

1 **Revision 2**

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

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6 **Abstract**

7 The crystal structure of nickelskutterudite, (Ni,Co,Fe)As₃, cubic, $Im\bar{3}$, $Z = 8$: $a =$
8 $8.2653(6) \text{ \AA}$, $V = 564.65(7) \text{ \AA}^3$, has been refined to $R_1 = 1.4\%$ for 225 unique reflections $I >$
9 $2\sigma(I)$ collected on a Bruker X8 four-circle diffractometer equipped with fine-focus, sealed tube
10 MoK α radiation and an APEX-II CCD detector. This is the first report of the crystal structure of
11 nickelskutterudite. Nickelskutterudite, a member of the skutterudite group of isostructural
12 minerals, adopts a distorted perovskite structure with notably tilted octahedra and an unoccupied
13 to partially occupied icosahedral metal site. In the structure of nickelskutterudite, there is one
14 metal (B) site occupied by Ni, Co, or Fe in octahedral coordination with six As atoms. Procrystal
15 electron density analysis shows each As anion is bonded to two cations and two As anions,
16 resulting in a four membered ring of bonded As with edges 2.547 \AA and 2.475 \AA . The extreme
17 tilting of BA_6 octahedra is likely a consequence of the As-As bonding. The nickelskutterudite
18 structure differs from the ideal perovskite structure ($A_4B_4X_{12}$) in that As₄ anion rings occupy

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

21 Electron microprobe analyses of nickelskutterudite gave an empirical chemical formula
22 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 $NiAs_3$
23 nickelskutterudite, natural or synthesized, has not been reported. In nature, nickelskutterudite is
24 always observed with significant Co and Fe, reportedly because all non-bonded valence electrons
25 must be spin-paired. This suggests that nickelskutterudite must contain Co^{3+} and Fe^{2+} , consistent
26 with previous models since Ni^{4+} cannot spin-pair its seven non-bonded electrons, Co^{3+} and Fe^{2+} ,
27 which can spin-pair all non-bonded electrons, are required to stabilize the structure. No anion
28 deficiencies were found in the course of this study so, including the structurally necessary Co
29 and Fe, the chemical formula of nickelskutterudite (currently given as $NiAs_{3-x}$ by the IMA)
30 should be considered $(Ni,Co,Fe)As_3$.

31 **Introduction**

32 The skutterudite mineral group consists of minerals that exhibit cubic space group
33 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.
34 Skutterudite group minerals adopt a distorted perovskite structure with unoccupied *A* sites,
35 constructed from a framework of tilted, corner-linked BX_6 octahedra, bringing together four
36 anions in three-quarters of the otherwise vacant icosahedral cages, where they form rectangular
37 four member rings (Aleksandrov and Beznosikov 2007). Numerous synthetic compounds exist
38 which are isomorphous with skutterudite group minerals, and these materials fall into two
39 categories: (1) filled, which follow the general formula AB_4X_{12} , in which *A* is a large cation
40 partially to completely occupying the remaining quarter of the icosahedral cages, *B* is generally a

41 transition metal cation, and X is a P, As, or Sb anion; and (2) unfilled with the general formula
42 BX_3 . Synthetic filled skutterudite materials, such as $Tl_{0.5}Co_4Sb_{12}$ and $NdOs_4Sb_{12}$, have been
43 widely studied due to their particular thermoelectric properties including high Seebeck
44 coefficients, high electrical conductivity, and low thermal conductivity (Aleksandrov and
45 Beznosikov 2007; Chakoumakos and Sales 2006; Fukuoka and Yamanaka 2009; Návratil et al.
46 2010). We suspect that the structures of natural skutterudites can accommodate cations within
47 the icosahedral site.

48 The skutterudite mineral group currently consists of four members (with current IMA
49 formula): skutterudite ($CoAs_{3-x}$), nickelskutterudite ($NiAs_{3-x}$), ferroskutterudite [$(Fe,Co)As_3$], and
50 kieftite ($CoSb_3$). The IMA nomenclature commission currently defines the chemical formula for
51 skutterudite and nickelskutterudite as anion deficient, BX_{3-x} , after the work of Palache, Berman,
52 and Frondel (1944). Pauling (1978) suggested that the ideal formula of skutterudite be written
53 $Co_4(As_4)_3$, emphasizing the four member As rings.

54 The study of the skutterudite group has a long history, with skutterudite sensu stricto first
55 reported by Breithaupt (1827) and its chemical composition reported as $CoAs_3$ by Haidinger
56 (1845). Over the course of the next century, a series of mineral species were described in order to
57 account for the diversity of chemical compositions and physical properties exhibited by minerals
58 related to skutterudite (Vollhardt 1888). In particular a nickel-dominant phase was described by
59 Waller and Moses (1893) from the Bullard's Peak Mining District, Grant County, New Mexico,
60 and more recently an iron dominant phase was described by Spridonov et al. (2007). The 7th
61 edition of Dana's System by Palache, Berman and Frondel (1944), included a summary of the
62 skutterudite minerals, defining them as consisting of cubic RA_{3-x} minerals where $R = Fe, Co$ or

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

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

65 Ramsdell (1925) examined smaltite and chloanthite, which he considered to be
66 isostructural members of the series CoAs₂-NiAs₂, respectively, and distinct from skutterudite.
67 Ramsdell was, however, unable to solve the structure of either compound. Oftedal (1926) was
68 the first to report the crystal structure of skutterudite, and two years later he compared the
69 crystallography of skutterudite and a sample along the smaltite-chloanthite join (Oftedal 1928).
70 The powder diffraction patterns for skutterudite and smaltite-chloanthite observed by Oftedal
71 (1925) showed that they are isostructural, in spite of their chemical differences. Single-crystal
72 X-ray diffraction data collected by Oftedal (1925) led him to conclude that skutterudite, and
73 therefore smaltite-chloanthite, must follow the general formula RA_s_3 , where $R = \text{Co or Ni}$.
74 Holmes (1947) analyzed and summarized previous studies of the arsenides of cobalt, nickel, and
75 iron, and, based on Oftedal's work, concluded that the skutterudite structure is consistent with a
76 general formula of MA_s_3 , but the observed compositions frequently appeared to be anion
77 deficient. In the course of our study, it became clear that cation excess is more likely than anion
78 deficiency in the skutterudite structure, as illustrated by the various synthetic compounds
79 mentioned earlier.

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

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

94 **Experimental**

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

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

106 Single-crystal X-ray diffraction data were collected on a Bruker X8 APEX2 CCD X-ray
107 diffractometer equipped with graphite-monochromatized MoK α radiation using frame widths of
108 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of a cubic
109 unit cell. The intensity data were corrected for absorption effects by the multi-scan method using
110 the Bruker programs TWINABS for R100196 and SADABS for the remaining samples (Bruker
111 2007). Crystal and refinement data for all samples are presented in Table 2.

112 The crystal structure of nickelskutterudite was solved and refined using SHELX97 (Shel-
113 drick 2008) based on space group $Im\bar{3}$ (no. 204), yielding a reliability factor R of 1.4%, from
114 data collected on a twinned crystal ($0.05 \times 0.05 \times 0.04$ mm) removed from R100196. The
115 crystal is twinned according to a reflection on (110) with matrix $0\ 1\ 0 / 1\ 0\ 0 / 0\ 0\ 1$. This is a
116 $\{110\}$ merohedral twin of index 1, forming a “penetration twin” similar to the “iron cross” twins
117 seen in in pyrite. Arsenic was assigned to the Wyckoff position $24g [x\ y\ 0]$. Due to the inability
118 of X-ray data to distinguish Ni, Co, and Fe from one another, the three elements were assigned to
119 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
120 formula generated from microprobe data. Note, refining site $8c$ without constraining the ratios of
121 Ni, Co, and Fe to the empirical formula, but keeping the sum of the cations at 1.00, resulted in
122 differences of up to 16% from the microprobe generated formula. Constraining either Co or Fe,
123 not both, to the value of the empirical formula resulted in differences of only 3%.

124 The positions of all atoms were refined with anisotropic displacement parameters. The
125 refined coordinates and displacement parameters are listed in Table 3, and selected bond
126 distances and angles are in Table 4. Negligible residual electron density at the icosahedral site, *A*
127 (0, 0, 0), indicated that nickelskutterudite R100196 is unfilled. However, residual electron
128 density was seen at *A* for skutterudite R050593 and nickelskutterudite R100194. Site occupancy
129 refinement of *A* showed 0.01 metal (Co, Ni, or Fe) atom per formula unit in R050593 and
130 R100194.

131 Results

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

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

153 A system for the classification of octahedral tilt in perovskite derivative structures was
154 developed by Glazer (1972), and is applicable to the skutterudite structure (Mitchell 2002). A
155 brief summary of Glazer's classification is presented here; for an in-depth discussion of
156 octahedral tilt, the reader is referred to Glazer (1972). According to Glazer (1972), octahedral tilt
157 may be thought of as the combination of tilts about the three 4-fold axes of an octahedron. This
158 overall tilt is characterized according to magnitude and direction. Magnitude is the amount of tilt
159 about the three 4-fold axes, denoted *a* relative to [100], *b* relative to [010], and *c* relative [001],
160 and equality of tilt is shown by repeating the appropriate letter. Direction refers to tilt of
161 octahedra in successive layers along a given 4-fold axis, denoted as a superscript 0 for no tilt, +
162 for tilt in the same direction, and – for tilt in the opposite direction (Glazer 1972). NiAs₆
163 octahedra in nickelskutterudite (and MAs₆ octahedra in all other skutterudite structures) have
164 equal tilt about all three 4-fold axes, and the tilt of NiAs₆ octahedra in successive layers along
165 each axis is the same (Aleksandrov and Beznosikov 2007), so the Glazer tilt notation is *a*⁺*a*⁺*a*⁺.
166 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
167 Návrtil et al. (2010), where **a** is the unit cell edge and **d** is the metal-arsenic bond distance.

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

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

187 Discussion

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

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

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

209 The general formula of nickelskutterudite, $NiAs_3$, is not charged balanced assuming Ni^{2+} ,
210 Ni^{3+} or Ni^{4+} . Nickel (1969) suggested that in the skutterudite structure, Ni displays a charge of
211 +4 and As a charge of -3, which give an overall charge of -5. In order to compensate for this
212 charge imbalance, the anions form As_4 rings (Návratil et al. 2010; Patrik and Lutz 1999;
213 Takizawa et al. 1999). Tilting of $NiAs_6$ octahedra “stuffs” four As atoms into an icosahedral

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

216 The chemistry of two different nickelskutterudite samples were examined in this study:
217 R100194 (Schneeberg, Saxony, Germany), and R100196 (New Mexico, USA). Each contains
218 significant amounts of Co and Fe: R100194 empirical formula
219 $(\text{Ni}_{0.86}\text{Co}_{0.14}\text{Fe}_{0.01})_{\Sigma=1.01}(\text{As}_{2.99}\text{S}_{0.01})_{\Sigma=3.00}$, R100196 empirical formula
220 $(\text{Ni}_{0.62}\text{Co}_{0.28}\text{Fe}_{0.12})_{\Sigma=1.02}(\text{As}_{2.95}\text{S}_{0.05})_{\Sigma=3.00}$. The presence of significant Co and Fe may be explained
221 by the different electronic configurations of Ni^{4+} and Co^{3+} in the skutterudite structure. Nickel
222 (1969) notes that in the skutterudite structure, cations achieve complete spin-pairing of their non-
223 bonded *d*-electrons. For example, when Co^{3+} donates sufficient electrons to form pair bonds with
224 neighboring atoms, it has 6 non-bonded *d*-electrons which can be spin paired (Nickel 1969). In
225 order for Ni to be left with 6 non-bonded electrons, it must be quadrivalent, and if Ni^{4+} donates
226 sufficient electrons to form pair-bonds with all 6 neighboring atoms, it is left with 7 non-bonded
227 electrons, which cannot be fully spin-paired (Nickel, 1969).

228 **Implications**

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

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

239 Additionally, no anion deficiencies were found in skutterudite phases by either X-ray or
240 electron microprobe, supporting Roseboom's (1962) interpretation that anion deficient
241 skutterudite samples likely do not consist of a single phase. For these reasons, we propose the
242 chemical formula of nickelskutterudite (currently given as NiAs_{3-x} by the IMA) should be
243 $(\text{Ni},\text{Co},\text{Fe})\text{As}_3$.

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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.

Figure 2. A depiction of the crystal structure of nickelskutterudite as a primitive cubic lattice with white spheres representing metal atoms at lattice points. Three quarters of these cubes contain rectangular four membered rings of bonded As atoms indicated by green rods.

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.

Figure 1

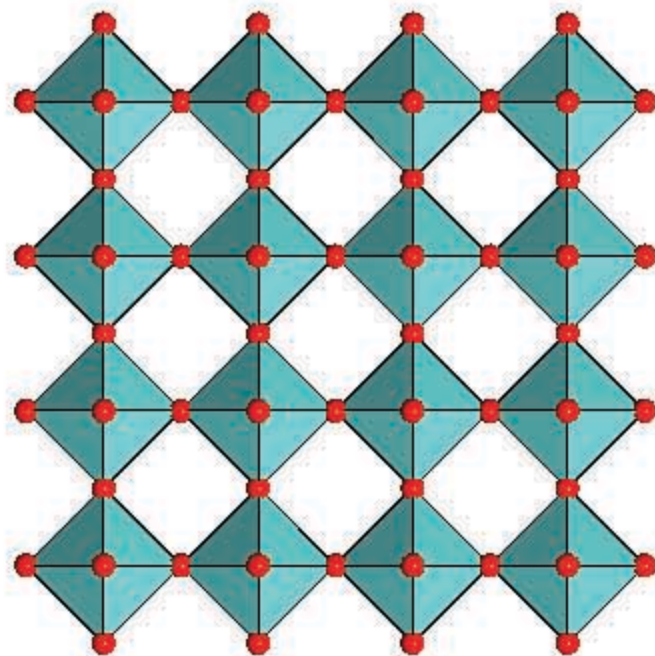
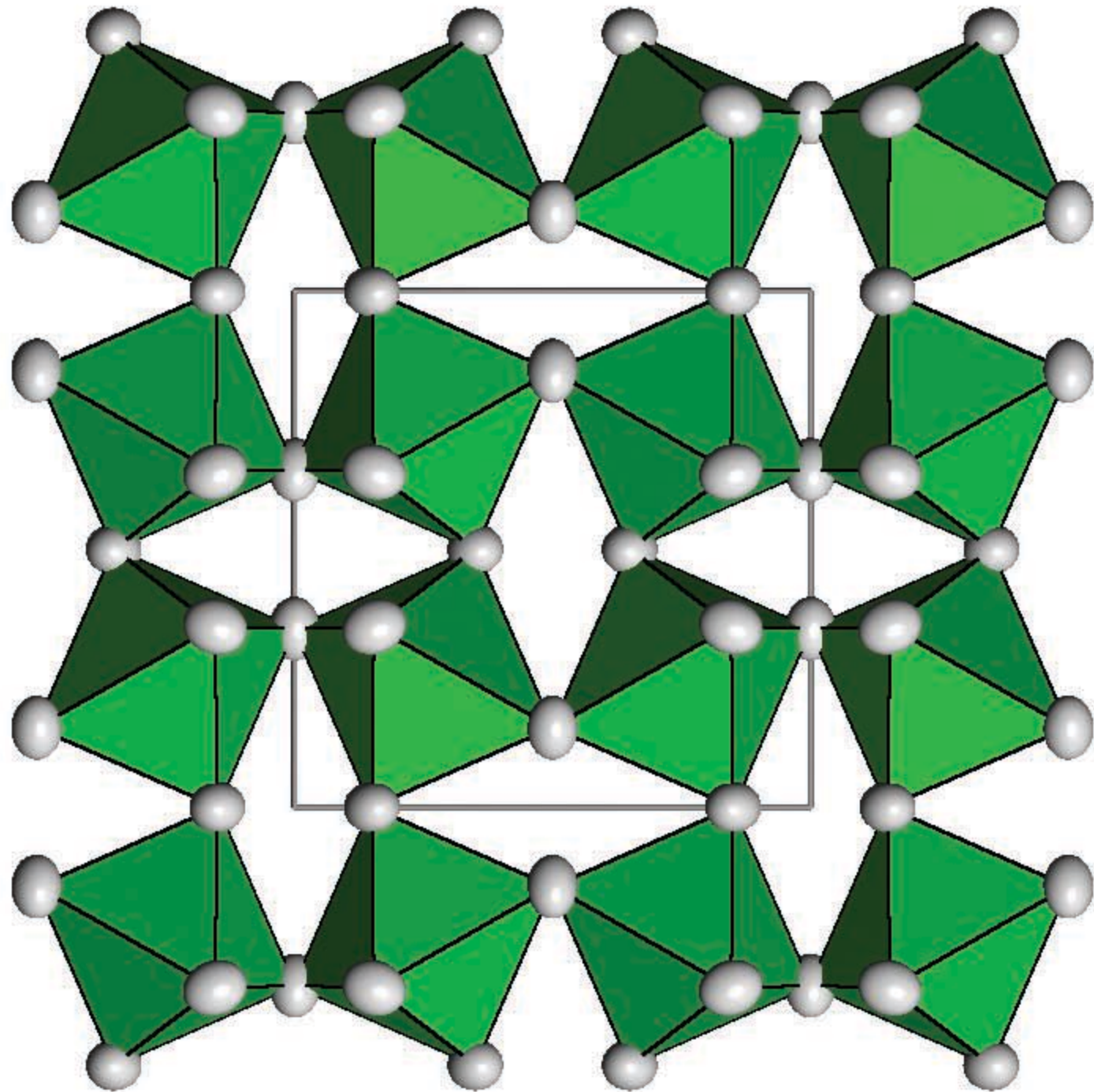


Figure 2

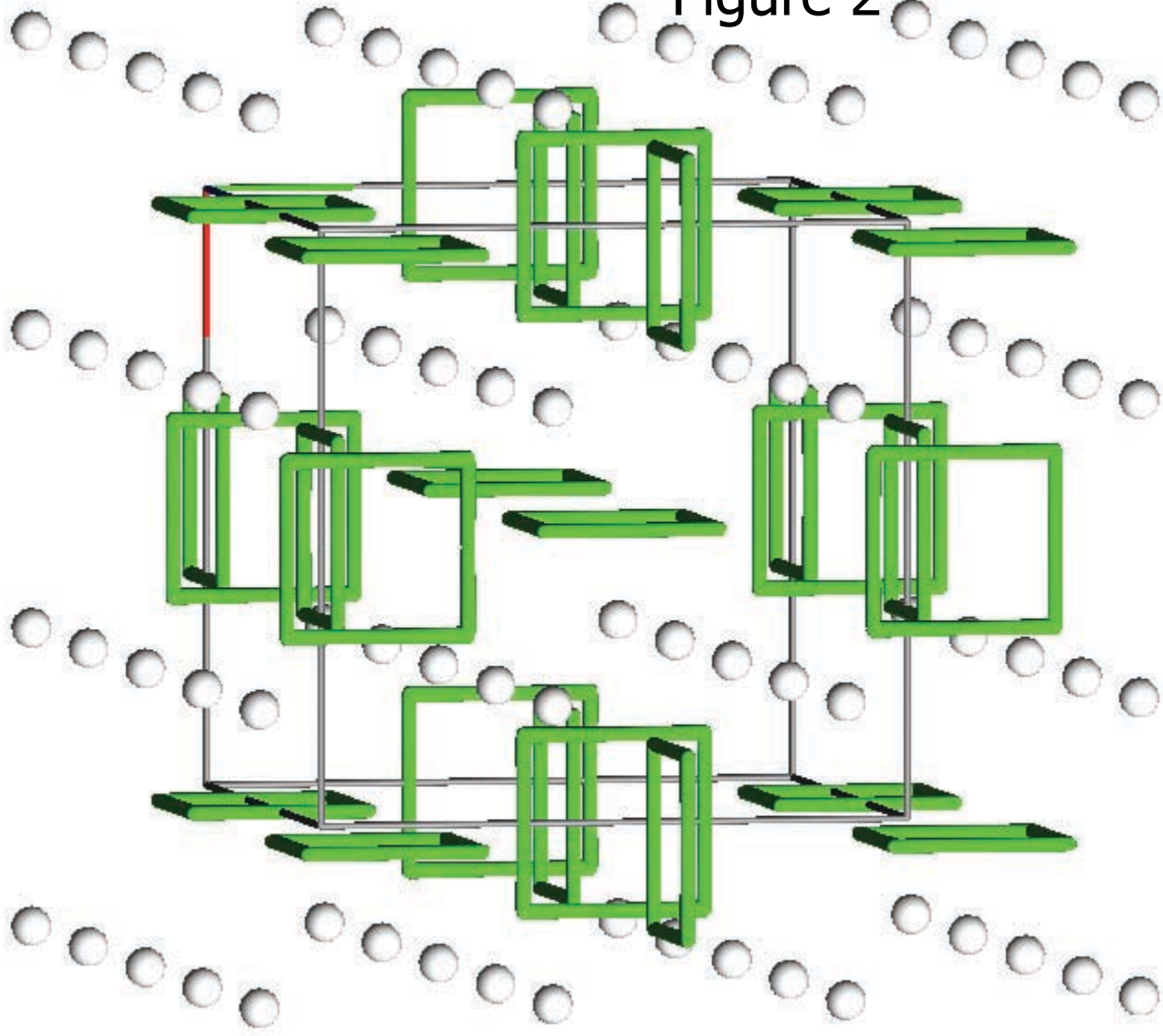
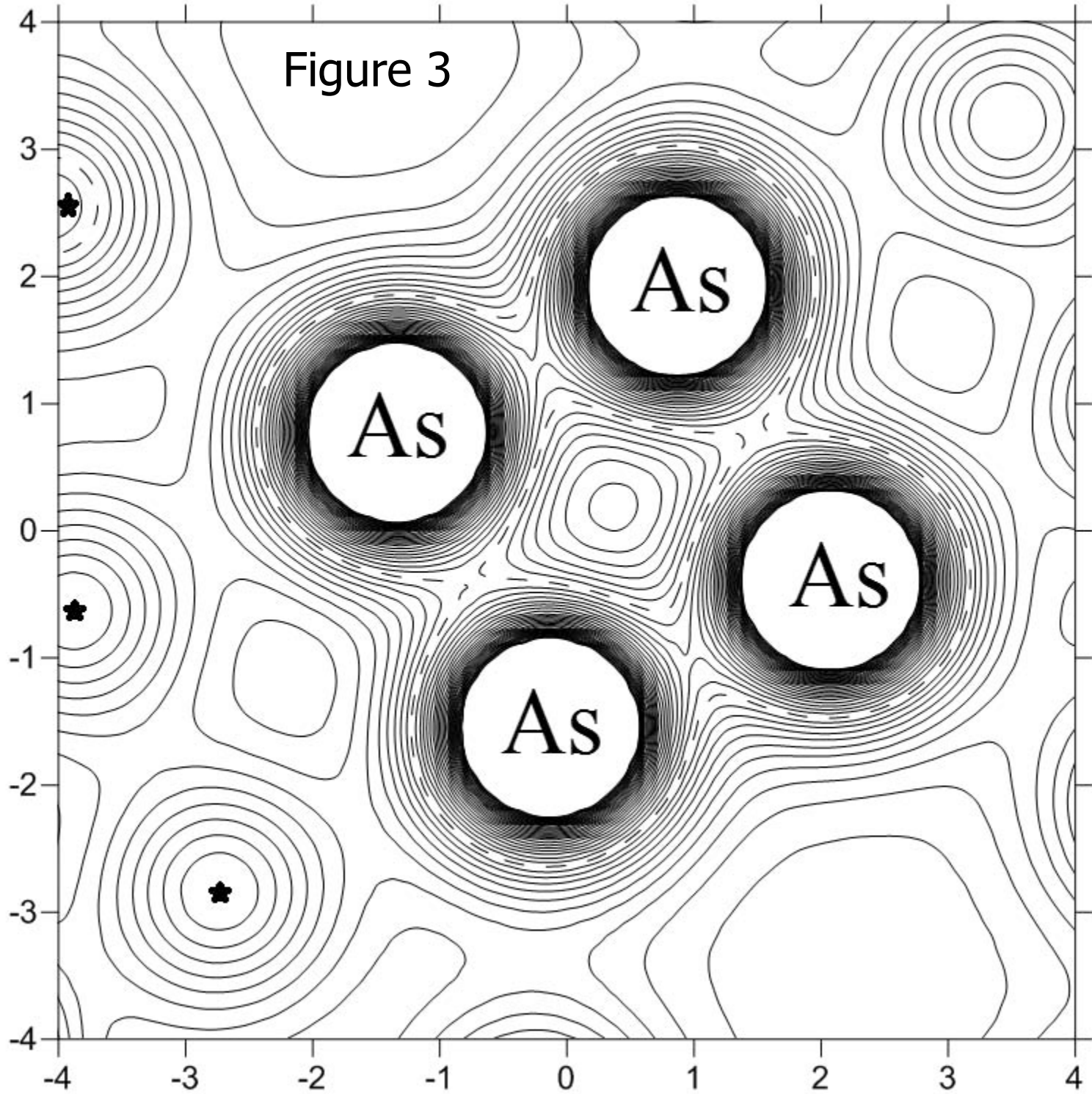


Figure 3



Octahedral Tilt vs X-X Bond Length

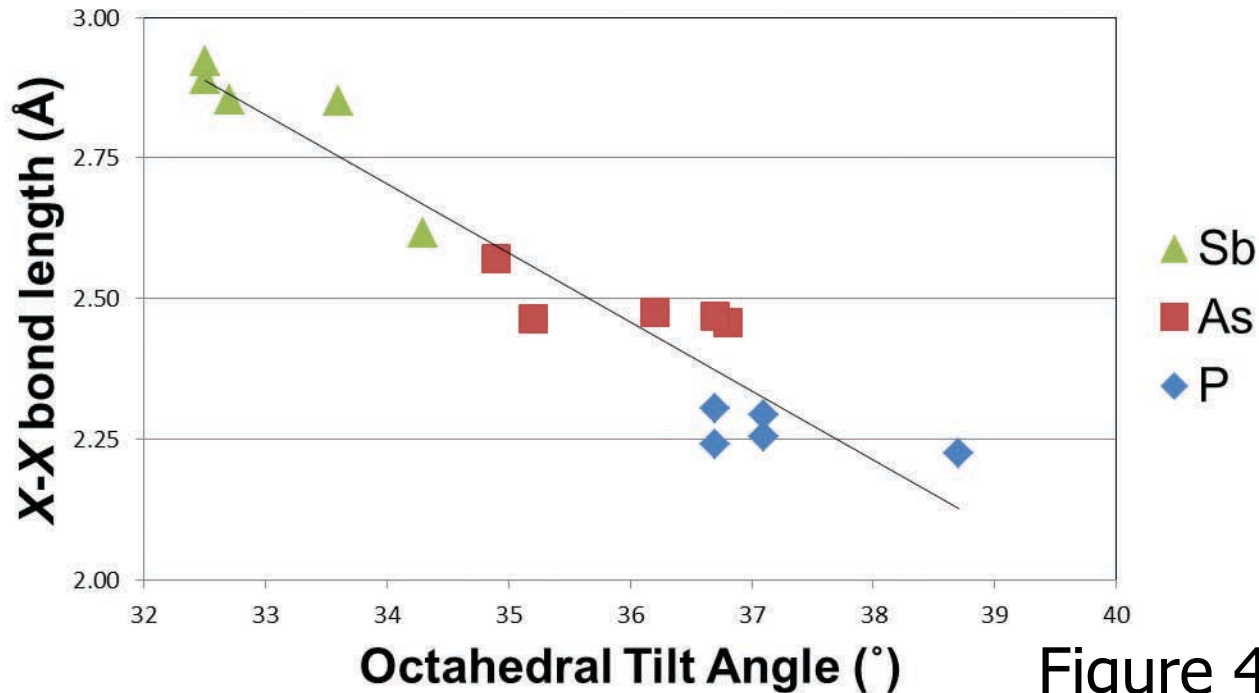


Figure 4

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

Revision 2

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 _{1.00} ^{M2} Fe _{0.01} As _{2.90} S _{0.10}	^{M1} Co _{1.00} As _{3.00}	^{M1} Ni _{1.00} ^{M2} Fe _{0.01} As _{3.00}	^{M1} Ni _{0.59} ^{M2} Co _{0.2499} ^{M2} Fe _{0.14} As _{3.00}
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	Shirotni 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	Shirotni 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	Návrtil et al. (2010)
Fe ₂ Pd ₂ Sb ₁₂	Sb	33.6	2.852	Návrtil 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)