

**Cu(Cu<sub>0.44</sub>Cr<sub>4.56</sub>)Ge<sub>2</sub>O<sub>12</sub>: a close-packed oxide with CuO<sub>4</sub> tetrahedra**Günther J. Redhammer,<sup>a\*</sup> Georg Roth<sup>b</sup> and Georg Amthauer<sup>a</sup><sup>a</sup>Department of Material Science, Division of Mineralogy, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria, and <sup>b</sup>Institute of Crystallography, RWTH Aachen University, Jägerstrasse 17/19, D-52056 Aachen, Germany  
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The structure of copper(I,II) pentachromium(III) germanate, Cu(Cu<sub>0.44</sub>Cr<sub>4.56</sub>)Ge<sub>2</sub>O<sub>12</sub>, contains one Cu position (*m2m*), one Ge position (*m*) and three Cr positions (*2/m, m* and *2*). The close-packed structure is described in terms of slabs of edge-sharing Cr<sup>3+</sup>O<sub>6</sub> octahedra and isolated CuO<sub>4</sub> and GeO<sub>4</sub> tetrahedra. These slabs are aligned parallel to the *bc* plane and are separated from each other by GeO<sub>4</sub> tetrahedra along *a*. The tetrahedral coordination observed for the Cu<sup>+</sup>/Cu<sup>2+</sup> ions represents an unusual feature of the structure. The Cr—O and Cu—O bond lengths are compared with literature data.

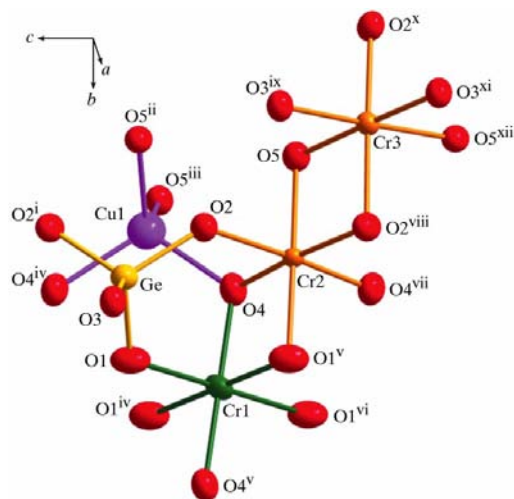
**Comment**

Cu(Cu<sub>0.44</sub>Cr<sub>4.56</sub>)Ge<sub>2</sub>O<sub>12</sub> was synthesized during our investigation of Cu-containing germanates (Redhammer & Roth, 2004a; Redhammer *et al.*, 2005). It represents a new structure type and, to the best of our knowledge, is the first copper chromium germanate reported. Lambert & Eysel (1968) were the only workers to study the CuO—Cr<sub>2</sub>O<sub>3</sub>—GeO<sub>2</sub> system previously and they noted the absence of ternary compounds. It may also be noted that Cr-containing germanates are also rare, with only seven entries in the current Inorganic Crystal Structure Database (ICSD, 2006), including cubic and tetragonal spinels (Hirota *et al.*, 1990; Isasi *et al.*, 1996) and pyroxene-type LiCrGe<sub>2</sub>O<sub>6</sub> (Redhammer & Roth, 2004b). In contrast, a larger number of copper germanates are known.

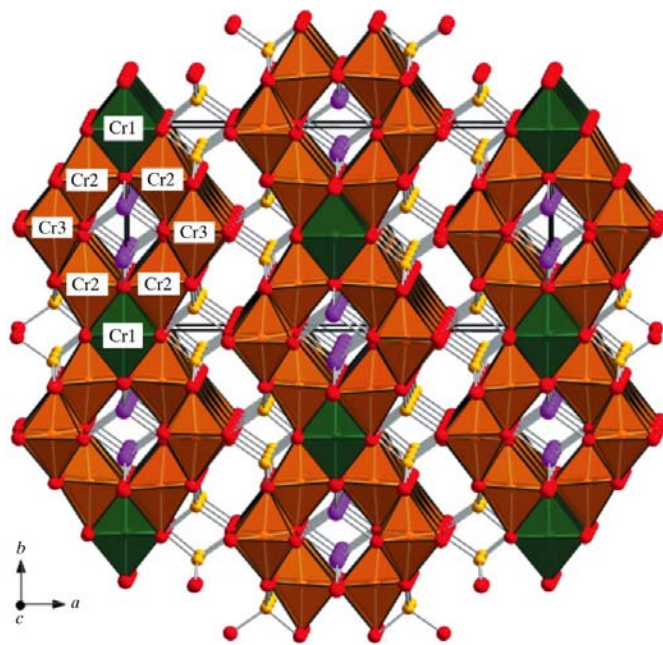
The asymmetric unit of the title crystal structure contains one Cu-, three Cr-, one Ge- and five O-atom positions (Fig. 1). The structure is built of edge-sharing CrO<sub>6</sub> octahedra that also share corners with CuO<sub>4</sub> and GeO<sub>4</sub> tetrahedra (Figs. 2 and 3). The basic unit of the structure is a (100) slab containing the Cu tetrahedra and Cr1—Cr3 octahedra, with adjacent slabs being linked to each other along *a* by the GeO<sub>4</sub> tetrahedra. An alternative description of the structure emphasizes the cubic close-packed arrangement of the O atoms (Fig. 3) and reveals a topology closely related to the spinel structure type and the orthorhombic *M*<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> structure type (Sauerbrei *et al.*,

1973). Indeed, the structure of the title compound can be described as a 1:1 intergrowth of spinel and *M*<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> slabs along the *a* axis (*i.e.* *M*<sub>2</sub>TO<sub>4</sub> + *M*<sub>3</sub>T<sub>2</sub>O<sub>8</sub> = *M*<sub>5</sub>T<sub>3</sub>O<sub>12</sub>, where *M* are octahedrally and *T* are tetrahedrally coordinated cations).

The bond lengths, the O—O edge lengths and the volume of the CrO<sub>6</sub> octahedron are all distinctly different from those of the Cr<sub>2</sub>O<sub>6</sub> and Cr<sub>3</sub>O<sub>6</sub> octahedra (Tables 1 and 2). The Cr1—O bond lengths vary between 1.941 (3) and 2.111 (2) Å, and this upper value is large for Cr<sup>3+</sup>—O bonds, as shown by an

**Figure 1**

A view of the asymmetric unit and some symmetry-related ellipsoids and the atom-numbering scheme. [Symmetry codes: (i)  $x, y, \frac{3}{2} - z$ ; (ii)  $x, -y, 1 - z$ ; (iii)  $1 - x, -y, \frac{1}{2} + z$ ; (iv)  $1 - x, y, \frac{3}{2} - z$ ; (v)  $x, 1 - y, 1 - z$ ; (vi)  $1 - x, 1 - y, -\frac{1}{2} + z$ ; (vii)  $1 - x, y, \frac{1}{2} - z$ ; (viii)  $x, y, \frac{1}{2} - z$ ; (ix)  $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (x)  $x, -y, -\frac{1}{2} + z$ ; (xi)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (xii)  $x, -y, -z$ .]

**Figure 2**

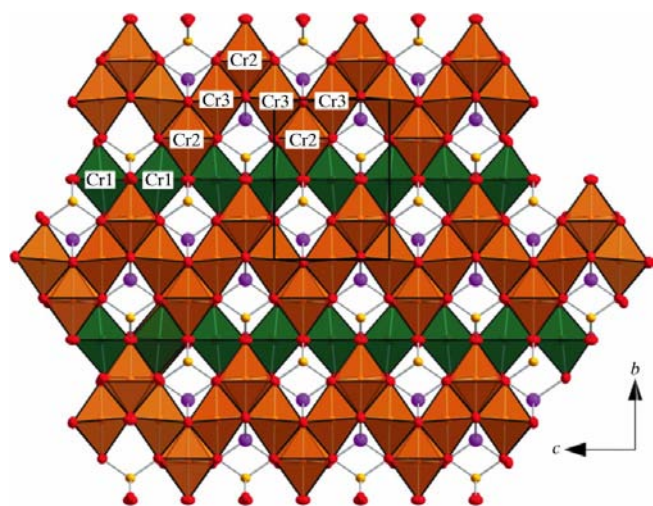
A view of the structure of the title compound along the *c* direction, showing the Cr1—Cr3 octahedra, the Ge sites (small spheres) and the Cu sites (large spheres).

evaluation of 925 individual bonds in 130 compounds in the ICSD that yielded a mean Cr—O value of 1.982 Å ( $\sigma = 0.089$  Å), with only a few bonds longer than 2.10 Å (Fig. 4a). The large mean Cr1—O bond length, the low bond-valence sum [ $S = 2.52$  valence units (v.u.); Brese & O'Keeffe, 1991] and the overpopulation of the Cr1 site when solely filled with Cr (see below) are all evidence for a mixed (Cr+Cu) occupancy of this site. Assuming valences of +3 and +2 for Cr and Cu, respectively, the refined content of  $\text{Cr}_{0.56}\text{Cu}_{0.44}$  yields a nominal valence of 2.56 v.u., in good agreement with the bond-valence sum  $S = 2.52$  v.u. While the bond-length distortion (BLD; Renner & Lehmann, 1986) is large for the  $\text{Cr1O}_6$  octahedron, the octahedral angle variance (OAV) and the quadratic octahedral elongation (QOE) (Robinson *et al.*, 1971) are the lowest of all three  $\text{CrO}_6$  octahedra (Table 2). The Cr1 site is thus regular in terms of the angular distortion, but shows a distinct tetragonal compression along the  $b$  axis.

The Cr2 site shows a more regular BLD, with typical Cr2—O bond lengths (Table 2 and Fig. 4a). Similar to Cr1, the Cr2 site is characterized by a high fraction of shared O—O edges. As a result, the Cr···Cr distances are shorter than 3.00 Å (Table 2). The  $\text{Cr3O}_6$  octahedron has the smallest number of shared edges, with the most regular BLD and the largest angular distortion and quadratic elongation (Table 2).

The most unusual feature of the structure is the tetrahedral coordination of the Cu1 site with  $m2m$  symmetry. Given the  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  mixing on the Cr1 site, it follows that the Cu1 site must be occupied by  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  for charge balance. This is also supported by the bond-valence sum, which is significantly higher than 1 v.u. (Table 2). The  $\text{Cu1O}_4$  tetrahedron is almost ideal, with small distortion parameters (Table 2) and nearly ideal bond angles (Table 1). Interestingly, it is more regular than the  $\text{GeO}_4$  tetrahedron.

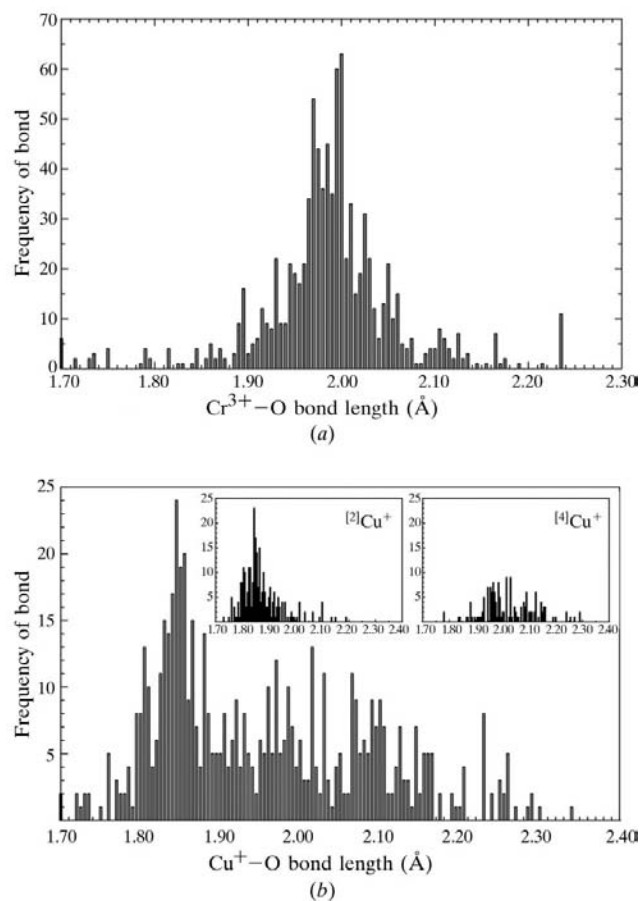
Copper is not frequently found in a tetrahedral coordination. An evaluation of 170 compounds in the ICSD containing 600 individual  $\text{Cu}^+$ —O bonds showed the following distribu-



**Figure 3**  
A view of the structure of the title compound along the  $a$  direction.

tion of coordination environments: threefold ( $\sim 5\%$ ), sixfold ( $\sim 5\%$ ) and fourfold ( $\sim 18\%$ ), with the remaining  $\sim 72\%$  in twofold coordination. Among the four-coordinated  $\text{Cu}^+$  ions, approximately one third are in a square-planar environment and two thirds in a tetrahedral environment. The individual  $\text{Cu}^+$ —O bond lengths are scattered between 1.70 and 2.30 Å (Fig. 4b), with a distribution strongly influenced by the coordination geometry. For twofold coordination, the majority of data lie between 1.80 and 1.93 Å (average value = 1.867 Å,  $\sigma = 0.072$ ) (inset in Fig. 4b). For square-planar coordination, one finds a rather narrow distribution with an average bond length of 1.946 Å ( $\sigma = 0.052$ ). For tetrahedral coordination, the bond lengths are between 1.83 and 2.28 Å (average value = 2.045 Å,  $\sigma = 0.094$ ). The  $\text{Cu1}$ —O bonds in the title compound match the average tetrahedral  $\text{Cu}^+$ —O bond length very well. In most compounds containing  $\text{Cu}^+\text{O}_4$  tetrahedra, these are strongly distorted (flattened) and only spinels, such as  $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (Vandenberghe *et al.*, 1976) or  $\text{CuFe}_5\text{O}_8$  (Mexmain, 1971), contain regular tetrahedra. This again illustrates the relationship between the spinel structure type and the title compound.

As in the case of  $\text{Cu}^+$ , tetrahedral coordination for  $\text{Cu}^{2+}$  is rare, due to the specific electronic configuration of the cation



**Figure 4**  
Histogram plots of (a) 925 individual  $\text{Cr}^{3+}$ —O bond lengths and (b) 600  $\text{Cu}^+$ —O bond lengths, taken from the ICSD. The histogram groups have a width of 0.005 Å. [2] and [4] superscripts in the inset denote two- and fourfold oxygen coordination, respectively.

(Jahn–Teller distortion). Only a few examples are known, such as akermanite-type  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  (Tovar *et al.*, 1998), spinel-type  $\text{CuCr}_2\text{O}_4$  and  $\text{CuRh}_2\text{O}_4$  (Dollase & O'Neill, 1997), or pollucite-type  $\text{Cs}_2\text{CuSi}_5\text{O}_{12}$  (Heinrich & Baerlocher, 1991). The  $\text{Cu}^{2+}\text{O}_4$  tetrahedra are distinctly flattened in all these structures. Thus, the almost ideal tetrahedral coordination of Cu in the title compound can indeed be regarded as a rather unusual feature of the structure. However, it should be noted that the atomic displacement of Cu1 is rather large, a fact that might indicate split sites for Cu1 (see *Refinement* section).

Although the  $\text{GeO}_4$  tetrahedron, with site symmetry  $m$ , is more distorted than the  $\text{CuO}_4$  tetrahedron (Table 2), it is still rather regular. By comparison, the  $\text{GeO}_4$  tetrahedra in  $\text{Ca}_{7.96}\text{Cu}_{0.04}\text{Ge}_5\text{O}_{18}$  (Redhammer *et al.*, 2006),  $\text{CaZn}_2\text{Ge}_2\text{O}_7$  (Redhammer & Roth, 2006),  $\text{CaCuGe}_2\text{O}_6$  (Redhammer *et al.*, 2005) or  $\text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13}$  (Redhammer & Roth, 2004a) all exhibit larger polyhedral distortions, especially in terms of the tetrahedral angle variance and quadratic tetrahedral elongation. The longest Ge–O bond in the title compound is Ge–O1, which is 0.02 Å longer than Ge–O2 or Ge–O3 (Table 2). Atom O1 is bonded to one Ge and three Cr atoms, while atoms O2 and O3 are bonded to one Ge and two Cr atoms only. With four bonds contributing to the bond-valence sum of O1, individual bonds to O1 are expected to be weaker, and hence longer. Stronger repulsions between  $\text{Ge}^{4+}$  and the three neighbouring  $\text{Cr}^{3+}$  ions around O1 may also be responsible for the longer Ge–O1 bond.

## Experimental

The title compound was found by chance in an attempt to grow crystals of  $\text{Cu}_2\text{Cr}_2\text{Ge}_4\text{O}_{13}$ , an analogue of  $\text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13}$  (Redhammer *et al.*, 2005), by slow cooling from the melt. For this purpose, a stoichiometric homogenous mixture of CuO,  $\text{Cr}_2\text{O}_3$  and  $\text{GeO}_2$  was carefully ground in an agate mortar and placed in a small open platinum tube (length 30 mm, internal diameter 5 mm). This assemblage was transferred to a high-temperature furnace, slowly heated to 1773 K at a rate of 1 K  $\text{min}^{-1}$ , held at this temperature for 12 h to homogenize the melt and cooled to 1323 K at a rate of 0.03 K  $\text{min}^{-1}$ . The products consisted mainly of  $\text{CuGeO}_3$ ,  $\text{GeO}_2$ , minor  $\text{Cr}_2\text{GeO}_5$  and some very small prismatic to needle-like black crystals of the title compound (less than 5% by volume). Semi-quantitative energy-dispersive X-ray (EDX) analysis showed that only Cu, Cr, Ge and O were present. The average composition from ten analyses of three different crystals was (in atom% and normalized to 100): 7.47 (9) Cu, 22.20 (11) Cr, 9.97 (7) Ge and 60.36 (21) O, yielding a formula of  $\text{Cu}_{1.48}\text{Cr}_{4.41}\text{Ge}_{1.98}\text{O}_{12}$ . Due to the small size of the crystals, we were unable to perform an electron microprobe analysis. According to Breuer *et al.* (1986), the reduction of CuO to  $\text{Cu}_2\text{O}$  takes place at 1293 K in air. The presence of  $\text{Cu}^+$  in the title compound is therefore not unexpected based on the synthesis conditions.

### Crystal data

$\text{Cu}(\text{Cu}_{0.44}\text{Cr}_{4.56})\text{Ge}_2\text{O}_{12}$	$Z = 4$
$M_r = 665.78$	$D_x = 5.305 \text{ Mg m}^{-3}$
Orthorhombic, <i>Cmcm</i>	Mo $K\alpha$ radiation
$a = 17.176 (2) \text{ \AA}$	$\mu = 16.49 \text{ mm}^{-1}$
$b = 8.2272 (10) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 5.8996 (7) \text{ \AA}$	Needle, black
$V = 833.68 (17) \text{ \AA}^3$	$0.09 \times 0.03 \times 0.03 \text{ mm}$

### Data collection

Bruker SMART APEX diffractometer	4822 measured reflections
Rotation, $\omega$ scans at four different $\varphi$ positions	595 independent reflections
Absorption correction: numerical via equivalents using <i>X-SHAPE</i> (Stoe & Cie, 1996)	481 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.55$ , $T_{\max} = 0.61$	$R_{\text{int}} = 0.042$
	$\theta_{\max} = 28.8^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.053$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.90 \text{ e \AA}^{-3}$
595 reflections	$\Delta\rho_{\min} = -0.71 \text{ e \AA}^{-3}$
62 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Cu1–O4	2.026 (3)	Cr1–Cr2	2.9004 (7)
Cu1–O5 <sup>i</sup>	2.038 (3)	Cr2–Cr3	2.9587 (7)
Ge–O2	1.755 (2)	Cr2–O5	1.939 (4)
Ge–O3	1.757 (3)	Cr2–O4	1.965 (2)
Ge–O1	1.778 (4)	Cr2–O1 <sup>iv</sup>	2.002 (4)
Cr1–O4	1.941 (3)	Cr2–O2	2.004 (2)
Cr1–O1	2.111 (2)	Cr3–O5	1.974 (2)
Cr1–Cr1 <sup>ii</sup>	2.9498 (4)	Cr3–O2 <sup>v</sup>	1.985 (2)
Cr3–Cr3 <sup>iii</sup>	2.9498 (4)		
O4 <sup>vi</sup> –Cu1–O4	110.36 (19)	O2–Ge–O3	111.72 (9)
O4 <sup>vi</sup> –Cu1–O5 <sup>i</sup>	109.59 (7)	O2–Ge–O1	109.10 (10)
O5 <sup>i</sup> –Cu1–O5 <sup>vii</sup>	108.1 (2)	O3–Ge–O1	105.44 (17)
O2–Ge–O2 <sup>vi</sup>	109.64 (15)		

Symmetry codes: (i)  $x, -y, -z + 1$ ; (ii)  $-x + 1, -y + 1, z + \frac{1}{2}$ ; (iii)  $x, y, -z - \frac{1}{2}$ ; (iv)  $x, -y + 1, -z + 1$ ; (v)  $x, -y, z - \frac{1}{2}$ ; (vi)  $x, y, -z + \frac{3}{2}$ ; (vii)  $-x + 1, -y, -z + 1$ .

**Table 2**

Selected structural and polyhedral distortion parameters for the title compound.

	Ge	Cu1		Cr1	Cr2	Cr3
$\langle T-O \rangle$ (Å)	1.762	2.032		2.055	1.980	1.980
$\langle O-O \rangle$ (Å)	2.876	3.318		2.906	2.780	2.797
BLD† (%)	0.41	0.30		3.68	1.18	0.21
Volume (Å <sup>3</sup> )	2.800	4.31		11.47	10.22	10.20
TAV‡ (°)	5.323	0.55		12.84	29.47	34.16
TQE§	1.0013	1.0001		1.0068	1.0085	1.0096
$S^\parallel$ (v.u.)	3.86	1.28		2.52	3.01	3.00

† Bond-length distortion,  $\text{BLD} = (100/n) \sum_{i=1}^n \{[(X-O)_i - \langle X-O \rangle] / \langle X-O \rangle\}$ , where  $n$  = number of bonds,  $(X-O)_i$  = central cation–oxygen length and  $\langle X-O \rangle$  = average cation–oxygen bond length (Renner & Lehmann, 1986). ‡ Tetrahedral angle variance,  $\text{TAV} = \sum_{i=1}^n (\Theta_i - 109.47)^2 / 5$ , with  $\Theta_i$  = individual O–T–O tetrahedral bonding angle (Robinson *et al.*, 1971). § Tetrahedral quadratic elongation,  $\text{TQE} = \sum_{i=1}^n (l_i/l_o)^2 / 4$ , where  $l_i$  = centre-to-vertex distance for a regular tetrahedron whose volume is equal to that of the undistorted tetrahedron with bond length  $l_o$  (Robinson *et al.*, 1971). ¶ Bond-valence sum  $S$  (Brese & O'Keeffe, 1991). †† Octahedral angle variance,  $\text{OAV} = \sum_{i=1}^n (\Theta_i - 90)^2 / 11$  (Robinson *et al.*, 1971). ††† Octahedral quadratic elongation,  $\text{OQE} = \sum_{i=1}^n (l_i/l_o)^2 / 6$ , where  $l_o$  = centre to vertex distance for a regular octahedron whose volume is equal to that of the undistorted octahedron with bond length  $l_o$  (Robinson *et al.*, 1971).

Structure solution using Patterson methods yielded the Cu, Cr and Ge positions, and the O atoms were located from residual electron-density analysis in subsequent refinement cycles. Full anisotropic

refinement on  $F^2$  using fixed site occupancies for the metal sites led to a final  $wR_2$  value of 9.3% and a formula of  $\text{Cu}^+\text{Cr}_5^{3+}\text{Ge}_2\text{O}_{12}$ . Releasing the site occupancies of all metal sites resulted in a drastic drop of  $wR_2$  to 5.4%, with occupancies of 0.249 (3), 0.499 (3), 0.497 (3) and 0.495 (4) for the Cu, Ge, Cr2 and Cr3 sites, respectively. However, the Cr1 occupancy of 0.279 (3) was significantly above 0.25, indicating that either Ge or Cu also occupied this site. Since the bond-valence sum for Cr1 was significantly below 3.0 and  $\text{Ge}^{4+}$  distinctly prefers tetrahedral coordination, it was concluded that Cu was present on the Cr1 site, at a final occupancy of  $\text{Cu}_{0.44}\text{Cr}_{0.56}$ .

As the displacement parameter for the Cu1 site is almost twice as large as those for the Ge and Cr1–Cr3 sites, the Cu1 occupancy was checked carefully in the final refinement cycles. No reduced occupancy and no substitution by lighter Cr atoms could be detected. The sum formula of  $\text{Cu}_{1.44}\text{Cr}_{4.56}\text{Ge}_2\text{O}_{12}$  resulting from the structure refinement agrees well with the semi-quantitative energy dispersive X-ray analysis.

The large displacement parameter of the Cu1 site could possibly be the result of positional disorder, which has also been investigated. By fixing  $U$  to a value of  $0.008 \text{ \AA}^2$  (close to the  $U$  values of the other cation sites), the Cu1 site can be split into three subsites, *viz.* Cu1a at  $4c$  [ $\frac{1}{2}$ , 0.124 (6),  $\frac{3}{4}$ ], Cu1b at  $8g$  [0.492 (1), 0.138 (2),  $\frac{3}{4}$ ] and Cu1c at  $8f$  [ $\frac{1}{2}$ , 0.112 (2), 0.776 (7)], with occupancies of 0.09 (2), 0.07 (2) and 0.08 (3), respectively. Such disorder may reflect the fact that the regular tetrahedral coordination of the unsplit Cu1 site is not ideally suited to either  $\text{Cu}^+$  or  $\text{Cu}^{2+}$ . The Cu1b and Cu1c positions correspond to distorted tetrahedral coordination environments, with Cu–O bond lengths ( $\text{\AA}$ ) of  $1.97 (1) \times 2$ ,  $2.00 (1)$  and  $2.21 (1)$  for Cu1b, and of  $1.96 (2)$ ,  $1.99 (2) \times 2$  and  $2.21 (4)$  for Cu1c. The refinement of this split model yields  $R$  indices similar to those of the unsplit model but is only stable with constrained displacement parameters for Cu1a–Cu1c.

Data collection: *SMART-Plus* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3029). Services for accessing these data are described at the back of the journal.

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