneracy. The extent to which this lowers the electronic entropy depends on by how much the loss of symmetry splits the orbitals in energy. This is not known, but the splitting energy is likely to be minimal in CuAl₂O₄ since the symmetry reduction is only slight (the octahedral site has the perfect symmetry when the oxygen positional parameter in the spinel structure, u, is 0.2625). Nevertheless, with no orbital degeneracy in the octahedral site, the electronic entropy of disordering would be -9.13 J/K.mol, in excellent agreement with the value observed in the β =0 model.

The alternative to this fairly large entropy of disorder is a large positive β parameter. O'Neill and Navrotsky (1983, 1984) suggested from an assessment of the empirical evidence available at the time that the value of the β parameter for most 2-3 spinels was about –20 kJ/mol. Subsequent work has in many cases confirmed the validity of this approximation (O'Neill et al., 1991; O'Neill, 1992, 1994), although exceptions have been found: Fe Al₂O₄ has $\beta = +19.7\pm3.4$ kJ/mol (Harrison et al., 1998), while Mg Al₂O₄ has +4.7±2.0 kJ/mol at zero pressure, but, interestingly, -20±13 kJ/mol at 2.6 GPa (Méducin et al., 2004). The reason for why a fairly modest pressure should have such a large effect

on the cation distribution in MgAl₂O₄ is not understood. Overall, though, since the exceptions are in a minority, the value of -20 kJ/mol continues to be a good initial guess for this parameter. The value found from the best fit with σ constrained to be zero (i.e., +45 kJ/mol) thus appears rather anomalous, although this is of course not a reason for excluding it. At present, there is no way to discriminate between whether the effect of temperature on the cation distribution in CuAl₂O₄ is due to a large non-configurational entropy or an unusually large and positive β parameter.

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Figure Captions

Figure 1. The observed (+), calculated (solid line) and difference powder neutron diffraction profiles for CuAl₂O4. The diffraction peak labelled with "*" at $2\theta \sim 27.15^{\circ}$ is due to the furnace.

Figure 2. The degree of inversion versus temperature in $CuAl_2O_4$ spinel. The solid curve is the least-squares best fit to the high-temperature in-situ neutron diffraction data between 600°C and 1000°C inclusive, assuming zero nonconfigurational entropy of disordering ($\sigma = 0$). The dashed curve is the fit to the same data with $\beta = 0$. Error bars are \pm one standard deviation in x.



Figure 1.

Tal	ble	1.

Sample	SM1(900)	SM2(1200)	SM3(600)	SM2/600	SM2/900	SM2/1000	SM2
Time (hrs)	132	70	26	242	15	0.5	0.16
X	0.360(13)	0.390(17)	0.378(5)	0.358(9)	0.355(7)	0.360(9)	0.391
u	0.2603(3)	0.2614(6)	0.2600(2)	0.2609(4)	0.2609(3)	0.2613(3)	0.260
B _{tet}	0.45(9)	1.31(7)	0.34(5)	1.51(5)	1.36(4)	1.31(5)	1.19(
B _{oct}	0.47(9)	1.34(7)	0.47(5)	1.44(5)	1.15(3)	1.16(5)	1.17(
B _{ox}	0.68(13)	2.06(12)	1.01(6)	2.05(10)	1.92(6)	1.76(8)	1.67(
$R_F/R_P(\%)$	2.0	3.5		2.4	1.9	2.8	2.3
$R_w/R_{Bragg}(\%)$	3.0	4.4	3.9	3.1	2.6	3.3	3.6
# refl	Rietveld	30	Rietveld	31	31	31	31

Table 2. Results from high-temperature neutron diffraction

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T (°C)	$a_{o}(A)^{a}$	u ^b	X ^c	В
20	8.081	0.2615	0.352	0.5
100	8.085	0.2614	0.364	0.6
200	8.092	0.2614	0.361	0.7
300	8.099	0.2613	0.364	0.8
400	8.105	0.2614	0.364	0.9
500	8.111	0.2614	0.371	1
600	8.119	0.2615	0.367	1.1
700	8.127	0.2614	0.381	1.3
800	8.136	0.2614	0.385	1.4
900	8.144	0.2611	0.402	1.6
1000	8.153	0.2611	0.405	1.6

experiments.

^a normalised to $a_0 = 8.0812$ Å at 20°C. Uncertainty ± 0.001 Å

^b ±0.0001 ^c ±0.005