

Article

Twinning, Superstructure and Chemical Ordering in Spryite, $\text{Ag}_8(\text{As}^{3+}_{0.50}\text{As}^{5+}_{0.50})\text{S}_6$, at Ultra-Low Temperature: An X-Ray Single-Crystal Study

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Abstract: Spryite ($\text{Ag}_{7.98}\text{Cu}_{0.05}\text{S}_{8.03}(\text{As}^{5+}_{0.31}\text{Ge}_{0.36}\text{As}^{3+}_{0.31}\text{Fe}^{3+}_{0.02})\text{S}_{5.97}$, and ideally $\text{Ag}_8(\text{As}^{3+}_{0.5}\text{As}^{5+}_{0.5})\text{S}_6$, is a new mineral recently described from the Uchucchacua polymetallic deposit, Oyon district, Catajumbo, Lima Department, Peru. Its room temperature structure exhibits an orthorhombic symmetry, space group $\text{Pna}2_1$, with lattice parameters $a = 14.984(4)$, $b = 7.474(1)$, $c = 10.571(2)$ Å, $V = 1083.9(4)$ Å³, $Z = 4$, and shows the coexistence of As^{3+} and As^{5+} distributed in a disordered fashion in a unique mixed position. To analyze the crystal-chemical behaviour of the arsenic distribution at ultra-low temperatures, a structural study was carried out at 30 K by means of in situ single-crystal X-ray diffraction data (helium-cryostat) on the same sample previously characterized from a chemical and structural point of view. At 30 K, spryite still crystallizes with orthorhombic symmetry, space group $\text{Pna}2_1$, but gives rise to a $a \times 3b \times c$ superstructure, with $a = 14.866(2)$, $b = 22.240(4)$, $c = 10.394(1)$ Å, $V = 3436.5(8)$ Å³ and $Z = 4$ ($\text{Ag}_{24}\text{As}^{3+}\text{As}^{5+}\text{Ge}^{4+}\text{S}_{18}$ stoichiometry). The twin laws making the twin lattice simulating a perfect hexagonal symmetry have been taken into account and the crystal structure has been solved and refined. The refinement of the structure leads to a residual factor $R = 0.0329$ for 4070 independent observed reflections [with $F_o > 4\sigma(F_o)$] and 408 variables. The threefold superstructure arises from the ordering of As^{3+} and (As^{5+} , Ge^{4+}) in different crystal-chemical environments.

Keywords: twinning; chemical ordering; superstructure; spryite; argyrodite-type compounds; ultra-low temperature



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1. Introduction

Spryite, ideally $\text{Ag}_8(\text{As}^{3+}_{0.5}\text{As}^{5+}_{0.5})\text{S}_6$, is a new mineral belonging to the argyrodite group recently described from the Uchucchacua polymetallic deposit, Oyon district, Catajumbo, Lima Department, Peru [1]. Argyrodite-type compounds allow for a large structural and chemical heterogeneity with the general formula $A^{m+}_{[(12-n-y)/m]}B^{n+}Q^{2-}_{6-y}X^{-}_y$, where A is a mono- or di-valent twofold or threefold coordinated cation such as Cu^+ , Ag^+ , Li^+ , Cd^{2+} , Hg^{2+} , B is a tri-, tetra-, or penta-valent tetrahedral cation, like Al^{3+} , Ga^{3+} , Si^{4+} , Ge^{4+} , Sn^{4+} , Ti^{4+} , P^{5+} , As^{5+} , Sb^{5+} , Nb^{5+} , Ta^{5+} , and Q and X are respectively chalcogenide or halide anions [2]. Natural and synthetic argyrodites have drawn attention over time for their peculiar physical properties, such as superionic conduction, and their potential application as electrolytes, e.g., [3]. In this respect, spryite represents an exception since it does not behave as a superionic conductor [1]. The absence of such property was attributed to the presence of As^{3+} in the structure, another unique feature of spryite. As^{3+} was not considered as a possible cation for the B site in the argyrodite-type structure because of the presence of the lone-pair electrons that do not allow tetrahedral coordination. It is thus not surprising that, before the description of spryite, only Al^{3+} , Ga^{3+} , and Fe^{3+} were reported as trivalent cations in argyrodites [4–6]. In spryite trivalent and pentavalent, As (together with Ge^{4+}) share the same split sites with slightly different atomic coordinates. On the

one hand, As^{3+} is split toward three S atoms to produce AsS_3 pyramids, analogously to sulfosalts [7]. On the other hand, As^{5+} and Ge^{4+} sit in the tetrahedral site typically occupied by Ge in argyrodite-type compounds [8]. The presence of disordered As^{3+}S_3 pyramids might be responsible for the absence of superionic conduction, since they can hinder the mobility of the Ag cations that in argyrodites-like structures are highly delocalized over all the available sites, even at room temperature [9]. In fact, this mineral is characterized by a network of non-interacting Ag cation, with all sites fully occupied. Temperature dependence is another peculiar aspect of spryite. Argyrodite-type compounds usually show three phase transitions as a function of temperature. The high temperature phase has space group $F-43m$, that transforms to $P2_13$. On further cooling, these compounds apparently adopt again the $F-43m$ space group, but actually have an orthorhombic symmetry, such as $Pna2_1$, $Pnam$, or $Pmn2_1$ [7]. Conversely, spryite was shown to maintain the orthorhombic structure from 90 to 500 K [1], thus representing a unique case in the argyrodite family. Considering the peculiar structural features and temperature dependence of spryite, we investigated its crystal structure at 30 K, in order to understand the effects of ultra-low temperature on the structure and to verify if the disordered As/Ge position present in the room-temperature structure could give rise to some localized ordering and thus to a possible superstructure at ultra-low temperature.

2. X-ray Crystallography

The same crystal of spryite used to study the temperature behaviour in the range 90–500 K (chemical composition $(\text{Ag}_{7.98}\text{Cu}_{0.05})_{\Sigma=8.03}(\text{As}^{5+}_{0.31}\text{Ge}_{0.36}\text{As}^{3+}_{0.31}\text{Fe}^{3+}_{0.02})_{\Sigma=1.00}\text{S}_{5.97}$ [1]) was mounted on an Oxford Diffraction Xcalibur 3 diffractometer (Oxford Diffraction, Oxford, UK) (Enhance X-ray source, X-ray $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$), fitted with a Sapphire 2 CCD detector and an Oxford cryostream cooler (helium-cryostat). The temperature was lowered at 30 K and, before the measurement, the sample was held at that temperature for about 30 min. The diffraction pattern at 30 K was consistent with an orthorhombic symmetry but additional reflections leading to a threefold $\mathbf{a} \times 3\mathbf{b} \times \mathbf{c}$ commensurate superstructure were observed (i.e., $a \approx 14.9 \text{ \AA}$, $b \approx 22.2$, $c \approx 10.4 \text{ \AA}$). To account for a potential reduction of symmetry for the low-temperature structure of spryite and given the fact that the crystal is intimately twinned, a relatively high $\sin(\theta)/\lambda$ cutoff and a high redundancy were chosen in the recording setting design. Intensity integration and standard Lorentz-polarization correction were performed with the *CrysAlis* software package [10,11]. The diffraction quality was found to be excellent, thus indicating that no deterioration of the crystal occurred even at ultra-low temperature. All the collected data are plotted down the $\mathbf{c}$ -axis and shown in Figure 1. A strong hexagonal pseudo-symmetry of the X-ray reflections is evident, which is due to the pervasive twinning giving rise to a pseudo-cubic, face-centered cell with $a \approx 10.5 \text{ \AA}$ at room temperature [1] and to a pseudo-hexagonal cell with $a \approx 7.5$ and $c \approx 10.5 \text{ \AA}$ at 30 K.

The values of the equivalent pairs were averaged. The merging R for the ψ -scan data set decreased from 0.1506 before absorption correction to 0.0355 after this correction. The analysis of the systematic absences ($0kl$: $k + l = 2n$; $h0l$: $h = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) are consistent with the space groups $Pnam$ ($Pnma$ as standard) and $Pna2_1$. Statistical tests on the distribution of $|E|$ values strongly indicate the absence of an inversion centre [$|E^2 - 1| = 0.695$], thus suggesting the choice of the space group $Pna2_1$. To decide the correct space group for the low-temperature superstructure we also analyzed the maximum orthorhombic *klassengleiche* subgroups of the $Pna2_1$ room-temperature space group. We noticed that there is only one subgroup with $\mathbf{b}' = 3\mathbf{b}$, that is $Pna2_1$, and thus the superstructure was solved in this space group.

The position of most of the atoms was determined from the three-dimensional Patterson synthesis. A least-squares refinement, by means of the program SHELXL-97 [12], using these heavy-atom positions and isotropic temperature factors, yielded an R factor of 0.2005. Three-dimensional difference Fourier synthesis yielded the position of the remaining sulfur atoms. The introduction of anisotropic temperature factors for all the

atoms led to $R = 0.0329$ for 4070 observed reflections [$F_o > 4\sigma(F_o)$] and $R = 0.0346$ for all 4705 independent reflections. Neutral scattering factors for Ag, As, Ge, and S were taken from the International Tables for X-ray Crystallography [13].

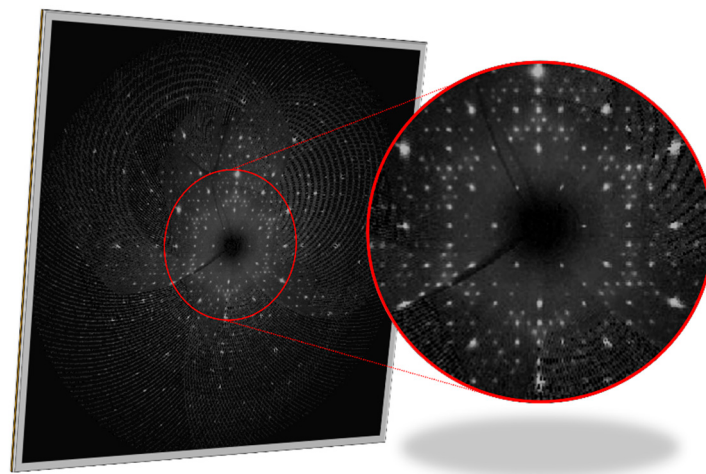


Figure 1. Hexagonal pseudo-symmetry in the X-ray diffraction pattern of spryite at 30 K due to the pervasive twinning.

In order to better model the twinning occurring in spryite [1], we then took into account the twin law, which makes the twin lattice (L_T) hexagonal (twinning by reticular merohedry [14]) using the program JANA2006 [15]. For details of this kind of twinning and on the averaging of equivalent reflections for twins in JANA, see the appendix in [16]. Remarkably, the same set of twin matrices (referred to the orthorhombic cell) were used either at 30 K or at room temperature [1]. Once again, the structure refinement was initiated in the orthorhombic supercell. After several cycles, the structure could be smoothly refined without any damping factor or restrictions. The residual value converged to $R = 0.0329$ for 4070 observed reflections [$F_o > 4\sigma(F_o)$] and $R = 0.0346$ including all the 4705 collected reflections in the refinement. Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 1.90 a-d $1.67 \text{ e}^-/\text{\AA}^3$, respectively. Experimental details and R indices are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are shown in Table 2. The Crystallographic Information File (CIF) of the structure is deposited as Supplementary Materials.

Table 1. Experimental and refinement details for spryite at 30 K.

Spryite	
Temperature	30(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	$a = 14.866(2)$ Å $b = 22.240(4)$ Å $c = 10.3940(10)$ Å
Volume	$3436.5(8)$ Å ³
Z	4
Density (calculated)	6.549 Mg/mm ³
Crystal size	$0.040 \times 0.030 \times 0.020$ mm ³
Theta range for data collection	4.78 to 30.00°
h,k,l ranges	$-20 \leq h \leq 20, -31 \leq k \leq 31, -14 \leq l \leq 14$
Reflections collected	38705
Independent reflections	4705 [$R_{\text{int}} = 0.0355$]
Data/restraints/parameters	4705/1/408
Goodness of fit on F^2	1.052
Final R indices [$F_o > 4\sigma(F_o)$]	$R1 = 0.0329, wR2 = 0.0670$
R indices (all data)	$R1 = 0.0346, wR2 = 0.0678$
Extinction coefficient	0.000301(17)
Largest diff. peak and hole	1.90 and -1.67 e.Å ⁻³
Twin matrices (referred to the orthorhombic cell)	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1/2 & 1/4 & 1/2 \\ -1 & -1/2 & 1 \\ 1 & -1/2 & 0 \end{bmatrix} \begin{bmatrix} 1/2 & -1/4 & 1/2 \\ 1 & -1/2 & -1 \\ 1 & 1/2 & 0 \end{bmatrix}$ $\begin{bmatrix} 0 & -1/2 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1/2 & 1/4 & -1/2 \\ 1 & -1/2 & -1 \\ 1 & 1/2 & 0 \end{bmatrix} \begin{bmatrix} 1/2 & 1/4 & -1/2 \\ 1 & 1/2 & 1 \\ -1 & 1/2 & 0 \end{bmatrix}$
Twin fractions	0.28(3), 0.20(2), 0.16(2), 0.14(2), 0.12(2), 0.10(2)

Table 2. Atom coordinates and equivalent isotropic displacement parameters (Å²) for spryite.

Site	x/a	y/b	z/c	U_{eq}
Ag1A	0.1257(3)	0.07361(17)	0.3742(5)	0.0383(5)
Ag1B	0.1269(2)	0.40562(13)	0.3764(4)	0.0359(4)
Ag1C	0.1269(4)	0.7341(3)	0.3739(6)	0.0393(6)
Ag2A	0.06183(4)	0.07485(2)	0.83671(6)	0.02599(11)
Ag2B	0.05993(4)	0.40511(2)	0.83817(6)	0.02494(11)
Ag2C	0.06321(3)	0.73552(2)	0.83630(6)	0.02402(11)
Ag3A	0.43197(5)	0.02050(3)	0.01921(7)	0.03304(14)
Ag3B	0.43246(4)	0.35041(3)	0.01990(7)	0.02850(13)
Ag3C	0.43262(5)	0.68067(4)	0.01956(9)	0.03866(17)
Ag4A	0.2768(4)	0.1662(3)	0.0834(8)	0.0290(10)
Ag4B	0.27687(4)	0.50675(14)	0.08245(6)	0.0286(4)
Ag4C	0.2770(5)	0.8364(4)	0.0819(9)	0.0391(16)
Ag5A	0.41845(5)	0.03021(3)	0.69619(9)	0.03584(14)
Ag5B	0.41848(4)	0.36017(3)	0.69717(8)	0.03396(13)
Ag5C	0.41868(4)	0.70034(3)	0.69693(7)	0.02805(12)
Ag6A	0.27281(4)	0.12823(3)	0.68399(7)	0.02865(12)
Ag6B	0.27274(5)	0.46785(3)	0.68435(9)	0.03504(13)
Ag6C	0.27304(4)	0.79812(3)	0.68428(7)	0.02883(12)

Table 2. Cont.

Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i>
Ag7A	0.01698(4)	0.0045(6)	0.60282(8)	0.0387(10)
Ag7B	0.0175(4)	0.3339(3)	0.6021(6)	0.0249(9)
Ag7C	0.0168(5)	0.6639(3)	0.6036(8)	0.0351(15)
Ag8A	0.25877(4)	0.04283(3)	0.90577(8)	0.03030(13)
Ag8B	0.25881(4)	0.37291(3)	0.90561(8)	0.03138(13)
Ag8C	0.25860(4)	0.70268(3)	0.90549(7)	0.02573(12)
As ⁵⁺	0.37565(4)	0.07852(3)	0.34985(10)	0.02252(13)
Ge	0.37583(4)	0.40121(3)	0.34959(10)	0.01968(12)
As ³⁺	0.37990(3)	0.78942(3)	0.29965(11)	0.02286(12)
S1A	0.1227(8)	0.1644(5)	0.9763(8)	0.030(3)
S1B	0.12244(14)	0.5046(18)	0.9770(3)	0.037(3)
S1C	0.1221(10)	0.8341(6)	0.9774(13)	0.046(4)
S2A	−0.00394(18)	0.09037(11)	0.2315(3)	0.0388(5)
S2B	−0.00418(18)	0.42044(11)	0.2316(3)	0.0380(5)
S2C	−0.00434(16)	0.75029(10)	0.2313(3)	0.0358(5)
S3A	0.37300(17)	0.15601(12)	0.4794(3)	0.0362(5)
S3B	0.37279(16)	0.48499(10)	0.4791(3)	0.0379(5)
S3C	0.37272(16)	0.81480(14)	0.4788(3)	0.0327(5)
S4A	0.25826(17)	0.07751(13)	0.2306(3)	0.0380(5)
S4B	0.25859(18)	0.40740(13)	0.2300(3)	0.0402(5)
S4C	0.25859(18)	0.73719(13)	0.2306(3)	0.0407(5)
S5A	0.3861(7)	0.1054(4)	0.8663(12)	0.0334(10)
S5B	0.3867(9)	0.4357(5)	0.8691(16)	0.0322(11)
S5C	0.3855(13)	0.7631(10)	0.879(2)	0.0398(19)
S6A	0.12309(13)	0.08887(10)	0.6117(3)	0.0320(4)
S6B	0.12280(14)	0.42869(10)	0.6117(3)	0.0351(5)
S6C	0.12278(14)	0.75866(10)	0.6112(3)	0.0337(4)

3. Description of the Low-Temperature Structure and Discussion

The low-temperature structure solution of spryite showed that the atomic arrangement of the mineral at 30 K is topologically identical to that observed at room temperature [1] with the cation ordering being limited to small portions of the structure only. Indeed, the solution revealed that As³⁺, As⁵⁺, and Ge⁴⁺ are ordered into three specific sites. Indeed, the unique mixed (As, Ge) position in the room-temperature structure (Wyckoff position 4a) transforms into three 4a Wyckoff positions in the low-temperature structure hosting As³⁺, As⁵⁺, and Ge, respectively. This does not lead to any reduction of symmetry as the space group (*Pna2*₁) remains the same as the room-temperature structure. In the structure, Ag occupies sites with coordination ranging from quasi-linear to almost tetrahedral connected into a framework (Figure 2 and Table 3). In particular, 10 Ag atoms are fourfold coordinated, 11 are threefold and 3 are twofold coordinated. As in the ambient temperature structure, the average bond length increases from the twofold to the fourfold coordination: the average Ag-S distance ranges from 2.569 to 2.722 Å for the almost tetrahedral geometry, from 2.475 to 2.562 Å for the trigonal geometry, and from 2.337 to 2.428 Å for the quasi-linear geometry. Each Ag site gives rise to three sites in the ultra-low temperature structure maintaining the coordination present at room temperature, e.g., the fourfold coordinated Ag2 corresponds to three fourfold coordinated Ag2A, Ag2C, Ag3C. The almost tetrahedral Ag1 is the only exception, since it is related to a fourfold coordinated Ag1C and two threefold coordinated Ag1A and Ag1B. The analysis of the crystal-chemical characteristic of the Ag-environments indicates that the As/Ge chemical ordering observed in the low-temperature crystal structure of spryite does not affect significantly the geometry of their coordination polyhedra, highlighting a clear similarity with the low temperature structure.

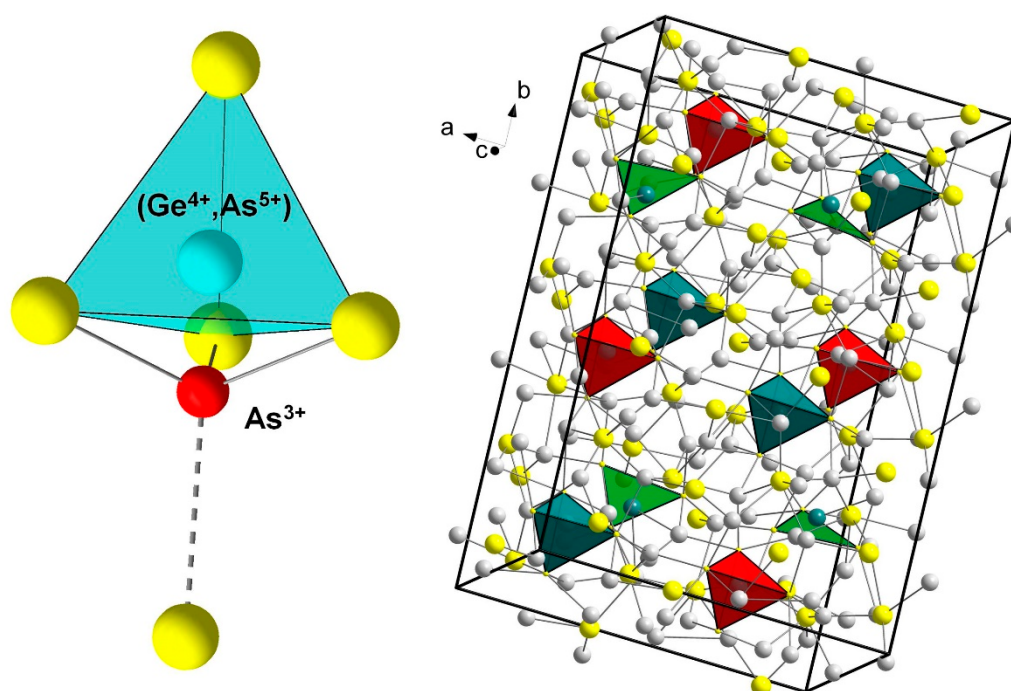


Figure 2. Left: Portion of the crystal structure of spryite at room temperature highlighting the disorder between the M1 and M2 positions (As^{3+} , As^{5+} and Ge^{4+}) at room temperature. In light blue the M1 tetrahedron (As^{5+} and Ge^{4+}) and with a red sphere the M2 atom (As^{3+}). Right: The crystal structure of spryite at 30 K; Ag and S atoms are given as white and yellow spheres, respectively. Light blue and red tetrahedra are filled by As^{5+} and Ge^{4+} , respectively, whereas green polyhedra are filled by As^{3+} . The unit cell and the orientation of the structure are outlined.

Table 3. Selected bond distances [$\text{\AA}$] and angles ($^\circ$) for spryite at 30K.

Atoms	Distance	Atoms	Distance
Ag1A-S2A	2.460(6)	Ag6A-S6A	2.507(2)
Ag1A-S4A	2.474(5)	Ag6A-S4C	2.515(3)
Ag1A-S6A	2.492(6)	Ag6A-S5A	2.586(12)
<Ag1A-S>	2.475	Ag6A-S3A	2.669(3)
Ag1B-S4B	2.480(5)	<Ag6A-S>	2.569
Ag1B-S2B	2.484(4)	Ag6B-S6B	2.510(2)
Ag1B-S6B	2.499(5)	Ag6B-S4A	2.528(3)
<Ag1B-S>	2.488	Ag6B-S3B	2.629(3)
Ag1C-S4C	2.461(6)	Ag6B-S5B	2.659(16)
Ag1C-S2C	2.477(7)	<Ag6B-S>	2.582
Ag1C-S6C	2.527(6)	Ag6C-S6C	2.517(2)
Ag1C-S5A	2.870(12)	Ag6C-S4B	2.521(3)
<Ag1C-S>	2.584	Ag6C-S3C	2.626(3)
Ag2A-S6A	2.529(3)	Ag6C-S5C	2.74(2)
Ag2A-S1A	2.624(11)	<Ag6C-S>	2.601
Ag2A-S5B	2.636(13)	Ag7A-S6A	2.453(10)
Ag2A-S3B	2.670(3)	Ag7A-S2A	2.506(12)
<Ag2A-S>	2.615	Ag7A-S3B	2.511(3)
Ag2B-S6B	2.587(3)	<Ag7A-S>	2.490
Ag2B-S5A	2.611(11)	Ag7B-S2C	2.313(6)
Ag2B-S3C	2.678(3)	Ag7B-S3A	2.509(6)
Ag2B-S1B	2.80(3)	Ag7B-S6B	2.627(6)
<Ag2B-S>	2.699	<Ag7B-S>	2.483
Ag2C-S3A	2.497(3)	Ag7C-S2B	2.307(8)

Table 3. Cont.

Atoms	Distance	Atoms	Distance
Ag2C-S6C	2.554(3)	Ag7C-S3C	2.548(8)
Ag2C-S5C	2.68(2)	Ag7C-S6C	2.634(7)
Ag2C-S1C	2.780(13)	<Ag7C-S>	2.496
<Ag2C-S>	2.628	Ag8A-S5A	2.384(7)
Ag3A-S6B	2.399(3)	Ag8A-S3B	2.462(3)
Ag3A-S5A	2.560(11)	<Ag8A-S>	2.428
Ag3A-S2B	2.739(3)	Ag8B-S5B	2.389(10)
Ag3A-S1B	2.919(8)	Ag8B-S3C	2.464(3)
<Ag3A-S>	2.654	<Ag8B-S>	2.427
Ag3B-S6C	2.396(3)	Ag8C-S5C	2.33(2)
Ag3B-S5B	2.553(14)	Ag8C-S3A	2.344(3)
Ag3B-S2A	2.732(3)	<Ag8C-S>	2.337
Ag3B-S1A	2.882(12)	As ⁵⁺ -S1B	2.11(3)
<Ag3B-S>	2.722	As ⁵⁺ -S4A	2.141(3)
Ag3C-S6A	2.402(3)	As ⁵⁺ -S2B	2.168(3)
Ag3C-S5C	2.45(2)	As ⁵⁺ -S3A	2.187(3)
Ag3C-S2C	2.843(3)	<As⁵⁺-S>	2.152
Ag3C-S1C	2.870(15)	S1B-As ⁵⁺ -S4A	111.4(4)
<Ag3C-S>	2.641	S1B-As ⁵⁺ -S2B	110.6(3)
Ag4A-S4A	2.511(8)	S4A-As ⁵⁺ -S2B	110.09(12)
Ag4A-S1A	2.548(14)	S1B-As ⁵⁺ -S3A	103.2(7)
Ag4A-S6C	2.557(7)	S4A-As ⁵⁺ -S3A	110.48(11)
<Ag4A-S>	2.539	S2B-As ⁵⁺ -S3A	110.81(10)
Ag4B-S6A	2.375(3)	Ge-S1C	1.998(13)
Ag4B-S1B	2.544(2)	Ge-S4B	2.145(3)
Ag4B-S4B	2.703(4)	Ge-S2A	2.177(3)
<Ag4B-S>	2.541	Ge-S3B	2.299(3)
Ag4C-S1C	2.545(18)	<Ge-S>	2.155
Ag4C-S6B	2.556(8)	S1C-Ge-S4B	116.5(4)
Ag4C-S4C	2.707(10)	S1C-Ge-S2A	115.3(5)
<Ag4C-S>	2.551	S4B-Ge-S2A	109.55(13)
Ag5A-S1B	2.426(10)	S1C-Ge-S3B	102.5(4)
Ag5A-S5A	2.481(12)	S4B-Ge-S3B	105.74(10)
Ag5A-S2B	2.778(3)	S2A-Ge-S3B	106.06(9)
<Ag5A-S>	2.562	As ³⁺ -S3C	1.949(3)
Ag5B-S1C	2.433(13)	As ³⁺ -S2C	2.061(2)
Ag5B-S5B	2.498(15)	As ³⁺ -S4C	2.262(3)
Ag5B-S2C	2.780(2)	As ³⁺ -S3C	1.949(3)
<Ag5B-S>	2.570	<As(3)-S>	2.055
Ag5C-S5C	2.40(2)		
Ag5C-S1A	2.505(9)		
Ag5C-S2A	2.778(3)		
<Ag5C-S>	2.561		

Bold = mean polyhedral bond distances.

As³⁺ forms AsS₃ pyramids, typical of sulfosalts, and (Ge⁴⁺, As⁵⁺) links four sulfur atoms in a tetrahedral coordination. Given the close scattering power between As and Ge—and their corresponding site geometry—it is hard to say which tetrahedron is dominated by As (or Ge). Bond-valence considerations do not help in this case as the mean tetrahedral distances and the mean tetrahedral angles are very close: 2.152 and 2.155 Å and 109.4 and 110.9°, for the AsS₄ and GeS₄, respectively (Table 3). However, the slightly smaller value for the AsS₄ tetrahedron seems in agreement with the slightly shorter As⁵⁺-S distance (2.169 Å—see discussion in [17]) than that observed for GeS₄ in pure argyrodite (i.e., 2.212 Å; [8]). Furthermore, the analysis of the angle variance (σ^2) and the quadratic elongation (λ) of the two tetrahedra [18] reveals strong differences: AsS₄ tetrahedra exhibit a $\sigma^2 = 9.86$ and $\lambda = 1.0030$, while GeS₄ tetrahedra exhibit a $\sigma^2 = 31.33$ and $\lambda = 1.0094$. The general higher distortion introduced by the entry of Ge⁴⁺ in crystal structures [8] represents a further

corroboration of the right assignment of As^{5+} and Ge^{4+} in the two tetrahedra of spryite at ultra-low temperature.

4. Conclusions

Our investigation shows that the crystal structure of cooled spryite is very close to that observed at room temperature. Spryite is also characterized by pervasive twinning, thus requiring an accurate structural characterization. We demonstrate by means of an in situ data collection at 30 K that there is an ordering between As^{3+} and $(\text{As}^{5+}, \text{Ge}^{4+})$, leading to a threefold superstructure. Spryite confirms its uniqueness in the argyrodite family of compounds, since it maintains its orthorhombic symmetry on a large temperature range, together with a network of non-interacting Ag cations, an unusual feature in argyrodite-like compounds. The characterization of Ag coordination geometries allows to confirm that the low-temperature structure and the room-temperature one are geometrically very similar to each other.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2075-163X/11/3/286/s1>, file: Supplementary Materials CIF.

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