Refinement of the crystal structure of $K_8Ge_{44}\square_2$, *an intermetallic clathrate I*

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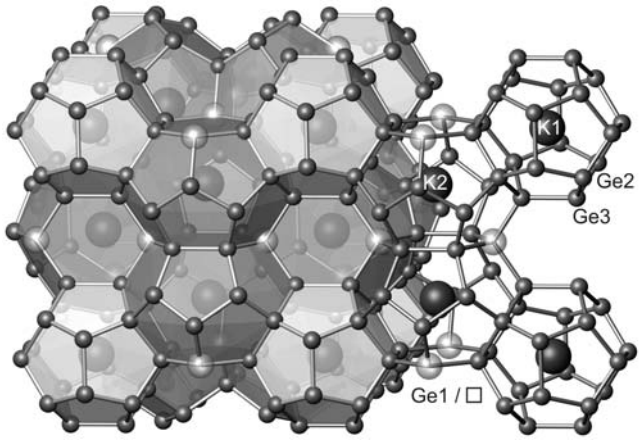

Abstract
$Ge_{44}K_8$, cubic, $Pm\bar{3}n$ (no. 223), a = 10.686(4) Å, V = 1220.2 Å^3, Z = 1, $R_{gt}(F)$ = 0.036, $wR_{obs}(F)$ = 0.043, T = 295 K.

Source of material
3.49 g (89.3 mmol) of K and 2.16 g (29.8 mmol) of Ge powder were welded under argon atmosphere in a Nb ampoule. The ampoule was sealed under argon in a silica tube, heated within 12 h to 930 °C, annealed for 120 h at this temperature and cooled down within 40 h to room temperature. After evaporation of potassium under dynamic vacuum at $p = 10^{-2}$ mbar and $T \geq 200$ °C, the reaction product consisted mainly of column-shaped crystals of $K_8Ge_{44}\square_2$, 1 - 2 mm in length. A small amount of K_4Ge_4 was found as an impurity phase. $K_8Ge_{44}\square_2$ is stable against HNO_3 but dissolves in nitrohydrochloric acid.

Discussion
A clathrate-I phase in the system K-Ge was first obtained by Hohmann, who investigated phases formed by thermal decomposition of K_4Ge_4 on heating under vacuum. The reflections of a clathrate I phase are undoubtedly present in the reported X-ray diffraction pattern [1]. Later on, Cros *et al*. identified the clathrate phase in the X-ray powder pattern of a similar product. Moreover, a careful investigation of the reflection intensities pointed to the presence of vacancies in the Ge framework and the composition K_7Ge_{45} was reported [2]. However, a redetermination of the crystal structure based on X-ray single crystal data revealed the composition K_8Ge_{46} [3], which has been used in literature thereafter [4,5]. In this structure model, the Ge framework consists only of four-bonded atoms so that the valence of the Ge atoms is saturated according to the (8-*N*)-rule. To explain the chemical bonding, it was discussed whether the excess electrons delivered by K^+ cations occupy antibonding states or remain localized at the K atoms. Finally, this question was answered, when the Zintl-Klemm concept was applied to predict the vacancy concentration in the Ge_{46} famework: The valence electrons of the K atoms are transferred to the Ge atoms forming three-bonded Zintl-anions $(3b)Ge^{1-}$. A vacancy □ in the framework is surrounded by four $(3b)Ge^{1-}$ and has to host four electron pairs which account for the electron excess from the alkaline metals. The octet rule is fulfilled for the composition $[K^+]_8[\square(Ge^-)_4]_2[Ge^0]_{36}$ [6-8].
The here presented redetermination of the crystal structure reveals the expected partial occupancy of the Ge1 site 6*c* of ≈ 2/3, whereas the site 16*i* of Ge2 and the site 24*k* of Ge3 atoms are fully occupied. The composition of the clathrate phase was determined to be $K_8Ge_{44.05(5)}\square_{1.95(5)}$. The accumulation of defects at site 6*c* can be explained, because the Ge1 atoms connect always two planar Ge_6-rings and provide therefore an unfavorable environment for Ge atoms due to the strong deviation of the bond angles from the tetrahedral values [9]. Atoms at site 6*c* are only connected to atoms at site 24*k*, which means that the Ge3 atoms surround either a Ge1 atom or a defect. Therefore, the large anisotropic displacement parameter of the Ge3 atoms results from a superposition of two different local environments. If a Ge atom is located at a 6*c* position, the bond distance to the neighbouring Ge3 atoms is in accordance with the typical bond length d(Ge—Ge) of ≈ 2.5 Å. On the other hand, if a 6*c* position is vacant, the Ge3 atoms are shifted towards the defect and the distance d(□—Ge3) amounts to only ≈ 2.2 Å.
An occupancy refinement of both split positions Ge31 (occ. ≈ 0.7) and Ge32 (occ. ≈ 0.3) provides another independent crystallographic proof for the defect concentration at site 6*c* [10] which is in particular an important tool for the refinement of ternary clathrates with heteroatomic frameworks [11]. The framework defects in $K_8Ge_{44}\square_2$ have been confirmed in recent works from powder diffraction data [12,13]. Moreover, the validity of the split atom model has been proven by the detection of superstructures with ordered defect arrangement (space group $Ia\bar{3}d$) for the clathrate-I phases $Rb_8Sn_{44}\square_2$ [14], $Cs_8Sn_{44}\square_2$ [15] and $Ba_8Ge_{43}\square_3$ [9,16,17]. Interestingly, vacancies occur for the larger tetrel elemenst but not for the corresponding silicide. This may be traced back to too short Si—Si distances which would push up the lone pair impurity states too high up in energy.
The clathrate-I structure in space group $Pm\bar{3}n$ is built up from two kinds of polyhedra centred by K atoms: The Ge_{20} dodecahedra centred (000) form an *I*-lattice complex [18] while the Ge_{24} tetrakaidecahedra centred at (¼½0) form a *W*-lattice complex.

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Alternatively, the clathrate-I structure can be described as a rod packing of tetrakaidecahedra interconnected by common hexagonal faces along [100] and by 8 common pentagonal faces. The dodecahedra share their pentagonal faces with 12 different tetrakaidecahedra.

Table 1. Data collection and handling.

Crystal:	metallic grey column, size 0.1 × 0.1 × 0.1 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	288.3 cm^{-1}
Diffractometer, scan mode:	Syntex P1, $\omega/2\theta$
$2\theta_{max}$:	75.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	583, 473
Criterion for I_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 4\,\sigma(F_{obs})$, 473
$N(param)_{refined}$:	20
Programs:	WinCSD [19], ATOMS [20]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	2*a*		0	0	0	0.020(1)	U_{11}	U_{11}	0	0	0
K(2)	6*d*		¼	½	0	0.020(2)	0.042(2)	U_{22}	0	0	0
Ge(1)	6*c*	0.676(8)	¼	0	½	0.014(1)	0.0129(6)	U_{22}	0	0	0
Ge(2)	16*i*		0.18353(6)	*x*	*x*	0.0175(3)	U_{11}	U_{11}	–0.0020(2)	U_{12}	U_{12}
Ge(31)	24*k*	0.71(1)	0	0.3053(2)	0.1170(4)	0.0149(7)	0.016(1)	0.0153(8)	0	0	0.001(1)
Ge(32)	24*k*	0.29(1)	0	0.3383(6)	0.126(1)	0.017(2)	0.019(3)	0.019(3)	0	0	0.003(3)

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