A new formula and crystal structure for nickelskutterudite, \((\text{Ni},\text{Co},\text{Fe})\text{As}_3\), and occupancy of the icosahedral cation site in the skutterudite group

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**ABSTRACT**

We propose a new formula for the mineral nickelskutterudite, based on our observation that either (or both) Co or Fe\textsuperscript{3+} are essential structure constituents. The crystal structure of nickelskutterudite, \((\text{Ni},\text{Co},\text{Fe})\text{As}_3\), cubic, \(I\overline{m}3\), \(Z = 8\): \(a = 8.2653(6)\ \text{Å}, V = 564.65(7)\ \text{Å}^3\), has been refined to \(R_b = 1.4\%\) for 225 unique reflections \(I > 2\sigma(I)\) collected on a Bruker X8 four-circle diffractometer equipped with fine-focus, sealed tube MoK\(\alpha\) 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 and 2.475 Å. The extreme tilting of \(B\text{As}_6\) octahedra is likely a consequence of the As-As bonding. The nickelskutterudite structure differs from the ideal perovskite structure \((A_BX_{12})\) in that \(A\text{As}_4\) 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 \((AB_X_{12})\).

Electron microprobe analyses of nickelskutterudite gave an empirical chemical formula of \((\text{Ni}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.1})\text{As}_{3.0}\). Normalized to three anions. Pure \(\text{NiAs}_3\) 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\textsuperscript{3+} and Fe\textsuperscript{2+}, consistent with previous models since Ni\textsuperscript{3+} cannot spin-pair its seven non-bonded electrons, Co\textsuperscript{3+} and Fe\textsuperscript{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 \(\text{NiAs}_{3.4}\) by the IMA) should be considered \((\text{Ni},\text{Co},\text{Fe})\text{As}_3\).

**Keywords:** Skutterudite, icosahedral metal site, cobalt, nickel, octahedral tilt

**INTRODUCTION**

The skutterudite mineral group consists of minerals that exhibit cubic space group symmetry \(I\overline{m}3\) with ideal formula \(BX_4\) or \(BX_5\), 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 \(AB_X\text{As}_4\), 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 \(BX_4\). Synthetic filled skutterudite materials, such as \(\text{Ti}_8\text{Co}_2\text{Sb}_2\) and \(\text{NdOs}_8\text{Sb}_2\), 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; Navrátil 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 \((\text{CoAs}_3)\), nickelskutterudite \((\text{NiAs}_3)\), ferroskutterudite \((\text{FeCoAs}_3)\), and kiefite \((\text{CoSb}_3)\). The IMA nomenclature commission currently defines the chemical formula for skutterudite and nickelskutterudite as anion deficient, \(BX_{3.5}\), after the work of Palache et al. (1944). Pauling (1978) suggested that the ideal formula of skutterudite be written \(\text{Co}_4\text{As}_3\), 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 \(\text{CoAs}_3\) by Haidinger (1845). Over the course of the next century, a series of mineral species were described 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 Breithaupt (1827) and its chemical composition reported as \(\text{CoAs}_3\) by Haidinger (1845).

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The 7th edition of Dana’s System by Palache et al. (1944) included a summary of the skutterudite minerals, defining them as consisting of cubic \(R\text{As}_{3.1}\) minerals where \(R = \text{Fe}, \text{Co}, \text{or Ni}\). The IMA adopted
the Palache et al. (1944) anion deficient ideal chemical formulas. Ramsdell (1925) examined smalltite 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. Ofteid (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 smalltite-chloanthite join (Ofteid 1928). The powder diffraction patterns for skutterudite and smalltite-chloanthite observed by Ofteid (1926) showed that they are isostructural, in spite of their chemical differences. Single-crystal X-ray diffraction data collected by Ofteid (1926) led him to conclude that skutterudite, and therefore smalltite-chloanthite, must follow the general formula RAs$_3$, where R = Co or Ni. Holmes (1947) analyzed and summarized previous studies of the arsenides of cobalt, nickel, and iron, and, based on Ofteid’s work, concluded that the skutterudite structure is consistent with a general formula of MA$_5$, 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 presence 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 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 [(Co,Ni,Fe)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.

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demonstrate bonded O₆ rings in high-pressure ReO₃.

Concomitant with tilting of the octahedra is distortion of the octahedra. Measured As-Ni-As angles for Ni₆As₃ 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 X₆ 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 fourfold axes of an octahedron. This overall tilt is characterized according to magnitude and direction. Magnitude is the amount of tilt about the three fourfold axes, denoted a relative to [010], b relative to [001], 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 fourfold axis, denoted as a superscript 0 for no tilt, + for tilt in the same direction, and − for tilt in the opposite direction (Glazer 1972). Ni₆As₃ octahedra in nickelskutterudite (and MA₆As₃ octahedra in all other skutterudite structures) have equal tilt about all three fourfold axes, and the tilt of Ni₆As₃ 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(ϕ) = 3a/ (8d – 0.5), given in Navrátil 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 X₆ 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

![Figure 1](image1.png)

**Figure 1.** Representative image of the crystal structure of nickelskutterudite (left), viewed along [001]. Green octahedra represent Ni₆As₃ groups and As displacement parameters at 99% are represented by gray ellipsoids. Unit-cell edges are indicated by the gray square. A NiAs octahedron. This overall tilt is characterized according to magnitude and direction. Magnitude is the amount of tilt about the three fourfold axes, denoted a relative to [010], b relative to [001], 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 fourfold axis, denoted as a superscript 0 for no tilt, + for tilt in the same direction, and − for tilt in the opposite direction (Glazer 1972). Ni₆As₃ octahedra in nickelskutterudite (and MA₆As₃ octahedra in all other skutterudite structures) have equal tilt about all three fourfold axes, and the tilt of Ni₆As₃ 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(ϕ) = 3a/ (8d – 0.5), given in Navrátil et al. (2010), where a is the unit-cell edge and d is the metal-arsenic bond distance.

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bonding. Distances between As atoms in As$_4$ rings in nickelskutterudite measure 2.5467(6) 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 arsenolanaprite (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.

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). Figure 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 Chakoumakos 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 Navrátil 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 5). Table 4 and Figure 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$_{3.0}$, is not charged balanced assuming Ni$^{3+}$, Ni$^{2+}$, 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. To compensate for this charge imbalance, the anions form As$_6$ rings (Navrátil 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, U.S.A.). Each contains significant amounts of Co and Fe: R100194 empirical formula (Ni$_{0.85}$Co$_{0.15}$Fe$_{0.01}$)$_{2.01}$(As$_{2.89}$S$_{0.01}$)$_{2.01}$, R100196 empirical formula (Ni$_{0.85}$Co$_{0.18}$Fe$_{0.02}$)$_{2.02}$(As$_{2.95}$S$_{0.05}$)$_{2.00}$. The presence of significant Co and Fe may be explained by the different electronic configurations.

**FIGURE 3.** Procrystal electron density map of a rectangular four-membered ring of bonded As atoms, from 0.005 to 0.200 e/Å$^3$ in steps of 0.005 e/Å$^3$. The 0.055 e/Å$^3$ 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. (Color online.)
of Ni$^{2+}$ and Co$^{2+}$ 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 six non-bonded d-electrons, which can be spin paired (Nickel 1969). For Ni to be left with six non-bonded electrons, it must be quadrivalent, and if Ni$^{4+}$ donates sufficient electrons to form pair-bonds with all six neighboring atoms, it is left with seven 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 (Grytsiv et al. 2002; Borshchevsky et al. 1996; Nickel 1969). For comparison, pure CoAs$_2$ (clinoasphaltenite) crystallizes in the arsenopyrite-type structure ($P_2_1/c$) because of the unpaired, non-bonded electron of Co$^{2+}$ occupying a $\pi$ orbital (Yang et al. 2008). Incorporation of Ni$^{2+}$ and Fe$^{2+}$ into CoAs$_2$ results in crystallization of (Co,Ni,Fe)As$_2$ (safflorite) in the marcasite-type structure ($P_{nmm}$), explained by the ability of Fe$^{3+}$ 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$_3$ by the IMA) should be (Ni,Co,Fe)As$_3$.

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