

Synthesis, Structure, and Conductivity of the New Group IV Chalcogenides, KCuZrQ_3 ($Q = \text{S, Se, Te}$)

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The new compounds KCuZrQ_3 ($Q = \text{S, Se, Te}$) and KCuHfS_3 have been synthesized through direct reaction of the elements with a K_2Q_y flux. The compounds crystallize in space group $D_{2h}^{17}-Cmcm$ of the orthorhombic system with four formula units in cells of dimensions: $a = 3.730(2)$, $b = 13.915(7)$, and $c = 9.754(6)$ Å for KCuZrS_3 ; $a = 3.874(2)$, $b = 14.506(7)$, and $c = 10.159(5)$ Å for KCuZrSe_3 ; and $a = 4.088(1)$, $b = 15.299(5)$, and $c = 10.886(3)$ Å for KCuZrTe_3 ($T = 113$ K). From photographs taken at room temperature the cell parameters for KCuHfS_3 are $a = 3.70(6)$, $b = 14.24(2)$, and $c = 9.86(5)$ Å. The structures of the KCuZrQ_3 compounds have been determined from single-crystal X-ray methods. The KCuZrQ_3 structure is composed of $\frac{2}{3}[\text{CuZrQ}_3^-]$ layers separated by K^+ cations that are coordinated by eight atoms in a bicapped trigonal prismatic arrangement. The Cu atoms are tetrahedrally coordinated and the Zr atoms are octahedrally coordinated by Q atoms. Within the $\frac{2}{3}[\text{CuZrQ}_3^-]$ layer, the tetrahedra share edges with four adjacent octahedra. The crystal structure is related to FeUS_3 or its structural anti-type Pd_3Te_2 , with Cu atoms occupying the tetrahedral sites that remain unoccupied in the parent structures. Electrical conductivity measurements indicate that KCuZrS_3 is an insulator; KCuZrSe_3 undergoes a metal-to-semiconductor transition at 50 K; and KCuZrTe_3 is a metal. © 1992 Academic Press, Inc.

Introduction

A number of ternary alkali metal-transition metal-chalcogenides (1-5) and more recently quaternary group V chalcogenides (6-8) have been synthesized by the reactive flux technique. As we first demonstrated for the $\text{K}_2\text{S/S}$ system (1), this technique utilizes a low-melting alkali metal (A)/chalcogen (Q) flux that reacts with added metal or metals (M) to afford a product containing A , M , and Q . These reactive fluxes (A_xQ_y/Q) have recently been extended to include $A =$ alkali metal or Cu and $Q = \text{S, Se, Te}$. The materials synthesized by this method often exhibit chalcogen-chalcogen bonding and unusual

structure types, including one-dimensional chains (1, 2, 4, 5, 9, 10), three-dimensional structures (10, 11), and molecular species (12). The synthesis of new ternary group IV and V chalcogenides (3, 13-16) and more recently quaternary group V sulfides and selenides (6-8) in this laboratory led to the investigation of quaternary group IV chalcogenides. Here we describe the syntheses, structures, and electrical conductivities of a new class of group IV quaternary chalcogenides KCuZrQ_3 ($Q = \text{S, Se, Te}$).

Experimental

Synthesis. The compounds KCuMS_3 ($M = \text{Zr, Hf}$) were prepared by the reactive

flux method. The binary starting material K_2S was synthesized from reaction of stoichiometric amounts of elemental K (Alfa, 99%) and S (AESAR 99.9999%) in liquid ammonia under an argon atmosphere. $KCuZrS_3$ was prepared by combining powders of the elements Cu (30 mg, 0.47 mmole; Aldrich 99.999%), Zr (43 mg, 0.47 mmole; AESAR 99%), and S (99 mg, 3.07 mmole) with K_2S (78 mg, 0.71 mmole). All reaction mixtures (vide infra) were loaded into quartz tubes in a dry box under an Ar atmosphere, evacuated to approximately 10^{-4} Torr, and sealed. $KCuHfS_3$ was prepared by a combination of K_2S (52 mg, 0.47 mmole) with elemental powders of Cu (20 mg, 0.31 mmole), Hf (112 mg, 0.63 mmole; AESAR 99.6%), and S (66 mg, 2.05 mmole).

$KCuZrSe_3$ was prepared similarly. The starting material K_2Se was made from the reaction of elemental K and Se (Aldrich, 99.999%) in stoichiometric quantities in liquid ammonia under an argon atmosphere. Powders of the elements Cu (29 mg, 0.46 mmole), Zr (42 mg, 0.46 mmole), and Se (108 mg, 1.37 mmole) were loaded together with K_2Se (72 mg, 0.46 mmole) and placed in a quartz tube.

For the synthesis of $KCuZrTe_3$ the binary compound K_2Te_3 was synthesized by reaction of the elements in stoichiometric quantities at 650°C for 3 days in an evacuated, sealed quartz tube. Single crystals resulted from reactions of K_2Te_3 (Te, AESAR, 99.5%), Cu, Zr, and Te in the atomic ratios of 1 : 2 : 1 : 3 or 1 : 2 : 2 : 5.

For the reactions containing S or Se, the tubes were heated in a furnace from room temperature to 500°C over 7 hr and held at 500°C for 24 hr. The furnace was then heated to 850°C over 4 hr and held there for 4 days before being cooled to room temperature at 4°C/hr. For the reactions containing Te, the tubes were heated in a furnace at 650°C for 6 days and then ramped to 900°C to heat for 4 days. The furnace was cooled at the rate

of 3°C/hr to 450°C and then to room temperature at 90°C/hr.

In all the reactions single crystals formed in the presence of a melt. Red needles of both $KCuZrS_3$ and $KCuHfS_3$ were obtained by washing the flux away in water. Black needles of $KCuZrSe_3$ and long bronze plates of $KCuZrTe_3$ were manually extracted from the solidified melts that formed in their respective reactions. The approximate compositions of the crystals were determined by a microprobe analysis with an EDAX (energy dispersive analysis by X-rays)-equipped Hitachi S570 scanning electron microscope. Analysis confirmed the presence of all four elements in the approximate ratios of 1 : 1 : 1 : 3, 1 : 1 : 1 : 3, and 1 : 2 : 1 : 5 for the quaternary sulfides, selenide, and telluride. These compounds appear to be stable in water and air. We have not succeeded in synthesizing the remaining members of the series ($KCuHfSe_3$ and $KCuHfTe_3$).

Conductivity measurements. Single crystals of $KCuZrQ_3$ ($Q = S, Se, Te$) ranging in length from 0.5 to 1.0 mm were mounted with Ag paint on Al wires with graphite extensions. The compositional integrity of the mounted single crystals was checked by EDAX. Four probe ac (27 Hz) resistivity measurements along the needle axis (*a*) were made according to procedures previously described (17).

Structure determinations of $KCuZrQ_3$ ($Q = S, Se, Te$). For all three substances preliminary cell constants and Laue symmetry *mmm* were determined from the analysis of Weissenberg photographs. The systematic absences (*hkl*, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) are consistent with the orthorhombic space groups $D_{2h}^{17}-Cmcm$, $C_{2v}^{12}-Cmc2_1$, and $C_{2v}^{16}-C2cm$. For each compound the final cell parameters were determined from a least-squares analysis of the setting angles of 25 reflections that had been automatically centered at 113 K on a Picker diffractometer operated from a PC (18). For

TABLE I
CRYSTAL DATA AND INTENSITY COLLECTION FOR KCuZrS_3 , KCuZrSe_3 , and KCuZrTe_3

Formula	KCuZrS_3	KCuZrSe_3	KCuZrTe_3
Formula mass (amu)	290.04	430.74	576.66
Space group	$D_{2h}^{17}-Cmcm$	$D_{2h}^{17}-Cmcm$	$D_{2h}^{17}-Cmcm$
a (Å)	3.730(2) ^a	3.874(2) ^a	4.088(1) ^a
b (Å)	13.915(7)	14.506(7)	15.299(5)
c (Å)	9.754(6)	10.159(5)	10.886(3)
V (Å ³)	506.3	570.9	680.8
Z	4	4	4
ρ_x (g cm ⁻³)	3.81	5.01	5.63
T of data collection (K) ^b	113	113	113
Radiation	Graphite monochromated $\text{MoK}\alpha$ ($\lambda(K\alpha_1) = 0.7093$ Å)	Graphite monochromated $\text{MoK}\alpha$ ($\lambda(K\alpha_1) = 0.7093$ Å)	Graphite monochromated $\text{MoK}\alpha$ ($\lambda(K\alpha_1) = 0.7093$ Å)
Crystal shape	Needle $0.15 \times 0.03 \times 0.03$ mm bounded by {100}, {010}, {001}	Needle $0.25 \times 0.02 \times 0.04$ mm bounded by {100}, {010}, {001}	Plate $0.39 \times 0.02 \times 0.22$ mm bounded by {100}, {010}, {001}
Crystal volume (mm ³)	1.35×10^{-4}	2.0×10^{-4}	1.4×10^{-4}
Linear absorption coefficient (cm ⁻¹)	81	239	178
Transmission factors ^c	0.767–0.814	0.411–0.569	0.062–0.753
Detector aperture (mm)	Horizontal, 6.5; vertical, 6.3; 32 cm from crystal	Horizontal, 5.3; vertical, 5.7; 32 cm from crystal	Horizontal, 4.5; vertical, 5.1; 32 cm from crystal
Takeoff angle (degrees)	2.5	2.5	2.5
Scan type	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$
Scan speed (degrees min ⁻¹)	2.0 in 2θ	2.0 in 2θ	2.0 in 2θ
Scan range (degrees)	-0.7 to +0.9 in 2θ	-1.1 to +1.1 in 2θ	-0.7 to +1.4 in 2θ
$\lambda^{-1} \sin \theta$, limits (Å ⁻¹)	0.025–0.788, $2^\circ \leq 2\theta(\text{MoK}\alpha_1) \leq 68^\circ$	0.025–0.758, $2^\circ \leq 2\theta(\text{MoK}\alpha_1) \leq 65^\circ$	0.025–0.758, $2^\circ \leq 2\theta(\text{MoK}\alpha_1) \leq 65^\circ$
Background counts ^d	10 sec at each end of scan	10 sec at each end of scan	10 sec at each end of scan
Data collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
R factor	0.04	0.04	0.04
No. of data collected	4156	4141	4935
No. of unique data, including $F_0^2 < 0$	634	633	749
No. of unique data, with $F_0^2 > 3\sigma(F_0^2)$	462	486	698
No. of variables	24	24	26
R_{ave}	0.068	0.040	0.047
$R(F^2)$	0.044	0.038	0.068
$R_w(F^2)$	0.062	0.054	0.090
R (on F for $F_0^2 > 3\sigma(F_0^2)$)	0.024	0.018	0.028
Error in observation of unit weight (e ²)	0.95	0.91	1.94

^a Obtained from a refinement constrained so that $\alpha = \beta = \gamma = 90^\circ$.

^b The low-temperature system is based on a design by Huffman (32).

^c The analytical method as employed in the Northwestern absorption program, AGNOST, was used for the absorption correction (33).

^d The diffractometer was operated using the Indiana University PCPS system (18).

$Q = \text{S}$ and Se these reflections were in the range $25^\circ < 2\theta(\text{MoK}\alpha_1) < 35^\circ$ while for $Q = \text{Te}$ they were in the range $23^\circ < 2\theta(\text{MoK}\alpha_1) < 32^\circ$. Intensity data for all three compounds were collected at 113 K on a Picker diffractometer. Six standard reflections monitored every 100 reflections showed no significant change during the data collection. In each instance all members of $\{hkl\}$ were collected. Crystal data and other crystallographic details for the three structures are described in Table I.

All calculations on the three compounds KCuZrS_3 , KCuZrSe_3 , and KCuZrTe_3 were performed on a Stardent ST2500 computer with programs and methods standard in this laboratory (19). Conventional atomic scattering factors and anomalous dispersion corrections were used (20, 21). Intensity data were processed and corrected for absorption. Subsequent averaging of the data strongly favored the centrosymmetric space group $Cmcm$ over either of the possible noncentrosymmetric space groups. The

TABLE II
POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR
KCuZrS₃, KCuZrSe₃, and KCuZrTe₃

Atom	x	y	z	B_{eq}^a (Å ²)
A. KCuZrS ₃				
K	0	0.744047(76)	$\frac{1}{4}$	0.79(2)
Cu	0	0.463546(44)	$\frac{1}{4}$	0.56(1)
Zr	0	0	0	0.42(1)
S(1)	0	0.376990(59)	0.050725(88)	0.58(2)
S(2)	0	0.063604(88)	$\frac{1}{4}$	0.54(2)
B. KCuZrSe ₃				
K	0	0.747009(95)	$\frac{1}{4}$	1.79(3)
Cu	0	0.464522(58)	$\frac{1}{4}$	1.39(2)
Zr	0	0	0	0.98(1)
Se(1)	0	0.374904(26)	0.050771(38)	0.922(8)
Se(2)	0	0.066685(42)	$\frac{1}{4}$	0.95(1)
C. KCuZrTe ₃				
K	0	0.75110(12)	$\frac{1}{4}$	1.81(4)
Cu	0	0.464982(58)	$\frac{1}{4}$	0.85(2)
Zr	0	-0.000334(65)	0.026093(74)	0.64(2)
Te(1)	0	0.371654(22)	0.051945(26)	0.90(1)
Te(2)	0	0.069282(34)	$\frac{1}{4}$	1.64(1)

$$^a B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j \cdot a_j.$$

structures were solved with the use of the direct methods program SHELX-86 (22). The program STRUCTURE TIDY (23) was used to standardize the positional parameters. Each structure was refined by full-matrix least-squares techniques, the function $\sum w(F_0^2 - F^2)^2$ being minimized. Anisotropic thermal motion and an isotropic extinction parameter were included.

For KCuZrS₃ the final refinement led to a value of $R(F_0^2)$ of 0.044. The conventional R index (on F for $F_0^2 > 3\sigma(F_0^2)$) is 0.024. The final difference electron density map shows no features with a height greater than 1.1% that of a Zr atom. For KCuZrSe₃ the final refinement resulted in a value of $R(F_0^2)$ of 0.038. The conventional R index is 0.018. The final difference electron density map shows no peaks greater than 0.9% the height of a Zr atom. For KCuZrTe₃ refinement of the model that placed the Zr atom at (0, 0, 0) (Wyckoff position 4a) resulted in unreasonable anisotropic thermal parameters in

which $U_{33} \gg U_{22}, U_{11}$. A difference electron density map resulting from a least-squares refinement that excluded the Zr atom revealed a distinct peak centered at approximately (0, 0, 0.03). Thus a model of disorder was adopted that placed a Zr atom with half-occupancy on Wyckoff position 8f. Subsequent refinement resulted in a value of $R(F_0^2)$ of 0.068 and in more realistic anisotropic thermal parameters. The value for the conventional R index (on F for $F_0^2 > 3\sigma(F_0^2)$) is 0.028. The final difference electron density map indicates no features with a height greater than 1.3% that of a Zr atom. Why in the KCuZrQ₃ structure the Zr atom should apparently disorder for $Q = \text{Te}$, but not for $Q = \text{S}$ or Se is unclear.

For all three structures analysis of $\sum w(F_0^2 - F^2)^2$ as a function of F_0^2 , Miller indices, and setting angles shows no uncommon trends. Final values of atomic parameters and equivalent isotropic thermal parameters are summarized in Table II. Final

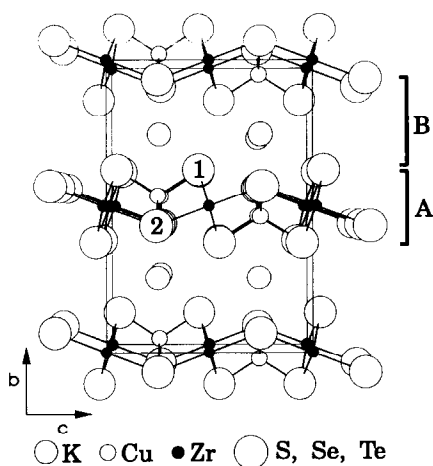


FIG. 1. View of KCuZrQ_3 down $[100]$ with layers and atoms labeled. Here and in Fig. 2 the atoms are shown as circles of arbitrary size.

anisotropic thermal parameters and structure amplitudes are available as supplementary material.¹

Weissenberg photography on the compound KCuHfS_3 indicates that it is isostructural to KCuZrQ_3 ($Q = \text{S, Se, Te}$) with a cell of dimensions $a = 3.70(6)$, $b = 14.24(2)$, and $c = 9.86(5)$ Å at 298 K.

Results and Discussion

The structure of KCuZrQ_3 ($Q = \text{S, Se, Te}$) consists of ${}^2_3[\text{CuZrQ}_3^-]$ layers separated by K^+ cations. The perspective view down the a axis given in Fig. 1 shows the stacking of the layers as well as the labeling scheme.

¹ See NAPS document No. 04950 for 12 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or \$7.75 for photocopy. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge of \$15 for this service. Foreign orders add \$4.50 for postage and handling, and \$1.50 for postage of any microfiche orders.

Figure 2 shows an isolated ${}^2_3[\text{CuZrQ}_3^-]$ layer as viewed down the b axis.

The structure comprises close-packed Q layers that extend orthogonal to $[010]$. Slab A (Fig. 1) is composed of Zr-centered octahedra and Cu-centered tetrahedra; slab B consists of K-centered bicapped trigonal prisms. Within the A slab, the octahedra are interconnected by edge sharing through two equatorial $Q(1)$ atoms in the $[100]$ direction and vertex sharing through the axial $Q(2)$ atom in the $[001]$ direction. These layers of octahedra are slightly buckled in the $[001]$ direction, giving rise to tetrahedral sites that are occupied by Cu atoms. The tetrahedra within this layer share edges with the four adjacent octahedra through a $Q(1)$ and a $Q(2)$ atom as shown in Fig. 2. As there is an absence of $Q-Q$ bonding in KCuZrQ_3 , slab B, ${}^1_3[\text{KQ}_3^{5-}]$, can be viewed as an undistorted ZrQ_3 layer, as found in the ZrQ_3 structure (24). Within Slab B, the K-centered bicapped trigonal prisms share triangular faces in the $[100]$ direction. Slab B is connected to slab A by edge sharing with both the tetrahedra and the octahedra.

Selected interatomic distances and angles for these new quaternary compounds

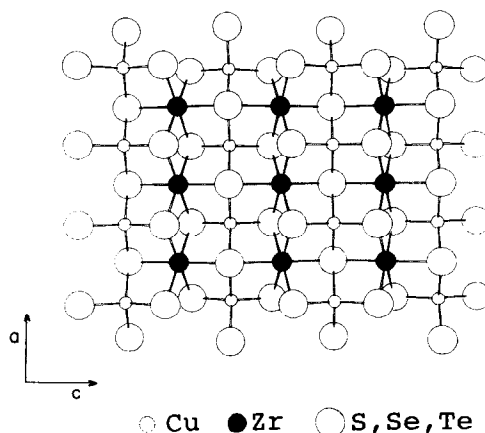


FIG. 2. Isolated ${}^2_3[\text{CuZrQ}_3^-]$ layer viewed down the $[010]$ direction.

TABLE III
SELECTED DISTANCES (Å) AND ANGLES (DEGREES)
FOR KCuZrS_3 , KCuZrSe_3 , and KCuZrTe_3

Q	S	Se	Te
$\text{K} \cdots 2Q(2)$	3.127(2)	3.255(2)	3.452(2)
$\text{K} \cdots 4Q(1)$	3.268(1)	3.360(1)	3.494(1)
$\text{K} \cdots 2Q(1)$	3.382(2)	3.530(2)	3.780(1)
$\text{Cu}-2Q(1)$	2.287(1)	2.406(1)	2.583(1)
$\text{Cu}-2Q(2)$	2.327(1)	2.439(1)	2.593(1)
$\text{Cu}-4\text{Zr}$	3.112(1)	3.235(1)	3.222(1)
$\text{Cu}-4\text{Zr}'$	—	—	3.670(1)
$\text{Zr}-2Q(1)$	2.579(1)	2.704(1)	2.845(1)
$\text{Zr}-2Q(1)$	2.579(1)	2.704(1)	2.962(1)
$\text{Zr}-Q(2)$	2.594(2)	2.718(1)	2.656(1)
$\text{Zr}-Q(2)$	2.594(2)	2.718(1)	3.180(1)
$Q(1) \cdots 2Q(2)$	3.573(2)	3.716(1)	3.970(1)
$Q(1) \cdots 2Q(2)$	3.742(2)	3.948(1)	4.237(1)
$Q(1) \cdots 2Q(1)$	3.730(2)	3.874(2)	4.088(1)
$Q(1) \cdots 2Q(1)$	4.117(2)	4.236(2)	4.394(1)
$Q(1) \cdots Q(1)$	3.888(3)	4.048(2)	4.304(1)
$Q(1) \cdots Q(1)$	3.564(2)	3.773(2)	4.086(1)
$Q(1)-\text{Cu}-Q(1)$	116.43(6)	114.57(5)	112.87(4)
$Q(1)-\text{Cu}-Q(2)$	108.37(2)	109.17(2)	109.89(1)
$Q(2)-\text{Cu}-Q(2)$	106.51(7)	105.16(6)	104.04(4)
$Q(1)-\text{Zr}-Q(1)$	92.62(5)	91.52(4)	87.28(4)
$Q(1)-\text{Zr}-Q(1)$	87.38(5)	88.49(4)	89.43(2)
$Q(1)-\text{Zr}-Q(2)$	92.64(3)	93.48(2)	100.70(3)
$Q(1)-\text{Zr}-Q(2)$	87.36(3)	86.52(2)	82.23(2)

KCuZrQ_3 are provided in Table III. These are generally unexceptional. For example, the $\text{Zr}-Q$ distances are narrower in range but compare well with those in the compounds ZrQ_3 : 2.602(3) to 2.724(4) Å ($Q = \text{S}$) (24), 2.71 to 2.87 Å ($Q = \text{Se}$) (25), and 2.771(3) to 3.467(4) Å ($Q = \text{Te}$) (24). Owing to the apparent disorder of the Zr position over two sites in KCuZrTe_3 there are twice as many distances involving Zr for $Q = \text{Te}$ as for $Q = \text{S}$ or Se. In the present compounds the ZrQ_6 octahedra and CuQ_4 tetrahedra are only slightly distorted.

The closest interlayer and intralayer $Q \cdots Q$ distances of 3.564(2), 3.716(1), and 3.970(1) Å for $Q = \text{S}$, Se, and Te, respectively, indicate there are no significant $Q-Q$ interactions. Thus, the formal oxidation states K(I) , Cu(I) , Zr(IV) , and $Q(-\text{II})$ may

be assigned; thus we would expect these compounds to be insulators or semiconductors. Indeed, the resistance at room temperature of a KCuZrS_3 crystal was beyond the measurement capabilities of our instrument and we therefore assume that the compound is an insulator. On the other hand, a plot of relative conductivity along the needle axis a as a function of temperature for the compounds KCuZrSe_3 and KCuZrTe_3 is given in Fig. 3. KCuZrTe_3 is a metal over the entire temperature range while KCuZrSe_3 displays metallic behavior down to 50 K, where there is a transition to semiconducting behavior. The conductivities at room temperature are 0.66 and 433 $\Omega^{-1} \text{cm}^{-1}$ for KCuZrSe_3 and KCuZrTe_3 , respectively. Metallic behavior in these compounds could arise from nonstoichiometry, a hypothesis invoked to explain unexpected metallic conductivities in the ternary tellurides Cu_2MTe_3 ($M = \text{Ti}$, Zr , Hf) (26). But from the structural evidence on the present compounds, any nonstoichiometry must be slight.

While KCuZrQ_3 apparently represents a new structure type, it is closely related to the known chalcogenides FeUS_3 (27) (Fig. 4) and AgTaS_3 (28), and the related anti-type

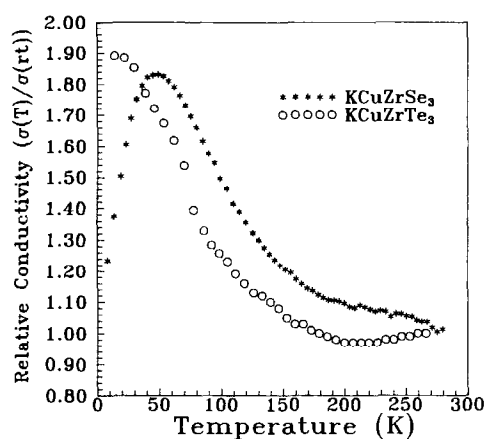


FIG. 3. Relative electrical conductivity ($\sigma(T)/\sigma(\text{rt})$) vs temperature as measured along the needle axis a for KCuZrSe_3 and KCuZrTe_3 .

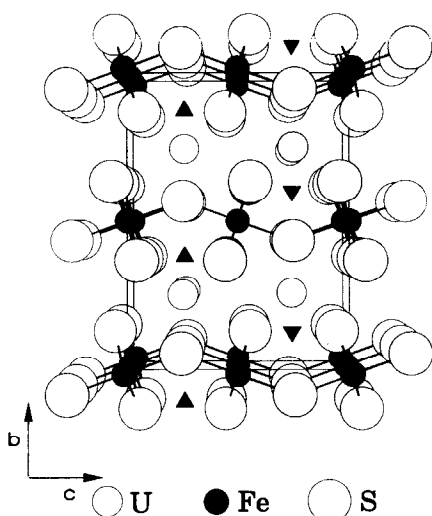


FIG. 4. View of the FeUS_3 structure down $[100]$ with vacant tetrahedral sites represented as closed triangles.

Pd_3Te_2 (29). As the structures of FeUS_3 , AgTaS_3 , and Pd_3Te_2 differ from that of KCuZrQ_3 only in the **A** slab, it is worthwhile considering the geometry of all available sites if no metal atoms were present in this slab. The nature of these sites is depicted in Fig. 5. For each chalcogen atom there are

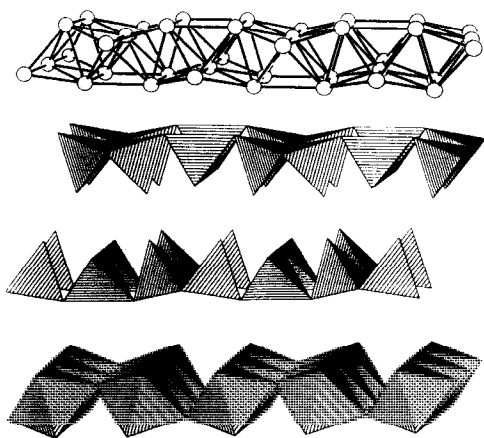


FIG. 5. Depiction of the possible octahedral and tetrahedral vacancies between layers of Q atoms in the **A** slab in KCuZrQ_3 .

two tetrahedral sites and one octahedral site. One tetrahedron points "up" and the other points "down." Owing to the buckling of the chalcogen layers there are two types of tetrahedra: the two edges of one tetrahedron are formed from two chalcogen atoms in opposite layers; in the other tetrahedron one triangular face is formed from three chalcogen atoms in the same layer. The tetrahedra in a given layer share vertices and edges and share faces with those of opposite orientation in the other layer. The arrangement of the octahedral sites is also depicted in Fig. 5. In the KCuZrQ_3 structure every third tetrahedral site and all octahedral sites are filled. In the FeUS_3 and AgTaS_3 structures the U atoms and Ta atoms, respectively, occupy the bicapped trigonal prismatic sites in the **B** slab and the Fe atoms and Ag atoms, respectively, fill the octahedral sites in the **A** slab. The available tetrahedral sites that are all filled in KCuZrQ_3 remain vacant in the FeUS_3 , AgTaS_3 , and Pd_3Te_2 structures; these sites are represented as closed triangles in Fig. 4. Thus the KCuZrQ_3 structure represents another example of Cu(I) insertion into a known chalcogenide framework (30).

We have successfully substituted Na for K in this structure. Initial results (31) indicate that NaCuTiS_3 and NaCuZrTe_3 crystallize in space group $D_{2h}^{16}-Pnma$ and are not isostructural to the KCuZrQ_3 compounds. Further work on these materials and on substitutional chemistry is in progress.

Acknowledgments

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