

Revision 2

The crystal structure of nickelskutterudite, (Ni,Co,Fe)As₃, and occupancy of the icosahedral cation site in the skutterudite group

Benjamin N. Schumer^a, Marcelo B. Andrade^b, Stanley H. Evans^a, and Robert T. Downs^a

^aDepartment of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, Arizona 85721-0077, USA

^bSão Carlos Institute of Physics, University of São Paulo, Caixa Postal 369, 13560-970, São Carlos, SP, Brazil

Correspondence e-mail: bschumer@email.arizona.edu

Abstract

The crystal structure of nickelskutterudite, (Ni,Co,Fe)As₃, cubic, $Im\bar{3}$, $Z = 8$: $a = 8.2653(6)$ Å, $V = 564.65(7)$ Å³, has been refined to $R_1 = 1.4\%$ for 225 unique reflections $I > 2\sigma(I)$ collected on a Bruker X8 four-circle diffractometer equipped with fine-focus, sealed tube MoK α radiation and an APEX-II CCD detector. This is the first report of the crystal structure of nickelskutterudite. Nickelskutterudite, a member of the skutterudite group of isostructural minerals, adopts a distorted perovskite structure with notably tilted octahedra and an unoccupied to partially occupied icosahedral metal site. In the structure of nickelskutterudite, there is one metal (B) site occupied by Ni, Co, or Fe in octahedral coordination with six As atoms. Procrystal electron density analysis shows each As anion is bonded to two cations and two As anions, resulting in a four membered ring of bonded As with edges 2.547 Å and 2.475 Å. The extreme tilting of BA_6 octahedra is likely a consequence of the As-As bonding. The nickelskutterudite structure differs from the ideal perovskite structure ($A_4B_4X_{12}$) in that As₄ anion rings occupy

three of the four icosahedral cages centered on the *A* sites. There are reported synthetic phases isomorphous with skutterudite with the other *A* site completely occupied by a cation (AB_4X_{12}).

Electron microprobe analyses of nickelskutterudite gave an empirical chemical formula of $(Ni_{0.62}Co_{0.28}Fe_{0.12})_{\Sigma=1.02}(As_{2.95}S_{0.05})_{\Sigma=3.00}$ normalized to three anions. Pure $NiAs_3$ nickelskutterudite, natural or synthesized, has not been reported. In nature, nickelskutterudite is always observed with significant Co and Fe, reportedly because all non-bonded valence electrons must be spin-paired. This suggests that nickelskutterudite must contain Co^{3+} and Fe^{2+} , consistent with previous models since Ni^{4+} cannot spin-pair its seven non-bonded electrons, Co^{3+} and Fe^{2+} , which can spin-pair all non-bonded electrons, are required to stabilize the structure. No anion deficiencies were found in the course of this study so, including the structurally necessary Co and Fe, the chemical formula of nickelskutterudite (currently given as $NiAs_{3-x}$ by the IMA) should be considered $(Ni,Co,Fe)As_3$.

Introduction

The skutterudite mineral group consists of minerals that exhibit cubic space group symmetry $Im\bar{3}$ with ideal formula BX_3 or B_4X_{12} , where *B* is Co, Ni, or Fe, and *X* is As or Sb. Skutterudite group minerals adopt a distorted perovskite structure with unoccupied *A* sites, constructed from a framework of tilted, corner-linked BX_6 octahedra, bringing together four anions in three-quarters of the otherwise vacant icosahedral cages, where they form rectangular four member rings (Aleksandrov and Beznosikov 2007). Numerous synthetic compounds exist which are isomorphous with skutterudite group minerals, and these materials fall into two categories: (1) filled, which follow the general formula AB_4X_{12} , in which *A* is a large cation partially to completely occupying the remaining quarter of the icosahedral cages, *B* is generally a

transition metal cation, and X is a P, As, or Sb anion; and (2) unfilled with the general formula BX_3 . Synthetic filled skutterudite materials, such as $Tl_{0.5}Co_4Sb_{12}$ and $NdOs_4Sb_{12}$, have been widely studied due to their particular thermoelectric properties including high Seebeck coefficients, high electrical conductivity, and low thermal conductivity (Aleksandrov and Beznosikov 2007; Chakoumakos and Sales 2006; Fukuoka and Yamanaka 2009; Návratil et al. 2010). We suspect that the structures of natural skutterudites can accommodate cations within the icosahedral site.

The skutterudite mineral group currently consists of four members (with current IMA formula): skutterudite ($CoAs_{3-x}$), nickelskutterudite ($NiAs_{3-x}$), ferroskutterudite [$(Fe,Co)As_3$], and kieftite ($CoSb_3$). The IMA nomenclature commission currently defines the chemical formula for skutterudite and nickelskutterudite as anion deficient, BX_{3-x} , after the work of Palache, Berman, and Frondel (1944). Pauling (1978) suggested that the ideal formula of skutterudite be written $Co_4(As_4)_3$, emphasizing the four member As rings.

The study of the skutterudite group has a long history, with skutterudite *sensu stricto* first reported by Breithaupt (1827) and its chemical composition reported as $CoAs_3$ by Haidinger (1845). Over the course of the next century, a series of mineral species were described in order to account for the diversity of chemical compositions and physical properties exhibited by minerals related to skutterudite (Vollhardt 1888). In particular a nickel-dominant phase was described by Waller and Moses (1893) from the Bullard's Peak Mining District, Grant County, New Mexico, and more recently an iron dominant phase was described by Spridonov et al. (2007). The 7th edition of Dana's System by Palache, Berman and Frondel (1944), included a summary of the skutterudite minerals, defining them as consisting of cubic RA_{3-x} minerals where $R = Fe, Co$ or

Ni. The IMA adopted the Palache, Berman, and Frondel (1944) anion deficient ideal chemical formulas.

$0 \leq x \leq \frac{1}{2}$		$\frac{1}{2} \leq x \leq 1$	
skutterudite	$(\text{Co,Ni})\text{As}_{3-x}$	smaltite	$(\text{Co,Ni})\text{As}_{3-x}$
nickel-skutterudite	$(\text{Ni,Co})\text{As}_{3-x}$	chloanthite	$(\text{Ni,Co})\text{As}_{3-x}$
ferrian skutterudite	$(\text{Fe,Ni,Co})\text{As}_{3-x}$	chathamite	$(\text{Fe,Ni,Co})\text{As}_{3-x}$

Ramsdell (1925) examined smaltite and chloanthite, which he considered to be isostructural members of the series CoAs_2 - NiAs_2 , respectively, and distinct from skutterudite. Ramsdell was, however, unable to solve the structure of either compound. Oftedal (1926) was the first to report the crystal structure of skutterudite, and two years later he compared the crystallography of skutterudite and a sample along the smaltite-chloanthite join (Oftedal 1928). The powder diffraction patterns for skutterudite and smaltite-chloanthite observed by Oftedal (1925) showed that they are isostructural, in spite of their chemical differences. Single-crystal X-ray diffraction data collected by Oftedal (1925) led him to conclude that skutterudite, and therefore smaltite-chloanthite, must follow the general formula $R\text{As}_3$, where $R = \text{Co}$ or Ni . Holmes (1947) analyzed and summarized previous studies of the arsenides of cobalt, nickel, and iron, and, based on Oftedal's work, concluded that the skutterudite structure is consistent with a general formula of $M\text{As}_3$, but the observed compositions frequently appeared to be anion deficient. In the course of our study, it became clear that cation excess is more likely than anion deficiency in the skutterudite structure, as illustrated by the various synthetic compounds mentioned earlier.

Roseboom (1962) studied the chemical variability of the skutterudite minerals by synthesizing a series of crystals. He reported some slightly anion deficient samples, even those synthesized in the presences of elemental As, but no deficiencies large enough to account for many of the analyses of natural skutterudites (references cited in Roseboom 1962). His synthetic Co samples exhibited maximum deficiencies of $\text{CoAs}_{2.94-2.96}$. He concluded that excess metal replaces deficient As. As well, just as observed in the natural samples, he could not synthesize end-member Ni or Fe skutterudite. Roseboom (1962) also concluded that the ubiquitous mixing of safflorite $[(\text{Co},\text{Ni},\text{Fe})\text{As}_2]$ with skutterudite in natural samples precludes any confidence in published chemical analyses done on samples without accompanying X-ray diffraction support.

Additional structural refinements of skutterudite have been reported by Ventriglia (1957), Mandel and Donahue (1971), and Kjekshus and Rakke (1974). Ventriglia (1957) is the first to mention distortion of the CoAs_6 octahedra to a form that more resembles trigonal prismatic than octahedral. This distortion was confirmed by Mandel and Donahue (1971). None of these studies mention occupancy of the icosahedral site.

Experimental

Four skutterudite group minerals were analyzed in this study: two nickelskutterudite samples (R100194, ruff.info/R100194 from Schneeberg, Germany; R100196, ruff.info/R100196 from Alhambra mine, Bullard's Peak Mining District, Grant County, New Mexico) and two skutterudite samples (R050593, ruff.info/R050593 from Bou Azzer, Morocco; R100195, ruff.info/R100195 from Skutterud, Norway). Chemistry was measured on a Cameca SX100 Electron Microprobe with beam conditions of 20 keV and 20 nA. Standards were NiAs (Ni and As), Co metal (Co), chalcopyrite (Fe), PbS (Pb and S), and AgBiS_2 (Ag and Bi). Trace

Sb was detected in sample R100196 at levels slightly lower than the standard deviation, 0.007(8) weight %. Each formula was normalized to three anions. Results of the electron microprobe are given in Table 1 and discussed further below. A portion of each sample analyzed by electron microprobe was removed for structure analysis.

Single-crystal X-ray diffraction data were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoK α radiation using frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of a cubic unit cell. The intensity data were corrected for absorption effects by the multi-scan method using the Bruker programs TWINABS for R100196 and SADABS for the remaining samples (Bruker 2007). Crystal and refinement data for all samples are presented in Table 2.

The crystal structure of nickelskutterudite was solved and refined using SHELX97 (Sheldrick 2008) based on space group $Im\bar{3}$ (no. 204), yielding a reliability factor R of 1.4%, from data collected on a twinned crystal (0.05 \times 0.05 \times 0.04 mm) removed from R100196. The crystal is twinned according to a reflection on (110) with matrix 0 1 0 / 1 0 0 / 0 0 1. This is a {110} merohedral twin of index 1, forming a “penetration twin” similar to the “iron cross” twins seen in pyrite. Arsenic was assigned to the Wyckoff position $24g$ [x y 0]. Due to the inability of X-ray data to distinguish Ni, Co, and Fe from one another, the three elements were assigned to M at the $8c$ position [$\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$], and the ratios of Ni, Co, and Fe were constrained to the empirical formula generated from microprobe data. Note, refining site $8c$ without constraining the ratios of Ni, Co, and Fe to the empirical formula, but keeping the sum of the cations at 1.00, resulted in differences of up to 16% from the microprobe generated formula. Constraining either Co or Fe, not both, to the value of the empirical formula resulted in differences of only 3%.

The positions of all atoms were refined with anisotropic displacement parameters. The refined coordinates and displacement parameters are listed in Table 3, and selected bond distances and angles are in Table 4. Negligible residual electron density at the icosahedral site, A (0, 0, 0), indicated that nickelskutterudite R100196 is unfilled. However, residual electron density was seen at A for skutterudite R050593 and nickelskutterudite R100194. Site occupancy refinement of A showed 0.01 metal (Co, Ni, or Fe) atom per formula unit in R050593 and R100194.

Results

As shown in Fig. 1, the structure of nickelskutterudite consists of corner-sharing MA_6 octahedral groups ($M = \text{Ni, Co, or Fe}$), similar to the octahedral groups in the $\alpha\text{-ReO}_3$ structure (space group $Pm\bar{3}m$, no. 221). However, the NiAs_6 octahedra are tilted about $[111]$ from the ideal orientation of octahedra in the ReO_3 structure, thereby emplacing As atoms into three quarters of the icosahedral cages (Aleksandrov and Beznosikov 2007, Návrtil et al. 2010). Each of these “stuffed” icosahedral cages contains four As atoms that are close enough to bond, forming a rectangular As_4 ring (Fig. 2). In filled skutterudite compounds, the remaining quarter of the icosahedral cages accommodate filling cations. In the ideal perovskite structure, ABX_3 , each icosahedral cage is occupied by an A cation, and there are no X_4 rings “stuffed” into the cages. In such a way, the filled skutterudite compounds, AB_4X_{12} , can be thought of as intermediaries between the ReO_3 and perovskite structures. Interestingly, Aleksandrov and Beznosikov (2007) reported that at pressure (~ 0.52 GPa), the ReO_3 structure deforms to the skutterudite structure. It would be interesting to demonstrate bonded O_4 rings in high-pressure ReO_3 .

Concomitant with tilting of the octahedra is distortion of the octahedra. Measured As-Ni-As angles for NiAs₆ octahedra in nickelskutterudite deviate significantly (~6 °) from 90° (Table 3), resulting in Ni coordination polyhedra that resemble trigonal prisms, as previously noted by Ventriglia (1957). Mitchell (2002) and Chakoumakos and Sales (2006) both describe octahedral distortion as a function of both octahedral tilt and anion-anion bonding within the skutterudite structure, dependent on composition. Consequently, octahedral distortion increases as anion-anion distances within the X₄ ring decreases from Sb to P.

A system for the classification of octahedral tilt in perovskite derivative structures was developed by Glazer (1972), and is applicable to the skutterudite structure (Mitchell 2002). A brief summary of Glazer's classification is presented here; for an in-depth discussion of octahedral tilt, the reader is referred to Glazer (1972). According to Glazer (1972), octahedral tilt may be thought of as the combination of tilts about the three 4-fold axes of an octahedron. This overall tilt is characterized according to magnitude and direction. Magnitude is the amount of tilt about the three 4-fold axes, denoted *a* relative to [100], *b* relative to [010], and *c* relative [001], and equality of tilt is shown by repeating the appropriate letter. Direction refers to tilt of octahedra in successive layers along a given 4-fold axis, denoted as a superscript 0 for no tilt, + for tilt in the same direction, and – for tilt in the opposite direction (Glazer 1972). NiAs₆ octahedra in nickelskutterudite (and MAs₆ octahedra in all other skutterudite structures) have equal tilt about all three 4-fold axes, and the tilt of NiAs₆ octahedra in successive layers along each axis is the same (Aleksandrov and Beznosikov 2007), so the Glazer tilt notation is *a*⁺*a*⁺*a*⁺. The angle of tilt φ is 36.20°, calculated according to the equation $\cos(\varphi) = 3\mathbf{a}/(8\mathbf{d} - 0.5)$, given in Návratil et al. (2010), where **a** is the unit cell edge and **d** is the metal-arsenic bond distance.

Distances between P, Sb, and As in X_4 rings within various synthetic skutterudite compounds were noted by Chakoumakos and Sales (2006) as comparable to distances between nearest neighbor atoms in elemental P, Sb, and As, consistent with $X-X$ bonding. Distances between As atoms in As_4 rings in nickelskutterudite measure 2.5467(6) Å and 2.4749(5) Å (average = 2.511 Å), similar to nearest neighbor distances of 2.517 Å within native arsenic (hexagonal As; Schiferl and Barrett 1969) and 2.493 Å in arsenolamprite (orthorhombic As; Smith et al. 1974), consistent with As-As bonding. Although the As_4 ring in skutterudite was described by Oftedal (1926) as having four equal sides, nickelskutterudite and skutterudite (Mandel and Donohue 1971) have rings with two different As-As distances, forming rectangles.

In order to test whether or not the As atoms are bonded in skutterudite, the procrystal electron density distribution was calculated using the experimental space group, unit cell dimensions, and atomic coordinates obtained from the single crystal x-ray diffraction data gathered in this study, as outlined by Gibbs et al. (2008), using the software SPEEDEN (Downs et al. 1996). Fig. 3 shows an electron density contour map in the plane of the As_4 ring. Bond paths and saddle points are located in the electron density along the sides of the ring. These saddle points represent (3,-1) bond critical points that satisfy the conditions of Bader (1998): a bonded pair of atoms exists if and only if a bond path and a saddle point exist in the electron density between them, demonstrating As-As bonded interactions in the As_4 ring of nickelskutterudite.

Discussion

To check for anion deficiency in our skutterudite samples, microprobe data were normalized to a cation-site sum of 1.00 and compared to the formulas generated by normalizing to an anion-site sum of 3.00 (Table 1). When the empirical formulas were normalized to a cation-

site sum of 1.00, the formulas were slightly anion deficient. The same formulas, when normalized to an anion-site sum of 3.00, showed a slight cation surplus. Site-occupancy refinement was used to check the validity of each result. Occupancy refinement of the anion site in all four samples showed full occupancy. Occupancy refinement of the *B* cation site showed full occupancy, while residual electron density was seen at the *A* site of R050593 and R100194, and refined to 0.01 metal atoms (Co, Ni, or Fe) per formula unit. Thus, the formulas normalized to 3.00 cations represent the observed structural state, and no anion deficiency is present in our samples.

A relationship was noticed between the degree of octahedral tilt and bond lengths within the X_4 rings. Mitchell (2002) and Chakumakos and Sales (2006) briefly mention the inversely proportional relationship between *X-X* interatomic distances and octahedral tilt, and when we calculated octahedral tilt for various skutterudite phases using the equation given by Návratil et al. (2010), it was seen that as the shortest *X-X* interatomic distance decreases, and therefore the smaller the ionic radius, the greater the octahedral tilt. Table 4 and Fig. 4 show this relationship for various skutterudite type compounds. Phosphides, with the shortest *X-X* bond length, show the greatest tilt, while antimonides, with the longest, show the least tilt, however there is some overlap between the phosphides and arsenides. This relationship begs the chicken-and-egg question: why do the MeX_6 octahedra tilt and why do the X_4 rings form?

The general formula of nickelskutterudite, $NiAs_3$, is not charged balanced assuming Ni^{2+} , Ni^{3+} or Ni^{4+} . Nickel (1969) suggested that in the skutterudite structure, Ni displays a charge of +4 and As a charge of -3, which give an overall charge of -5. In order to compensate for this charge imbalance, the anions form As_4 rings (Návratil et al. 2010; Patrik and Lutz 1999; Takizawa et al. 1999). Tilting of $NiAs_6$ octahedra “stuffs” four As atoms into an icosahedral

void, allowing them to form a four member, σ -bonded ring, with each As sharing one electron with two other As atoms for an overall charge of -4 (Patrik and Lutz 1999, Nickel 1969).

The chemistry of two different nickelskutterudite samples were examined in this study: R100194 (Schneeberg, Saxony, Germany), and R100196 (New Mexico, USA). Each contains significant amounts of Co and Fe: R100194 empirical formula $(\text{Ni}_{0.86}\text{Co}_{0.14}\text{Fe}_{0.01})_{\Sigma=1.01}(\text{As}_{2.99}\text{S}_{0.01})_{\Sigma=3.00}$, R100196 empirical formula $(\text{Ni}_{0.62}\text{Co}_{0.28}\text{Fe}_{0.12})_{\Sigma=1.02}(\text{As}_{2.95}\text{S}_{0.05})_{\Sigma=3.00}$. The presence of significant Co and Fe may be explained by the different electronic configurations of Ni^{4+} and Co^{3+} in the skutterudite structure. Nickel (1969) notes that in the skutterudite structure, cations achieve complete spin-pairing of their non-bonded d -electrons. For example, when Co^{3+} donates sufficient electrons to form pair bonds with neighboring atoms, it has 6 non-bonded d -electrons which can be spin paired (Nickel 1969). In order for Ni to be left with 6 non-bonded electrons, it must be quadrivalent, and if Ni^{4+} donates sufficient electrons to form pair-bonds with all 6 neighboring atoms, it is left with 7 non-bonded electrons, which cannot be fully spin-paired (Nickel, 1969).

Implications

Important concentrations of Co and Fe in natural NiAs_3 , and the apparent inability to synthesize pure NiAs_3 indicate that Co^{3+} and/or Fe^{2+} are required to stabilize the nickelskutterudite structure (Grystiv et al. 2002; Borshchevsky et al. 1996; Nickel 1969). For comparison, pure CoAs_2 (clinosaflorite) crystallizes in the arsenopyrite-type structure ($P2_1/c$) because of the unpaired, non-bonded electron of Co^{2+} occupying a π_b orbital (Yang et al. 2008). Incorporation of Ni^{2+} and Fe^{2+} into CoAs_2 results in crystallization of $(\text{Co,Ni,Fe})\text{As}_2$ (saflorite) in the marcasite-type structure ($Pnmm$), explained by the ability of Fe^{2+} and Ni^{2+} to spin-pair non-bonded electrons and thus achieve a lower energy, higher symmetry structure (Yang et al. 2008).

Further synthesis experiments could be used to constrain the amounts of Co^{3+} and/or Fe^{2+} necessary to stabilize the nickelskutterudite structure.

Additionally, no anion deficiencies were found in skutterudite phases by either X-ray or electron microprobe, supporting Roseboom's (1962) interpretation that anion deficient skutterudite samples likely do not consist of a single phase. For these reasons, we propose the chemical formula of nickelskutterudite (currently given as NiAs_{3-x} by the IMA) should be $(\text{Ni,Co,Fe})\text{As}_3$.

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Figure Captions

Figure 1. Representative image of the crystal structure of nickelskutterudite (left), viewed along [001]. Green octahedra represent NiAs_6 groups and As displacement parameters at 99% are represented by grey ellipsoids. Unit cell edges are indicated by the grey square. A representation of the crystal structure of $\alpha\text{-ReO}_3$, viewed along [001] (right), is included for the purpose of comparison.

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Figure 3. Procrystal electron density map of a rectangular four membered ring of bonded As atoms, from 0.005 to 0.200 $\text{e}/\text{\AA}^3$ in steps of 0.005 $\text{e}/\text{\AA}^3$. The 0.055 $\text{e}/\text{\AA}^3$ contour is dashed to emphasize the difference in electron density at the bond critical points associated with the different lengths of As-As bonds. The bond critical points are represented by saddles in the contours between bonded As atoms. Note three other As atoms at left (black stars), representing other four membered rings above and below the plane of the observed ring.

Figure 4. Graph showing the inverse relationship between octahedral tilt and shortest anion-anion ($X-X$) distance in X_4 rings in the skutterudite structure. As the $X-X$ distance, and therefore the size of the X atom, increases, octahedral tilt will decrease.

Table 1. Electron microprobe data for skutterudite and nickelskutterudite samples in weight percent.

Sample	R050593	R100195	R100194	R100196
Locality	Bou Azzer	Skutterud	Schneeberg	Alhambra mine
a-cell, Å	8.2060(10)	8.2070(4)	8.2876(5)	8.2653(6)
Ni	1.42(18)	1.04(2)	17.82(48)	12.76(90)
Co	17.68(20)	18.54(7)	2.88(44)	5.8(48)
Fe	2.1(18)	1.52(1)	0.25(7)	2.41(51)
Bi	nd*	0.34(13)	0.27(19)	0.34(20)
As	76.32(74)	78.00(12)	78.64(22)	77.95(24)
S	0.82(9)	0.31(6)	0.06(4)	0.59(11)
Sum	98.34	99.75	99.92	99.85

Formula

R050593 $(\text{Co}_{0.86}\text{Fe}_{0.11}\text{Ni}_{0.07})_{\Sigma=1.04}(\text{As}_{2.97}\text{S}_{0.03})_{\Sigma=3.00}$

R100195 $(\text{Co}_{0.90}\text{Fe}_{0.08}\text{Ni}_{0.05})_{\Sigma=1.03}(\text{As}_{2.97}\text{S}_{0.03})_{\Sigma=3.00}$

R100194 $(\text{Ni}_{0.85}\text{Co}_{0.14}\text{Fe}_{0.01})_{\Sigma=1.01}(\text{As}_{2.99}\text{S}_{0.01})_{\Sigma=3.00}$

R100196 $(\text{Ni}_{0.62}\text{Co}_{0.28}\text{Fe}_{0.12})_{\Sigma=1.02}(\text{As}_{2.95}\text{S}_{0.05})_{\Sigma=3.00}$

Note: *nd = not determined

Table 2. Summary of crystal data and refinement results for skutterudite and nickelskutterudite.

	Skutterudite (R050593, Morocco)	Skutterudite (R100195, Norway)	Nickelskutterudite (R100194, Germany)	Nickelskutterudite (R100196, New Mexico)
IMA-defined chemical formula	CoAs _{3-x}	CoAs _{3-x}	NiAs ₂₋₃	NiAs ₂₋₃
Effective structural formula	^{M1} Co _{0.99} ^{M2} Fe _{0.01} As _{2.90} S _{0.1}	^{M1} Co _{0.99} As _{3.00}	^{M1} Ni _{0.99} ^{M2} Fe _{0.01} As _{3.0}	^{M1} Ni _{0.59} ^{M2} Co _{0.2499} ^{M2} Fe _{0.14} As _{3.0}
Space group	<i>Im</i> -3 (No. 204)	<i>Im</i> -3 (No. 204)	<i>Im</i> -3 (No. 204)	<i>Im</i> -3 (No. 204)
<i>a</i> (Å)	8.2060(10)	8.2070(4)	8.2876(5)	8.2653(6)
<i>V</i> (Å ³)	552.6(1)	552.78(5)	569.23(6)	564.65(7)
<i>Z</i>	8	8	8	8
ρ_{calc} (g/cm ³)	6.719	6.818	6.615	6.675
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	40.41	41.49	41.07	41.04
2 θ range for data collection	≤68.75	≤68.28	≤68.44	≤68.65
No. of reflections collected	1279	1259	1205	1266
No. of independent reflections	232	224	231	234
No. of reflections with <i>I</i> > 2 σ (<i>I</i>)	214	215	220	225
No. of parameters refined	17	12	14	13
R(int)	0.02	0.019	0.022	0.033
Final <i>R</i> ₁ , <i>wR</i> ₂ factors [<i>I</i> > 2 σ (<i>I</i>)]	0.015, 0.036	0.011, 0.023	0.010, 0.023	0.014, 0.029
Final <i>R</i> ₁ , <i>wR</i> ₂ factors (all data)	0.018, 0.037	0.012, 0.023	0.012, 0.023	0.015, 0.029
Goodness-of-fit	1.106	1.209	1.12	1.001
Twin law				(0 1 0/1 0 0 /0 0 1)
Twin ratio				0.88/0.12

Table 3. Fractional atomic coordinates, equivalent isotropic displacement parameters, occupancies, and atomic displacement parameters (\AA^2) for skutterudite and nickelskutterudite.

Element	x	y	z	U_{eq} (\AA^2)	Occ. (<1)	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
R050593											
M*	0.25	0.25	0.25	0.00310(18)	0.989(4)	0.00310(18)	0.00310(18)	0.00310(18)	0.00047(11)	0.00047(11)	0.00047 (11)
Fe	0	0	0	0.000(15)	0.0127(9)						
As	0.15012(4)	0.34300 (5)	0	0.00452(14)	0.967(5)	0.00434(17)	0.0057(2)	0.00350(16)	0.00054(10)	0	0
S	0.121(3)	0.273(4)	0	0.009(6)*	0.033(5)						
R100195											
Co	0.25	0.25	0.25	0.00227(13)	1.00(3)	0.00227(13)	0.00227(13)	0.00227(13)	0.00013(8)	0.00013(8)	0.00013 (8)
As	0	0.15024(2)	0.34280 (2)	0.00316(8)	0.99(3)	0.00211(10)	0.00295(11)	0.00442(11)	0	0	0.00048 (6)
R100194											
Ni1	0.25	0.25	0.25	0.00529(12)		0.00529(12)	0.00529(12)	0.00529(12)	0.00026(8)	0.00026(8)	0.00026 (8)
Ni2	0	0	0	0.01(3)	0.008(6)						
As	0	0.34685(2)	0.14960 (2)	0.00613(8)		0.00503(10)	0.00752(11)	0.00584(11)	0	0	0.00073 (6)
R100196											
M**	0.25	0.25	0.25	0.00471(15)		0.00471(15)	0.00471(15)	0.00471(15)	0.00023(11)	0.00023(11)	0.00023(11)
As**	0.14972(3)	0.34594(3)	0	0.00585(9)		0.00562(15)	0.00734(14)	0.00459(15)	0.00074(8)	0	0

Notes: *M = Co + Fe.

**M = $\text{Ni}_{0.59(5)}\text{Co}_{0.280(10)}\text{Fe}_{0.14(6)}$.

**As = $\text{As}_{0.99}\text{S}_{0.01}$.

Table 4. Selected interatomic distances and angles for nickelskutterudite R100196. The Ni, Co, and Fe site is identified as *M*. The theoretical icosahedral bond length, *A*-As, is included for purposes of discussion even though *A* is not occupied.

	Distance, Å		Angle (°)
M—As	2.3634(2)	As ⁱ —M—As	84.008(9)
As—As ^{vii}	2.4749(5)	As ⁱ —M—As ⁱⁱ	95.992(9)
As—As ^{viii}	2.5467(6)	As—M—As ⁱⁱ	84.008(9)
		As ⁱ —M—As ⁱⁱⁱ	84.008(9)
		As—M—As ⁱⁱⁱ	95.992(9)
		As ⁱⁱ —M—As ⁱⁱⁱ	180.000(11)
		As ^{iv} —M—As ^v	84.007(9)
		M ^{vi} —As—M	121.928(11)
		M ^{vi} —As—As ^{vii}	110.531(6)
		M ^{vi} —As—As ^{viii}	109.604(6)
		As ^{vii} —As—As ^{viii}	90.0

Table 5. MX_6 octahedral tilt compared by anion (X) and shortest X-X interatomic distance for both filled and unfilled skutterudite phases.

Formula	Anion(X)	Tilt Angle	Shortest X-X Distance	Reference
YbFe ₄ P ₁₂	P	37.1	2.293	Shirotnani et al. (2006)
La _x Rh ₄ P ₁₂	P	38.7	2.224	Takeda et al. (2007)
CeFe ₄ P ₁₂	P	36.7	2.304	Shirotnani et al. (2006)
La _{0.2} Co ₄ P ₁₂	P	37.1	2.254	Zemni et al. (1986)
CoP ₃	P	36.7	2.240	Zemni et al. (1986)
(Ni,Co,Fe)As ₃	As	36.2	2.475	This Study
IrAs ₃	As	36.8	2.456	Kjekshus and Rakke (1974)
RhAs ₃	As	36.7	2.468	Kjekshus and Rakke (1974)
LaFe ₄ As ₁₂	As	34.9	2.570	Braun and Jeitschko (1980)
CoAs ₃	As	35.2	2.464	Mandel and Donahue (1971)
CoSb ₃	Sb	32.7	2.854	Schmidt, Kliche, and Lutz (1987)
Fe ₂ Ni ₂ Sb ₁₂	Sb	32.5	2.890	Návratil et al. (2010)
Fe ₂ Pd ₂ Sb ₁₂	Sb	33.6	2.852	Návratil et al. (2010)
IrSb ₃	Sb	34.3	2.617	Kjekshus and Rakke (1974)
NdFe ₄ Sb ₁₂	Sb	32.5	2.921	Evers et al. (1995)

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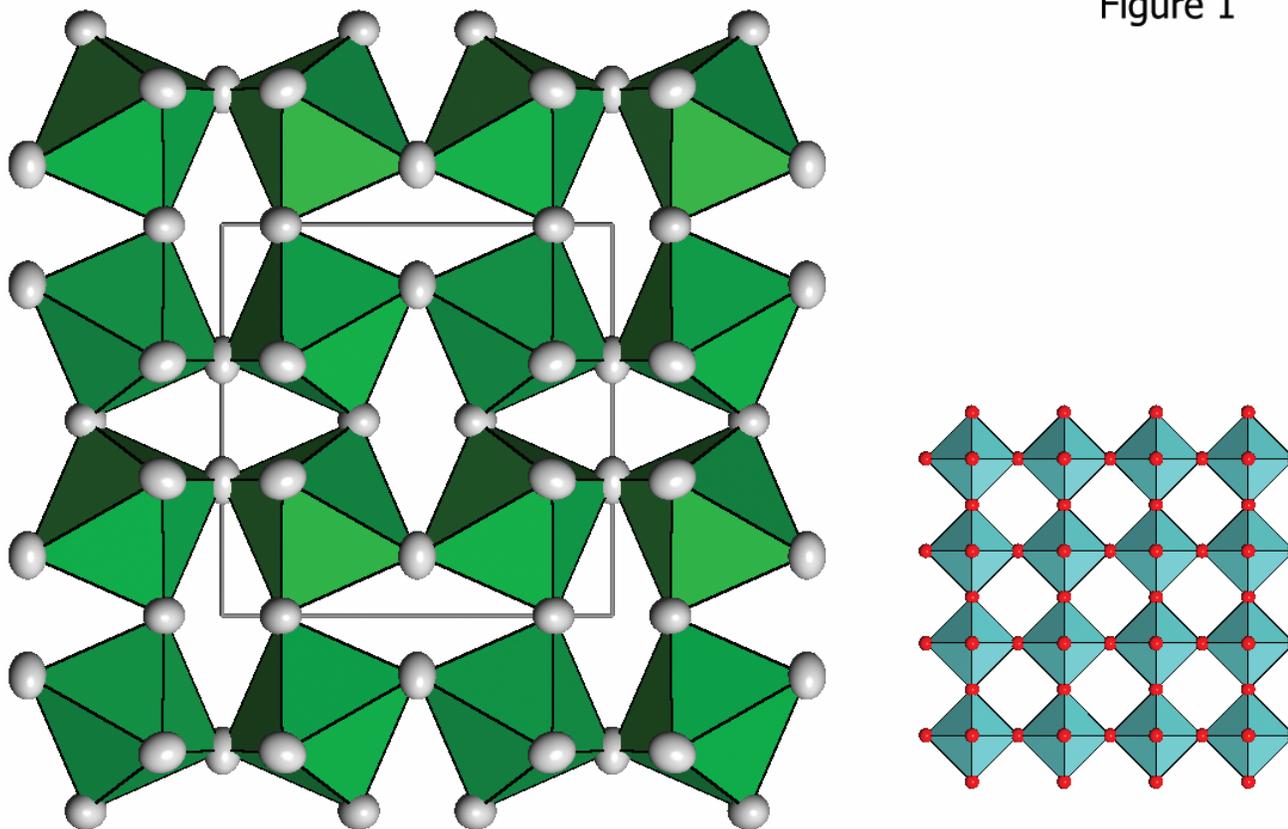


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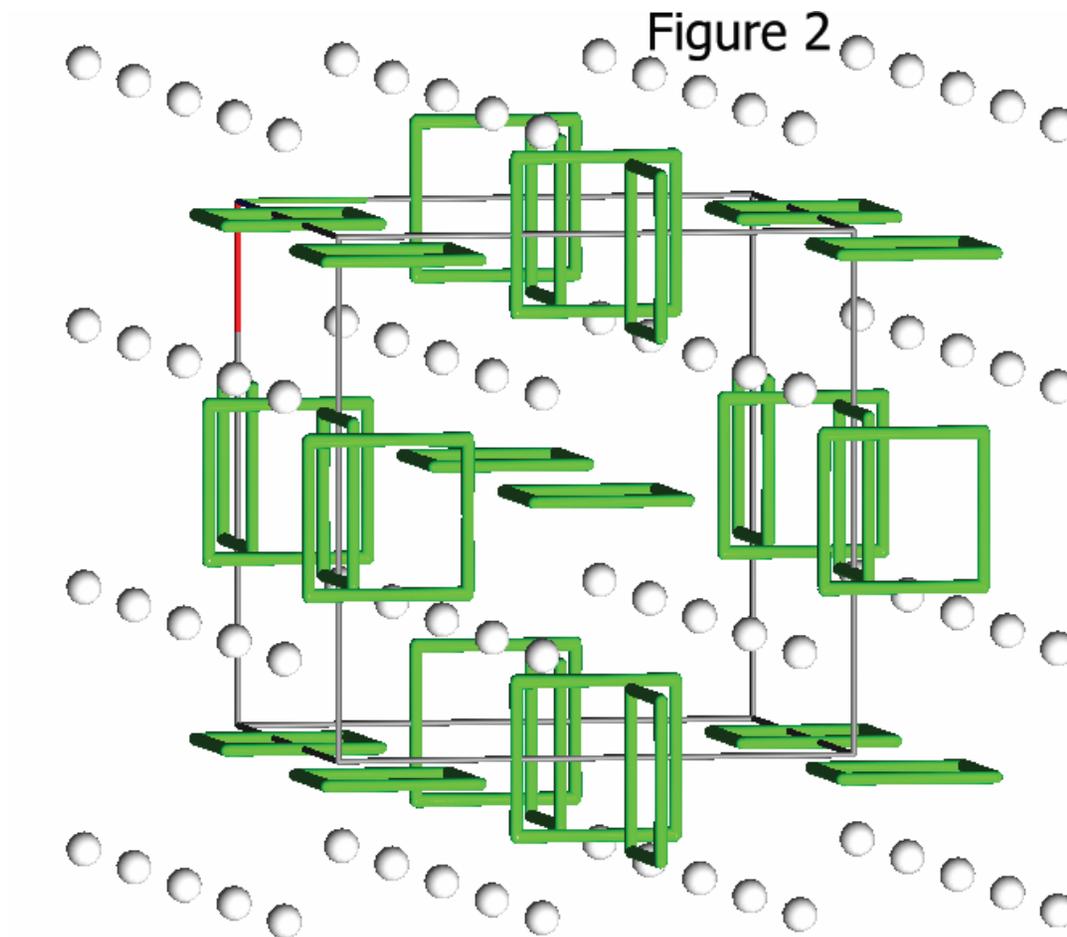


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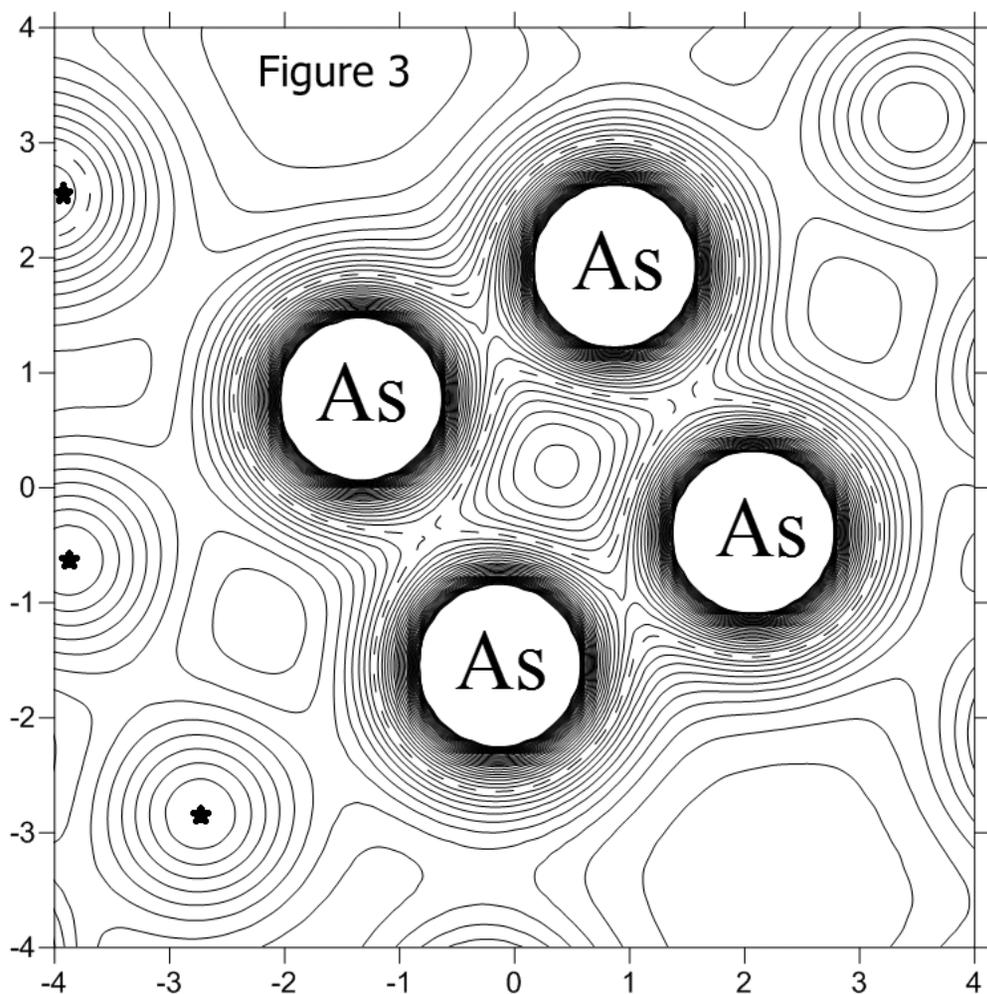


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