

X-ray data, optical anisotropism, and thermal stability of cobaltite, gersdorffite, and ullmannite

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SUMMARY. Data are presented from cobaltite (CoAsS), gersdorffite (NiAsS), and ullmannite (NiSbS) for cell size, compositional zoning, mineralogical association, X-ray diffraction powder intensities, and optical anisotropy. The presence of powder X-ray diffraction reflections 001 and 011 are related to the crystal structure type. The amount of distortion from cubic symmetry is related to the 001 reflection intensity and also to the optical anisotropism strength. These properties are related approximately to the thermal stability of the distorted crystal structure. This thermal stability increases with the substitution of cobalt for nickel, which decreases the cell size. An order-disorder change occurs before the distortion release in non-cubic gersdorffite (*P1*) with a large cell size, whereas only a distortion release is observed in cobaltite (*Pca2₁*) and non-cubic gersdorffite (*P1*) with a small cell size. Glaucodot (Co,Fe)AsS converted to cobaltite at 620 °C. No evidence was found to relate optical anisotropism of pyrite to deviations from cubic symmetry.

THE main mineral species in the *AXY* sulphide sub-class, which are closely related to pyrite, are cobaltite, gersdorffite, and ullmannite. Until recent crystal structure analyses, all these minerals were considered cubic because of their geometrically cubic cell, although optical anisotropism has been observed in them. The relationship between crystal structure, X-ray diffraction powder reflection intensities, and optical anisotropism needs to be investigated. Compositional variation may effect these properties. In addition, the relationship between the various gersdorffite structures needs to be investigated by heating experiments. Other related problems are the relationship of glaucodot (Co,Fe)AsS to cobaltite, and to examine if the observed optical anisotropy of pyrite is related to deviations from cubic symmetry.

To study these properties, six cobaltite samples, fourteen gersdorffite samples, four ullmannite samples, one glaucodot sample, and eighteen pyrite samples were obtained from museums.

Literature survey

The cell sizes for cobaltites recorded by Mechling (1921), Ramsdell (1925), de Jong (1926), Zachariassen (1927), Peacock and Berry (1940), Peacock and Henry (1948), Bokii and Tsinokev (1954), Onorato (1957), Bashenov (1958), Shishkin (1958), Silberman *et al.* (1958), Berry and Thompson (1962), Oftedal (1963), Giese and Kerr (1965), and Klemm (1965) range from 5.56 Å to 5.62 Å except that of Bokii and Tsinokev (1954) at 5.67 KX. X-ray diffraction powder reflection intensities for cobaltite have been recorded by Peacock and Henry (1948), Berry and Thompson (1962), and Giese and Kerr (1965). The optical anisotropy of cobaltite was initially described by Schneiderholm (1922); it is considered by Ramdohr (1960) to vary with deviation from cubic symmetry. All ten cobaltite samples examined by Klemm (1962)

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were optically anisotropic. Optically anisotropic cobaltite was heated by Flörke (1926) above 850 °C and became optically isotropic. This agrees with the crystal structure analyses of Giese and Kerr (1965) in which the orthorhombic structure ($Pca2_1$) with the non-metal atoms ordered changed to the cubic structure ($Pa3$) with non-metal atoms disordered upon heating to 850 °C.

The cell sizes for gersdorffites recorded by Ramsdell (1925), Olshausen (1925), Zachariassen (1927), Peacock and Berry (1940), Peacock and Henry (1948), Bernard (1958), Bokii and Tsinokev (1954), Yund (1962), and Klemm (1965) range from 5.60 Å to 5.72 Å. X-ray diffraction powder reflection intensities for gersdorffite have been recorded by Peacock and Henry (1948), and Yund (1962). The crystal structures of gersdorffite ($Pa3$, $P2_13$, and $P1$) are described by Bayliss and Stephenson (1967 and 1968), and Bayliss (1968). From polished-section studies, evidence by Ramdohr (1960) indicates a possible inversion and non-isometric character. This was confirmed by Klemm (1962), who noted areas of weak optical anisotropic colours in eight of his fourteen samples mainly as twin lamellae after (100) and (111) [?], often as zone structure and occasionally as grains.

The cell sizes for ullmannites recorded by Ramsdell (1925), Zachariassen (1927), Peacock and Berry (1940), Harcourt (1942), Bokii and Tsinokev (1954), Takeuchi (1957), and Berry and Thompson (1962) range from 5.88 Å to 5.93 Å and for corynite from 5.73 Å to 5.76 Å. X-ray diffraction powder reflection intensities for ullmannite have been recorded by Harcourt (1942) and Berry and Thompson (1962). The crystal structure of ullmannite ($P2_13$) is described by Takeuchi (1957). Areas of weak optical anisotropic colours were noted by Klemm (1962) in seven of his eight samples as mainly twin lamellae after (100) and (111) [?], often as zone structure, and occasionally as grains.

Discussion

Table I contains the geographic locations and collection numbers of cobaltite, gersdorffite, and ullmannite materials together with their cell sizes, which were determined from Debye-Scherrer photographs using the function of Nelson and Riley (1945).

The similar cell sizes and the semi-quantitative emission spectrographic analyses for cobaltite given in table I indicate little deviation from stoichiometric CoAsS. No compositional zoning for cobaltite was observed, as shown in table I, either optically in oil after etching with 10N HNO₃ or from X-ray diffraction powder data. Twinning occurs extensively in all cobaltites and a well-developed brecciated texture occurs in a few specimens. The mineralogical association as given in table I shows that cobaltite commonly occurs with quartz, mica, and chlorite, and the cobaltite with the largest unit cell size also occurs with safflorite.

The cell sizes of gersdorffite are similar to the cell size of 5.594 Å for synthetic stoichiometric NiAsS of Yund (1962). The two exceptions are Cobalt (BM 1922, 145) material with a Ni_{0.4}Co_{0.6}AsS composition and Sudbury (USNM R830) material with a Ni_{0.4}Co_{0.3}Fe_{0.3}AsS composition, which were determined from their cell sizes upon the diagram of Klemm (1965) and their semi-quantitative emission spectrographic data in table I. In most of these gersdorffites zoning was observed optically in oil as shown in table I, although it was detected in only four of these fourteen gersdorffites by powder X-ray diffraction. No correlation was found between optical and powder X-ray diffraction zoning results. The large 0.09 Å unit cell difference, the strong variation in optical properties, and the interstitial texture indicate that material from

TABLE I. *Semi-quantitative spectrographic analyses (in %), unit cell, optical anisotropy for natural samples of cobaltite, gersdorffite, and ullmannite; also end-*

| Cobaltite | Location | Ni | Co | Fe | Sb | As | S | Si | <i>a</i> Å |
|---------------------|--|-------|-----|-----|-----|-------|----|-----|-----------------------------------|
| CoAsS | Theoretical | — | 36 | — | — | 45 | 19 | — | — |
| UNSW 362 | N.S.W., Australia | 2 | 30 | 4 | nil | 40 | — | 0.4 | 5.5766 (3) |
| UNSW 361 | Cloncurry, Qld., Australia | — | — | — | — | — | — | — | 5.577 (2) |
| UNSW 61 | Bimbowrie, S.A., Australia | 1 | 30 | 4 | nil | 40 | — | 2 | 5.5780 (5) |
| UNSW 233 | Torrington, N.S.W., Australia | — | — | — | — | — | — | — | 5.5790 (5) |
| AM D24919 | Mt. Cobalt, Qld., Australia | — | — | — | — | — | — | — | 5.579 (2) |
| UNSW | S. Broken Hill, N.S.W., Australia | — | — | — | — | — | — | — | 5.581 (1) |
| Gersdorffite | | | | | | | | | |
| NiAsS | Theoretical | 36 | — | — | — | 45 | 19 | — | — |
| USNM R830 | Sudbury, Ontario, Canada | { 25 | 10 | 10 | nil | 40 | — | 1 | 5.616 (1) |
| BM 1917, 285 | | { — | — | — | — | — | — | — | { 5.628 (3) 90 % 5.68 (1) 10 % |
| BM 1922, 145 | Cobalt, Ontario, Canada | { 20 | 15 | 1 | nil | 50 | — | 0.3 | 5.63 (1) |
| AM D25174 | | { — | — | — | — | — | — | — | { 5.63 (1) 70 % 5.72 (1) 30 % |
| USNM R862 | (amoibite) Leichtenberg, Fichtelgebirge, Germany | 25-30 | 2 | 4 | 1 | 40 | — | 0.3 | 5.6849 (3) |
| BM 1929, 12 | Mitterburg, Salzburg, Austria | — | — | — | — | — | — | — | 5.6870 (8) |
| HMM | Wolfsberg, Harz, Germany | 25-30 | 2 | 1 | 1 | 40 | — | 2 | 5.6885 (3) |
| HMM | Hager a.d. Dill, Germany | — | — | — | — | — | — | — | { 5.693 (1) 70 % 5.68 (1) 30 % |
| BM 1434 | Musen, Westphalia, Germany | — | — | — | — | — | — | — | 5.694 (1) |
| BM 57562 | Lobenstein, Russ, Germany | — | — | — | — | — | — | — | 5.6941 (5) |
| USNM D650 | (dobschauite) Dobschau, Hungary* | — | — | — | — | — | — | — | { 5.69 (1) 40 % 5.72 (1) 60 % |
| BM 1933, 371 | Farvic Mine, Gwanda, Rhodesia | — | — | — | — | — | — | — | 5.6957 (5) |
| BM 1959, 462 | Cochabamba, Bolivia | — | — | — | — | — | — | — | 5.696 (1) |
| UNSW | Ferro, Slovakia | 25-30 | 2 | 6 | 1 | 40 | — | 0.2 | 5.7053 (3) |
| Ullmannite | | | | | | | | | |
| NiSbS | Theoretical | 28 | — | — | 57 | — | 15 | — | — |
| BM 69114 | Harzgerode, Harz Mts., Germany | 25-30 | 0.5 | 1 | >30 | 20-30 | — | 0.3 | 5.876 (1) |
| AM D9984 | Petersbach, Siegen, Germany | — | — | — | — | — | — | — | 5.894 (1) |
| AM D17751 | (willyamite) Broken Hill, N.S.W. | { 4 | 10 | 0.5 | 50 | 1 | — | — | 5.9203 (5) |
| AM D27860 | | { — | — | — | — | — | — | — | 5.9203 (5) |

* Now Dobšiná, Slovakia.

Cobalt (AM D25174) has two distinct minerals rather than zoning. The 0.03 Å unit cell difference in material from Dobschau (USNM D650) indicates a substantial composition variation, which agrees with the data of Goll (1937). The 0.01 Å unit cell difference in materials from Hager (HMM) and Sudbury (BM 1917, 285) indicates minor compositional variations. Differences up to 0.02 Å can be masked in poorly crystalline samples. Zoning frequently occurs in patches, often as a mottled pattern or in broad bands, and occasionally in concentric zones with both sharp and gradual boundaries. Zoning is expressed optically as a colour change from lilac-yellow (occasionally isotropic) to yellow (anisotropic). Twinning occurs in the gersdorffite from Leichtenberg and also occasionally in the gersdorffite from Lobenstein. The mineralogical association is given in table I. Gersdorffites with small cell sizes

tropism, X-ray diffraction powder intensities of hkl reflections, zoning, and mineralogical member composition. Numbers in parentheses represent probable error in last figure

| Aniso-tropy | | | | | | | | | | | Zoning | Associated minerals |
|-------------|-----|-----|-----|-----|-----|-----|-----|------------|-----|-----|--------|--|
| | 100 | 110 | 111 | 200 | 210 | 211 | 220 | 300 221 | 310 | 311 | | |
| strong | 50 | 5 | 5 | 100 | 50 | 20 | 8 | 10 | 1 | 50 | nil | |
| strong | 50 | 5 | 5 | 100 | 90 | 40 | 15 | 3 | 1 | 40 | nil | quartz |
| medium | 10 | 2 | 5 | 80 | 80 | 80 | 20 | 5 | 2 | 100 | nil | quartz |
| strong | 50 | 4 | 2 | 100 | 20 | 20 | 5 | 2 | 1 | 50 | nil | quartz, mica, chlorite |
| strong | 20 | 5 | 2 | 100 | 50 | 50 | 10 | 5 | 2 | 20 | nil | quartz |
| medium | 10 | 5 | 20 | 80 | 100 | 80 | 20 | 2 | 2 | 20 | nil | safflorite, quartz, mica, chlorite |
| medium | 10 | 5 | 10 | 100 | 75 | 80 | 15 | 1 | 3 | 75 | — | pyrrhotine, calcite |
| nil | — | 0 | 0 | 100 | 35 | 30 | 10 | 1 | 1 | 15 | medium | nickeline, chalcopyrite, pyrite, pyrrhotine, chlorite, magnetite |
| weak | 6 | 3 | 6 | 90 | 100 | 90 | 30 | 1 | 1 | 40 | medium | calcite |
| weak | 0 | 0 | 0 | 55 | 100 | 70 | 30 | 1 | 15 | 35 | strong | skutterudite, sphalerite, siderite, calcite |
| medium | 11 | 2 | 5 | 100 | 70 | 35 | 10 | 1 | 1 | 35 | medium | pyrite |
| weak | 1 | 9 | 2 | 100 | 50 | 25 | 9 | 1 | 8 | 30 | strong | skutterudite, dolomite |
| weak | 0 | 6 | 3 | 35 | 100 | 75 | 10 | 3 | 2 | 25 | — | chalcopyrite, pyrrhotine, calcite, quartz |
| weak | 3 | 10 | 6 | 80 | 100 | 60 | 20 | 3 | 3 | 60 | medium | pyrrhotine, galena, quartz |
| v. weak | 0 | 8 | 4 | 100 | 65 | 60 | 20 | 1 | 7 | 30 | medium | jamesonite, siderite |
| weak | 2 | 4 | 2 | 100 | 55 | 20 | 25 | 1 | 3 | 50 | medium | sphalerite, siderite |
| nil | — | — | 1 | 30 | 100 | 60 | 10 | 0 | — | 40 | weak | skutterudite, safflorite |
| nil | — | — | 1 | 35 | 45 | 100 | 15 | 1 | — | 70 | weak | siderite, quartz |
| nil | — | 7 | 4 | 75 | 75 | 45 | 20 | 1 | 1 | 100 | nil | safflorite, sphalerite |
| nil | — | — | 0 | 90 | 100 | 55 | 30 | 0 | — | 50 | strong | siderite, quartz |
| weak | — | 20 | 5 | 50 | 100 | 50 | 10 | 0 | 5 | 20 | medium | pendlandite, chalcopyrite |
| nil | — | 20 | 10 | 80 | 100 | 20 | 8 | 0 | 10 | 50 | nil | pyrrhotine, galena, quartz |
| weak | — | 50 | 8 | 80 | 100 | 50 | 10 | 1 | 10 | 50 | nil | chalcopyrite, tetrahedrite |
| nil | — | 20 | 8 | 20 | 100 | 50 | 20 | 1 | 8 | 50 | nil | |

commonly occur with calcite and sulphides such as pyrite and pyrrhotine. Gersdorffites with large unit cell sizes commonly occur with siderite and arsenides such as skutterudite and safflorite. Ubiquitous cobalt and iron occurs in most arsenic-rich environments, so the absence of arsenic-rich gersdorffite in nature is attributed to the formation of nickel-rich skutterudite. Synthetic skutterudite is described by Roseboom (1962). Of these accessory minerals, only siderite, which decomposes in carbon dioxide at 500 °C, indicates any limitation to formation temperature.

A wide composition range is indicated for ullmannite by the cell sizes and semi-quantitative emission spectrographic analyses in table I. This deviation from a NiSbS composition occurs by arsenic substitution for antimony in BM 69114 to NiSb_{0.7}As_{0.3}S and by cobalt substitution for nickel in AM D17751. Distinct zoning as shown in

table I was observed only in one polished section of ullmannite (BM 69114), where one phase is distinctly harder than the other.

The X-ray diffraction powder reflection intensities are recorded in table I for cobaltite, gersdorffite, and ullmannite. Since the indices and the d -spacings of a cubic mineral are easily calculated from its cell edge, only a single row of hkl reflections are tabulated. The three crystal structure types may be related to the presence of 001 and 011 reflections. The absence of both reflections 001 and 011 indicates a cubic structure with disordered non-metal atoms, for example Pa_3 cobaltite heated to 850 °C by Giese and Kerr (1965) and Pa_3 gersdorffite (UNSW) by Bayliss (1968). The absence of 001 reflection and presence of 011 reflection indicates a cubic structure with ordered non-metal atoms, for example, P_{213} gersdorffite (HMM, Wolfsberg) by Bayliss and Stephenson (1967) and P_{213} ullmannite by Takeuchi (1957). The presence of both 001 and 011 reflections indicates a non-cubic structure, for example, Pca_2_1 cobaltite by Giese and Kerr (1965) and $P1$ gersdorffite (USNM R862) by Bayliss and Stephenson (1968) with either ordered or disordered non-metal atoms.

The 001 reflection intensity is positively correlated with the optical anisotropism; both are given in table I. Both the 001 reflection intensity and the optical anisotropism strength are related to the distortion of the crystal structure from cubic symmetry caused by movement of the metal atoms off the three-fold axis. The weak optical anisotropism found in gersdorffite and ullmannite without detection of reflection 001 is interpreted as minor structure distortion below the level detectable by X-ray diffraction, provided that optical anisotropism is not caused during the polishing process (Gibbons, 1967).

Optical anisotropism is related approximately to the cell size. Materials with strong optical anisotropism have small cell sizes (cobaltite), materials with medium optical anisotropism have medium cell sizes (cobaltite and gersdorffite), materials with weak optical anisotropism have large cell sizes (gersdorffite and ullmannite), and optically isotropic materials have very large cell sizes (gersdorffite and ullmannite). The cell size is quantitatively related to composition as shown by Klemm (1965), where the cell size decreases with substitution of cobalt for nickel.

Thermal stability experimental results are presented in table II. The time dependence of reflection intensity changes is shown by cobaltite UNSW 233, where the 001 reflection intensity has gradually decreased in fourteen weeks at 700 °C to the stage reached after one week at 825 °C. After heating non-cubic gersdorffite ($P1$) samples to 600 °C, samples with large cell sizes had lost both reflections, samples with intermediate cell sizes had lost one reflection, and samples with medium cell sizes were unaffected. Similarly, after heating cobaltite (Pca_2_1) samples to 840 °C, samples with medium cell sizes had lost both reflections, samples with intermediate cell sizes were partially affected, and samples with small cell sizes were unaffected. This data indicates that the temperature at which the crystal-structure distortion release occurs (non-cubic to cubic structure change), which is interpreted from the disappearance of reflections 001 and 011, is quantitatively related to the cell size and hence to the chemical composition. Therefore the substitution of cobalt for nickel increases the thermal stability of the non-cubic distorted structure.

These thermal stability experiments also indicate order-disorder changes. The cubic gersdorffite ($P2_13$) with ordered non-metal atoms loses its 011 reflection when heated, which indicates an order-disorder change. In non-cubic gersdorffite ($P1$) with large cell size the structure distortion release occurs at a lower temperature than the order-disorder change. In cobaltite ($Pca2_1$) and in non-cubic gersdorffite ($P1$) with a small cell size the crystal structure distortion release occurs at a higher temperature,

TABLE II. Unit cell data and X-ray diffraction powder intensities for gersdorffite and cobaltite natural samples heated to various temperatures

| Cobaltite | a | 001 | 011 | Temp. | Time weeks | Gersdorffite | a | 001 | 011 | Temp. | Time weeks |
|-----------|---------|---|--|---|-----------------------------|--------------|---------|--|--|---------------------------|------------------|
| UNSW 361 | 5.577 Å | $\begin{cases} 50 \\ 25 \\ 8 \end{cases}$ | $\begin{cases} 5 \\ 1 \\ 1 \end{cases}$ | Room 825 °C 850 | — 1 1 | BM 1922, 145 | 5.633 Å | $\begin{cases} 6 \\ 6 \\ 2 \end{cases}$ | $\begin{cases} 3 \\ 3 \\ 2 \end{cases}$ | Room 550 °C 600 | — 1 1 |
| UNSW 362 | 5.577 | $\begin{cases} 50 \\ 10 \\ 3 \end{cases}$ | $\begin{cases} 5 \\ 5 \\ 0 \end{cases}$ | Room 825 850 | — 1 1 | USNM R862 | 5.685 | $\begin{cases} 8 \\ 3 \\ 2 \\ 0 \end{cases}$ | $\begin{cases} 2 \\ 1 \\ 0 \\ 0 \end{cases}$ | Room 550 600 550 | — 1 1 4 |
| UNSW 233 | 5.579 | $\begin{cases} 50 \\ 40 \\ 20 \\ 10 \\ 10 \\ 4 \end{cases}$ | $\begin{cases} 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 0 \end{cases}$ | Room 700 700 700 825 850 | — 2 4 14 1 1 | BM 57562 | 5.694 | $\begin{cases} 2 \\ 0 \\ 0 \end{cases}$ | $\begin{cases} 4 \\ 3 \\ 0 \end{cases}$ | Room 550 600 | — 1 1 |
| UNSW | 5.581 | $\begin{cases} 10 \\ 2 \\ 0 \end{cases}$ | $\begin{cases} 5 \\ 0 \\ 0 \end{cases}$ | Room 825 850 | — 1 1 | BM 1434 | 5.694 | $\begin{cases} 0 \\ — \\ — \end{cases}$ | $\begin{cases} 8 \\ 8 \\ 0 \end{cases}$ | Room 550 600 | — 1 1 |
| | | | | | | BM 1959, 462 | 5.696 | $\begin{cases} — \\ — \\ — \end{cases}$ | $\begin{cases} 7 \\ 6 \\ 0 \end{cases}$ | Room 550 600 | — 1 1 |

which appears to be after the order-disorder change. These crystal structure results are presented in fig. 1 diagrammatically, because exact reaction temperatures were not obtained due to sluggish transformations.

No change was noticed in the powder X-ray diffraction reflection intensities of ullmannite ($P2_13$) upon heating before its decomposition at 710 ± 5 °C. Ullmannite does not change into a structure with the non-metal atoms disordered ($Pa3$), because the atomic sizes of sulphur and antimony are greatly different.

Heating experiments were also undertaken on glaucodot (Co,Fe)AsS since it is considered a metastable form in relation to cobaltite by Klemm (1965) from his FeAsS-CoAsS-NiAsS ternary diagram results. Glaucodot from Hakansbo was determined by Ferguson (1947) to be orthorhombic $Cmmm$, but later Klemm (1965) redetermined it as monoclinic $P2_1/c$, the space group used for arsenopyrite by Morimoto and Clark (1961). The heating experiments in this study showed the partial conversion of glaucodot to cobaltite after 1 month at 630 ± 20 °C.

Optical anisotropy in pyrite has been discussed by Gibbons (1967). The distortions in the octahedral and tetrahedral angles of pyrite are similar to those of gersdorffite. Therefore the optical anisotropy in pyrite may result from a non-cubic structure in a similar manner to the optical anisotropy caused by the non-cubic structure of

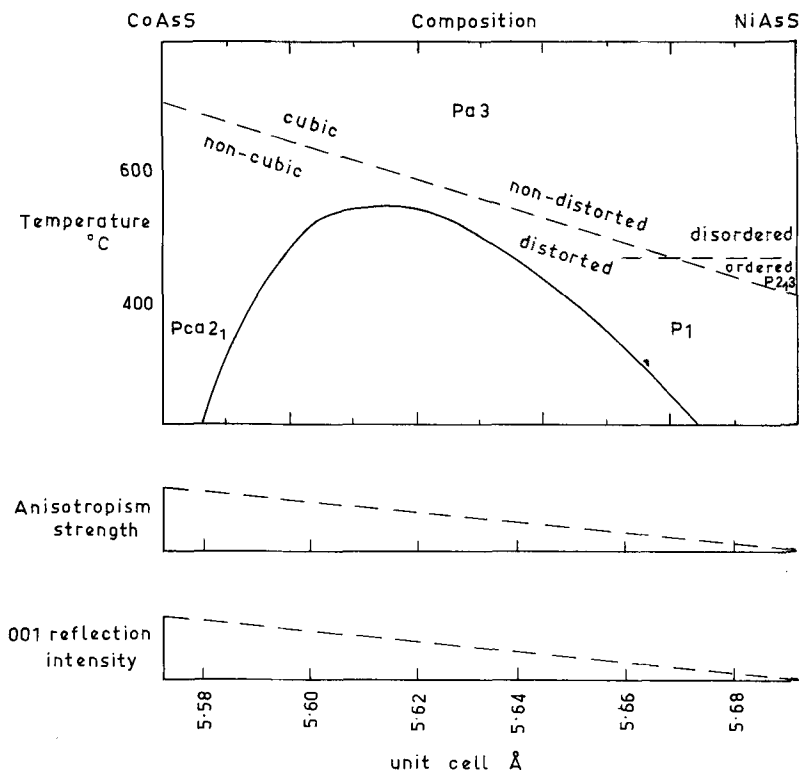


FIG. 1. Diagrammatic sketch to relate ordering and distortion in structure with composition, unit cell, and thermal stability, and their semi-quantitative relationship to anisotropy and 001 reflection intensity.

gersdorffite (*P1*). To investigate this possibility, eighteen pyrite samples taken from hydrothermal to sedimentary environments were examined. No trace of either 001 or 011 reflection was found in their X-ray diffraction powder patterns. However this non-cubic possibility remains since optical anisotropy appears to be a more sensitive detector of distortion than X-ray diffraction in the work on gersdorffite.

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