Structural stability of CuAl$_2$O$_4$ under pressure

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Abstract

Structural properties of CuAl$_2$O$_4$, which was recently argued to show unusual suppression of the Jahn–Teller distortions by the spin–orbit coupling, are investigated under pressures up to 6 GPa. Analysis of x-ray powder diffraction experiments shows that CuAl$_2$O$_4$ gets unstable and decomposes onto CuO and Al$_2$O$_3$ at pressures $\sim$6 GPa and temperature $\sim$1000 K. This finding is complemented by the density-functional theory $+ U$ + spin–orbit coupling calculations, which demonstrate that this instability is partially driven by a (relatively) large compressibility of strongly Jahn–Teller distorted CuO.

Keywords: spinels, spin–orbit-coupling, high pressure

(Some figures may appear in colour only in the online journal)

1. Introduction

The AB$_2$O$_4$ (A-divalent cation such as Cu, Co; B-trivalent cation, e.g., Al, Fe) family of spinel oxides is known for their unique physical properties, which have been attracting considerable attention over the years. There are multiferroics among them, e.g., CdV$_2$O$_4$ [1], CoCr$_2$O$_4$ [2], and FeCr$_2$O$_4$ [3, 4], materials with charge [5] and orbital ordering [6], some of these spinels show rather unusual distortions of the crystal structure, which can be accompanied by strong modifications of their magnetic properties and even opening the spin gap [7–9].

In fact two different sites are available for metals in spinels: octahedral and tetrahedral. In ‘normal’ spinels-A(B)$_2$O$_4$—B ions sit at octahedral positions, while in ‘inverse’ ones-B(AB)O$_4$—they are distributed equally between octahedral and tetrahedral voids (and of course an intermediate situation with random distribution is also possible). The transition metals (TM) can occupy both sites. While a lot of afford is now concentrated on studying the spinels with TMs having octahedral coordination, an opposite situation is equally interesting. In the present paper we study structural properties of CuAl$_2$O$_4$, where Cu$^{2+}$ ions preferably occupy tetrahedral sites. They have 3$d^9$ electronic configuration and in tetrahedral surrounding Cu 3$d$ orbitals are split onto three high-lying t$_{2g}$-levels separated from two low-lying e$_g$-levels. Therefore, there is one hole in the t$_{2g}$ manifold in CuAl$_2$O$_4$, which is susceptible to further Jahn–Teller distortions to lower the total energy. However, previous x-ray powder diffraction studies did not detect any indications of the Jahn–Teller effect in CuAl$_2$O$_4$ [10]. It was later shown theoretically that the absence of the Jahn–Teller distortions can be related with formation of the $j_{\text{eff}} = 1/2$ state [11, 12]. Thus, it was suggested that Cu$^{2+}$ ions behave in this material similar to Ir$^{4+}$ ions also having t$_{2g}^5$ electronic configuration. Strong spin–orbit splitting lifts degeneracy and puts a single hole onto the $j_{\text{eff}} = 1/2$ spin–orbital retaining only Kramers degeneracy, which can not be removed by the Jahn–Teller distortions, see e.g. [13]. Moreover, it was shown that suppression of the Jahn–Teller effect is not gradual, but there is a critical value of strength of the spin–orbit coupling above which distortions vanish [14, 15]. Possible stabilization of the $j_{\text{eff}} = 1/2$ state makes CuAl$_2$O$_4$ a unique system, which is similar to famous iridates [16, 17],
but based on the 3d transition metal Cu. First theoretical calculations indeed demonstrated that one might expect strong anisotropy of the exchange coupling and stressed importance of the frustration effects, since magnetic Cu\(^{2+}\) ions form strongly frustrated diamond lattice [11]. However, all these results are based on, first, the assumption that there is an ideal ordering of Cu\(^{2+}\) ions and they occupy only tetrahedral sites (i.e. this is normal spinel), while there are experimental evidences of antisite defects [10, 18]. Second, there is of course always competition between the Jahn–Teller effect and spin–orbit coupling and, e.g., theoretical calculations show that applying pressure one may shift the balance between these two factors and CuAl\(_2\)O\(_4\) is expected to show Jahn–Teller distortions already at pressure [12]. Third, because of antisite disorder observed in previous studies it is highly desirable to find alternative synthesis methods or ways, which would modify the distribution of Cu\(^{2+}\) cations between the tetrahedral and octahedral sites of the spinel structure. The high-pressure (HP) high-temperature annealing is one of such methods.

In this work we focused on experimental and theoretical investigations of structural properties of CuAl\(_2\)O\(_4\) under high pressure. Ex-situ x-ray powder diffraction studies showed that at temperatures above about 1070 K and pressure of 6 GPa CuAl\(_2\)O\(_4\) decomposes through a complex way to a final mixture of initial oxides CuO and Al\(_2\)O\(_3\). The density-functional theory (DFT) + U + spin–orbit coupling (SOC) calculations confirmed that CuAl\(_2\)O\(_4\) is unstable at high pressure.

2. Experimental details and results

CuAl\(_2\)O\(_4\) was prepared from a stoichiometric mixture of Al\(_2\)O\(_3\) (99.9%) and CuO (99.9%). The mixture was pressed into a pellet and annealed on Pt foil at 1193 K for 84 h and at 1293 K for 38 h in air with several intermediate grindings. This phase will be called ambient-pressure CuAl\(_2\)O\(_4\), and it had orange-brown color. As-prepared single-phase CuAl\(_2\)O\(_4\) was then annealed in Au capsules at 6 GPa and different temperatures for 2 h using a belt-type HP apparatus (where the annealing temperature was reached in 10–15 min). After the HP high-temperature treatments, the samples were quenched to room temperature (RT) by turning off current, and the pressure was slowly released. Such samples will be called HP samples. We emphasize that the melting point of Au is above about 1600 K at 6 GPa [19]; therefore, the HP annealing could be performed safely up to 1523 K in gold capsules.

X-ray powder diffraction (XRPD) data were collected at RT on an RIGAKU MiniFlex600 diffractometer using CuK\(\alpha\) radiation (2\(\theta\) range of 8–140\(^\circ\), a step width of 0.02\(^\circ\), and a scan speed of 1 deg min\(^{-1}\)). XRPD data were analysed by the Rietveld method using Riet-an-2000 [20].

CuAl\(_2\)O\(_4\) prepared at ambient pressure was single-phase and had sharp reflections on XRPD patterns. The structural analysis gave the following cation distribution [Cu\(_{0.676}\)Al\(_{0.324}\)]\(_8\)O\(_4\) in [10] or \(x = 0.36–0.39\) for [Cu\(_{1-x}\)Al\(_{x}\)]\(_8\)[Al\(_{2-x}\)Cu\(_x\)]\(_{16}\)O\(_4\) in [18]).

XRPD patterns of the samples annealed at 6 GPa and different temperatures are given on figure 1. The spinel structure remains after annealing at 6 GPa and 880 K (powdered sample had orange-brown color) or 1048 K (powdered sample had brown color).

However, the reflections of the spinel phase were significantly broadened, and additional reflections from Au (the capsule material) appeared. Particle size is unlikely to significantly decrease at such annealing conditions. Therefore, the broadening of the reflections could originate from the accumulation of huge stress. The appearance of Au could be caused by a small and gradual loss of oxygen or copper by CuAl\(_2\)O\(_4\) near contacts with Au, where oxygen or metallic copper attacks Au and damages the capsule material.

An increase of the annealing temperature to 1073 K (at 6 GPa) resulted in a partial decomposition: an XRPD pattern showed the presence of a spinel phase, Al\(_2\)O\(_3\), and reflections from unknown phase(s) (see figure 2). This powdered sample had black color, and the pellet looked like a solidified melt. Further increase of the annealing temperature to 1413 K or 1523 K resulted in the complete decomposition of CuAl\(_2\)O\(_4\) to
Figure 2. Experimental (crosses), calculated (red line), and difference x-ray powder diffraction patterns for CuAl$_2$O$_4$ annealed at 6 GPa and 1073 K. Possible Bragg reflections for Al$_2$O$_3$ and CuAl$_2$O$_4$ phases are shown by tick marks. The difference pattern emphasizes reflections from new phase(s).

Figure 3. Energy–volume curves for CuAl$_2$O$_4$, CuO, and Al$_2$O$_3$, obtained by fitting the third order Birch–Murnaghan equation of states to energy–volume data.

3. Computational methods

First-principles DFT calculations were conducted to investigate the stability of CuAl$_2$O$_4$ under pressure. The calculations of CuAl$_2$O$_4$, CuO, and Al$_2$O$_3$ compounds were carried out using the Vienna ab initio simulation package [22]. We utilized the projector augmented-wave method [23] with the Perdew–Burke–Ernzerhof type of exchange-correlation functional [24] within the general gradient approximation (GGA + U) [25]. Initial crystal structure parameters were taken for CuAl$_2$O$_4$ from [10] ($T = 40$ K), for CuO from [26] ($T = 293$ K) and for Al$_2$O$_3$ from [27]. They were relaxed for all calculated volumes. On site Coulomb repulsion parameter $U$ was chosen to be 9 eV, while intra-atomic Hund’s exchange 1 eV [12]. The cut-off energy was taken to be $E_{\text{cutoff}} = 560$ eV and $6 \times 6 \times 6$ Monkhorst–Pack grid of $k$-points was used during calculations. The SOC was included to the calculation scheme for CuAl$_2$O$_4$ and CuO.

Strictly speaking DFT is valid only for zero temperature, while majority of HP experimental work is performed at 300 K and above. Therefore, we would like to mention that there is always at least the 300 K difference between theoretical and experimental conditions. This temperature difference is sometimes responsible for different values of pressure when a phase transition is predicted from first-principles calculations and observed in experiments.
4. Theoretical study of structural stability

The total energy dependence on the unit cell volume for CuAl₂O₄, CuO, and Al₂O₃ was obtained by series of calculations, where it was varied between about −10% and +10%.

First of all, we see that equilibrium volumes \( V_0 \) obtained in our calculations are close to experimental ones, so that \( (V_0 - V_0^{\text{exp}})/V_0^{\text{exp}} \) is 0.031 for CuAl₂O₄ [10], 0.008 for CuO [26] and 0.027 for Al₂O₃ [27], which are very typical estimates for DFT [28]. The energy-volume curves for CuAl₂O₄, CuO, and Al₂O₃ compounds are given in figure 3.

Next we extracted other parameters of the equation of state (the zero pressure total energy \( E_0 \), the equilibrium volume \( V_0 \), and the bulk modulus \( B_0 \) by fitting the calculated energies versus volume to the third order Birch–Murnaghan equation of states [29]. Already at this level we see that compressibility (inverse of Bulk modulus) of CuO is much larger than in both CuAl₂O₄ and Al₂O₃ (table 1). The thermodynamic stability of CuAl₂O₄ was investigated by comparing the enthalpies of CuAl₂O₄ and CuO + Al₂O₃, which are shown in figure 4. One may see that in DFT + U + SOC calculations CuAl₂O₄ becomes unstable at pressures \( \sim 8 \) GPa, which is close to experimental \( P_c = 6 \) GPa.

It is instructive to study physical origin of this decomposition. For this in table 2 we present results of fitting of enthalpy by the third order polynomials

\[
H(P) = a \cdot P^2 + b \cdot P + c + d \cdot P^3
\]

for CuAl₂O₄, CuO, and Al₂O₃ compounds (here \( P \) stands for pressure).

By analyzing parameters of fitting, one can see that quadratic and cubic terms, characterized by coefficients \( a \) and \( d \) respectively, are much smaller than other terms (parametrized by \( b \) and \( c \)) and therefore these coefficients only weakly affect structural stability of the materials under consideration in a given pressure range.

One can see that the constant term \( (c) \) is much smaller for CuAl₂O₄ and this reflects structural stability of this material at normal conditions.

The linear term, characterized by positive coefficient \( b \), destabilizes all compounds, since the enthalpy grows in all of them due to this linear term. However, it increases very differently for CuAl₂O₄, CuO, and Al₂O₃. If \( b \) for mixture of CuO and Al₂O₃ would be larger than for CuAl₂O₄ then the later would be stable at any pressure. Our calculations show that this is not the case: \( b_{\text{CuAl2O4}} = 0.422 \) eV GPa \(^{-1} \), while \( b_{\text{CuO + Al2O3}} = 0.403 \) eV GPa \(^{-1} \) and this is one of the reasons why CuAl₂O₄ decomposes under pressure. One can also see that \( b \) coefficient for CuO is much smaller than for Al₂O₃ and therefore at pressures \( \sim 8 \) GPa, the largest contribution to relative (with respect to CuAl₂O₄) decrease of the enthalpy of the mixture CuO + Al₂O₃ (\( \delta H_{\text{CuO+Al2O3}} = -3.54 \) eV) is mostly due to CuO (\( \delta H_{\text{CuO}} = -2.36 \) eV). Thus, small \( b \) for CuO coefficient is one of the most important factors, which results in decomposition of CuAl₂O₄.

Interestingly, the compressibility of CuO has been studied experimentally in reference [26], where it was shown that it is very different for three different Cu–O bonds. The Cu\(^{2+} \) ions in this material have octahedral surrounding, but these octahedra are so elongated, that it even seems that Cu ions are in the middle of plaquetes, not octahedra, see figure 6.

The compressibility of long apical Cu–O bonds is much larger than others (which is rather natural) and this explains overall (relatively) large compressibility of CuO. We find at pressure 8 GPa that decrease of Cu–O bond length is only \( \sim 0.031 \) in CuAl₂O₄, while the longest bond in CuO changes much larger, on \( \sim 0.072 \) Å (two others decrease on 0.030 Å and 0.026 Å) in the same pressure range, see figure 5.

The second very important factor is the electronic correlations. We found that decrease of Hubbard \( U \) on 1 eV suppresses \( P_c \) down to \( \sim 4 \) GPa, so that the optimal \( U \) is \( \sim 8.5 \) eV. Detailed analysis shows that with decrease of \( U \) nearly does not change \( a \), \( b \), and \( d \) parameters in (1), but decreases \( c \) coefficient for CuO stronger than for CuAl₂O₄ (for

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Table 1. The equation of state parameters of CuAl₂O₄, CuO, and Al₂O₃ obtained by fitting the calculated GGA + U + SOC energies versus volume data to the third order Birch–Murnaghan equation of states.

|                | CuAl₂O₄ | CuO  | Al₂O₃ |
|----------------|---------|------|-------|
| \( E_0 \), eV  | −90.8   | −31.2| −224.5|
| \( V_0 \), Å   | 135.2   | 81.6 | 262.9 |
| \( B_0 \), GPa | 187.7   | 140.4| 230.8 |
| \( B_0' \)     | 4.2     | 4.7  | 4.04  |
Table 2. Parameters of fitting GGA + U + SOC enthalpies by the third order polynomials $a P^2 + b P + c + d P^3$ for CuAl$_2$O$_4$, CuO, and Al$_2$O$_3$. Here $P$ stands for pressure.

| Material     | $a$, (eV (GPa)$^{-2}$) | $b$, (eV (GPa)$^{-1}$) | $c$, eV | $d$, (eV (GPa)$^{-3}$) |
|--------------|------------------------|-------------------------|--------|------------------------|
| CuAl$_2$O$_4$| -0.001                 | 0.422                   | -45.378| 6.723 $\times 10^{-6}$ |
| CuO          | -0.0005                | 0.127                   | -7.808 | 4.547 $\times 10^{-6}$ |
| Al$_2$O$_3$  | -0.0006                | 0.274                   | -37.409| 2.773 $\times 10^{-6}$ |

Figure 5. Variation of lattice parameters with pressure in CuAl$_2$O$_4$, CuO, and Al$_2$O$_3$ as obtained in the DFT + U calculations. $U = 8$ eV, $c_{\text{CuO}} = -7.991$ eV, while $c_{\text{CuAl}_2\text{O}_4} = -45.779$ eV. Thus, we see that correlation effects stabilize CuAl$_2$O$_4$ under pressure. This is because of weaker hybridization of Cu 3$d$ states with O 2$p$ states in tetrahedral geometry of CuAl$_2$O$_4$.

Of course there are also other factors, which affect decomposition of CuAl$_2$O$_4$ under pressure. Corund (α-Al$_2$O$_3$) is a rather stable structure: constant coefficient $a$ for Al$_2$O$_3$ is very low and this also works for stabilization of CuO and Al$_2$O$_3$ mixture. One might expect that the close packed corundum structure is clearly more favourable than cubic packing of oxygen atoms in spinels, if we apply pressure, and a rather high temperature in our experiment also facilitates the decomposition.

It has to be also mentioned that present results rely on the crystal structure with the idealized atomic order—Cu ions occupy tetrahedral sites, while Al ions are octahedral. In real CuAl$_2$O$_4$ there is a certain degree of disorder between Cu and Al and this must be taken into account in further studies.

5. Conclusions

To sum up the stability of CuAl$_2$O$_4$ spinel under high pressure has been investigated in the present paper experimentally and theoretically. Our ex-situ x-ray powder diffraction study showed that this material decomposes at pressure of 6 GPa above about 1070 K onto the final mixture of CuO and Al$_2$O$_3$. The DFT + U + SOC calculations generally support this finding with critical pressure of $\sim$8 GPa for zero temperature and demonstrate that one of the important factors, which results in decomposition, is a compressibility of CuO. It is also shown that electronic correlations work in opposite direction additionally stabilizing CuO under pressure.

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