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ELECTRON MICROSCOPY STUDY OF TRANSITION METALS DISULFIDES WITH PYRITE STRUCTURE

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Résumé. — Les composés CuS_2 et NiS_x ($1,91 \leq x \leq 2,1$) ont été examinés par microscopie électronique afin de déterminer si les transitions magnétiques et électriques observées sont reliées à un changement de phase cristallographique. Pour CuS_2 , la transition magnétique à 160 K est liée à la formation d'une surstructure dont la nature est discutée. Dans les sulfures de nickel, par contre, il n'a pas été possible de mettre en évidence une quelconque influence de la stœchiométrie ou de la température (jusque ~ 130 K) sur la structure de ces composés.

Abstract. — The compounds CuS_2 and NiS_x ($1.91 \leq x \leq 2.1$) have been examined by electron microscopy in order to determine the correlation between magnetic/electrical transitions and possible crystallographic transformations. In CuS_2 the magnetic transition occurring at 160 K is found to be related to the formation of a crystallographic superstructure, the nature of which is discussed. In nickel disulfides, however, no influence is found of either stoichiometry or temperature (down to ~ 130 K) on the crystallographic structure.

1. Introduction. — During the last few years, the electrical and magnetic properties of transition metals disulfides with pyrite structure have been extensively studied, suggesting both in NiS_x [1, 2] and CuS_2 [3, 4] the possibility of structural modifications with either temperature or stoichiometry. This electron microscopy investigation is aimed at an experimental knowledge of these structures.

In CuS_2 the susceptibility becomes temperature dependent below $T_Q = 160$ K; correspondingly, the line width of the ^{63}Cu spectra increases strongly below T_Q (Fig. 1) and the copper quadrupolar spectrum is no longer resolved [3, 4]. It has been suggested that the transition might be a crystallographic one: Similar behaviour of the physical properties has been observed in some layered dichalcogenides (e. g. TaS_2 , TaSe_2 , NbS_2 , NbSe_2) [5, 6] where a superstructure resulting from the occurrence of a charge density wave has been detected by electron microscopy [7, 8, 9].

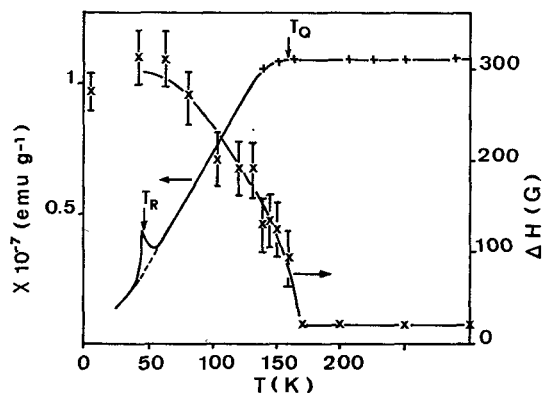
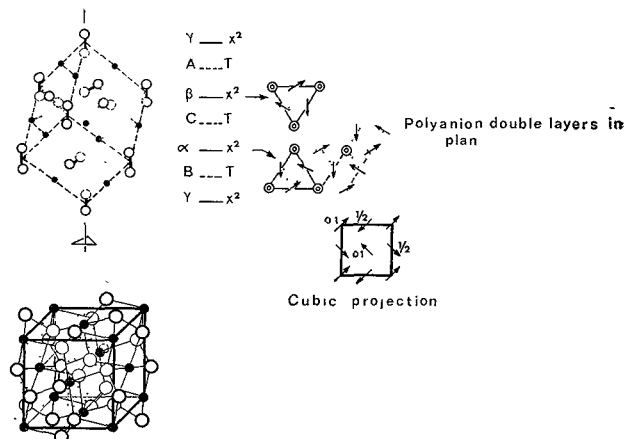


FIG. 1. — Temperature dependence of the bulk susceptibility (+) and ^{63}Cu NMR linewidth (x) in CuS_2 , after Krill *et al.* [4].

We show below that a superstructure is developed in CuS_2 below T_Q .

In NiS_x , the Ni vacancy concentration (up to 10 %) is correlated to a metal-insulator transition [1, 2] and the explanation of electrical resistivity and magnetic susceptibility suggested first the hypothesis of a two phase structure [2]. In contrast, we show below that both stoichiometry and temperature (down to 130 K) have no detectable influence on the crystal structure; that means that vacancies are not long range ordered, as it is confirmed in a recent Mössbauer spectroscopy study [10].

In the first part of this paper, we discuss of the crystallography of the pyrite structure and the corresponding possible electron diffraction patterns. The next part is devoted to the preparation of thin samples suitable for electron microscopy and the last section discuss the experimental results.



Standard cubic orientation

FIG. 2. — The pyrite structure, after Wilson and Yoffe [11].

2. **Crystallography.** — The pyrite structure is described figure 2. The cubic unit cell involves four cations at (000) , $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$ and eight anions at $\pm (uuu)$, $\pm (u + \frac{1}{2}, \frac{1}{2} - u, \bar{u})$, $\pm (\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u)$, $\pm (\frac{1}{2} - u, \bar{u}, u + \frac{1}{2})$. The lattice parameter a is between 5.5 and 6 Å and the value of u close to 0.4. So the structure can be described as follows [12] : starting from a rocksalt structure one places an anion pair upon each anion site and pulls these pairs apart along one of the body diagonals of the cube. In terms of the packing of (111) planes normal to one particular threefold axis of pyrite, this becomes... $A\gamma B\alpha C\beta A\gamma\dots$ with cations planes A, B, C, and S_2 pairs planes $\alpha, \beta, \gamma\dots$ From the cubic projection of figure 2, it can be seen that shear in a $\{001\}$ plane do not cut any S_2 pair. Therefore these planes are possible

glide planes of dislocations in these structures. This is compatible with the observation that $\{001\}$ planes are common cleavage planes in iron pyrite. Notice that dislocations with $\langle 100 \rangle$ Burgers vectors have been observed in Nickel pyrite [13].

Concerning the diffraction, structure factor calculations indicate that the following reflections are forbidden :

- $[hko]^*$ with h odd
- $[okl]^*$ with k odd
- $[hol]^*$ with l odd.

However some forbidden reflections can occur on the diffraction patterns ; this anomaly arises because of double diffraction effect (Fig. 3). So tilting experiments are needed in order to determine if extra spots are

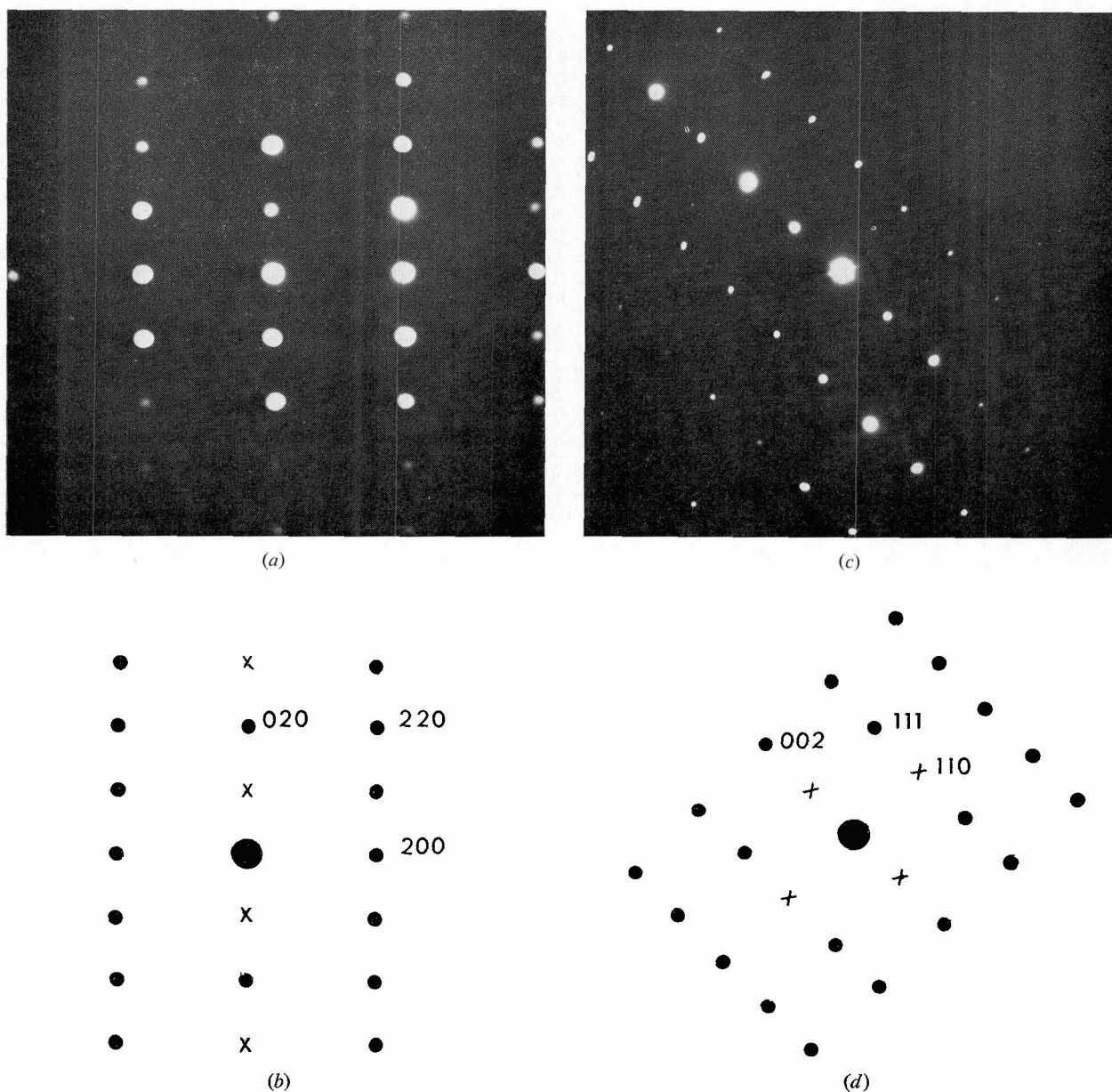


FIG. 3. — Double diffraction effect in diffraction patterns of $NiS_{1.94}$. a, b) $(001)^*$ section of reciprocal lattice ; c, d) $(110)^*$ section. Notice that (110) reflections do not appear on the (a) pattern ; they are due to double diffraction. \times double diffraction spots.

either superstructure spots or double diffractions spots. Notice that $[hko]^*$ reflections with h odd do not appear on the $(001)^*$ pattern, even by double diffraction (Fig. 3b).

3. Experimental methods. — The compounds NiS_x and CuS_2 are supplied by the Laboratoire de Structure Electronique des Solides de l'Université de Strasbourg. They are obtained by synthesis under very high pressure (65 kbar-1 000 °C). Typically the material is formed by slightly misoriented grains of size approximately $0.5 \mu m$ [13]. Classical methods (e. g. electro or chemical polishing; ion beam thinning) failed to produce in this case any reliable thin samples. Only a few observable foils of $NiS_{1.94}$ were obtained by electropolishing or ion beam thinning. Yet the energy of incident ions, in the last method, proved to be high enough to induce localized phase transformation $NiS_2 \rightarrow NiS$ and Ni_3S_2 within the sample (these phases are found only in ion beam thinned specimens, while the electropolished ones do not yield any evidences of them). These new phases have been identified both by systematic examinations of sections of reciprocal space and electron Debye-Scherrer pattern [13].

The specimens are examined in an electron microscope operating at 100 kV. The transformation $NiS_2 \rightarrow \beta NiS$ may also occur under the electron beam: it is apparent through the growth of small precipitates made visible by characteristic moiré pattern due to the small difference between interplanar distances of the two compounds (Fig. 4).

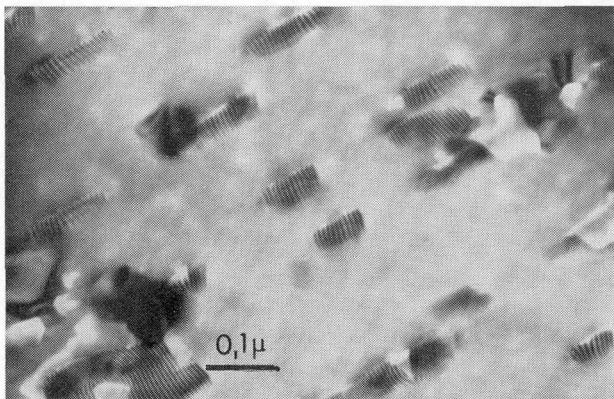


FIG. 4. — Moiré pattern due to the interference between $[020]_{pyrite}^*$ and $[0110]_{Nis}^*$ ($d_{020} = 2,84 \text{ \AA}$; $d_{0110} = 2,98 \text{ \AA}$).

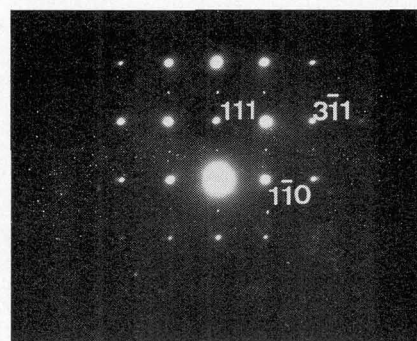
We expect that electron bombardment does not have any influence on the stoichiometry of samples having the pyrite structure, because the decrease of x in all the range $1.91 \leq x \leq 2.1$ is rather due to an increase of the Ni vacancy concentration, the S vacancy concentration being approximately constant [2].

Finally, sufficiently thin samples have been obtained by grinding and mouting the dispersed powder on carbon films.

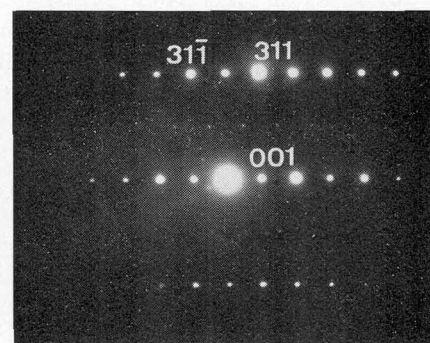
In order to determine the influence of temperature on structure, the samples have been mounted in a liquid nitrogen cooled stage. However some doubts arise on the true specimen temperature because of the poor thermal conductivity of the material.

4. Results. — The specimens are observed in order to determine either the presence of superstructures by means of microdiffraction techniques or the existence of structural defects due non stoichiometry.

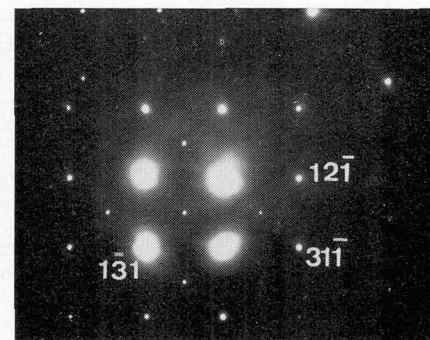
4.1 COPPER DISULFIDE. — When observing the specimen in the cold stage, a superstructure is present, characterized by new weak reflections $\langle 100 \rangle^*$, $\langle 110 \rangle^*$ and $\frac{1}{2} \langle 2m+1, 2n+1, 2p+1 \rangle^*$ with m, n, p integers (Fig. 5, 6). This transformation is reversible and the superstructure disappears by heating.



(a)



(b)



(c)

FIG. 5. — Superstructure appearing at low temperature in CuS_2 . a) $(11\bar{2})^*$ section; b) $(\bar{1}30)^*$ section; c) $(125)^*$ section. Notice the weak superstructure reflections $\frac{1}{2} \langle 2m+1, 2n+1, 2p+1 \rangle^*$.

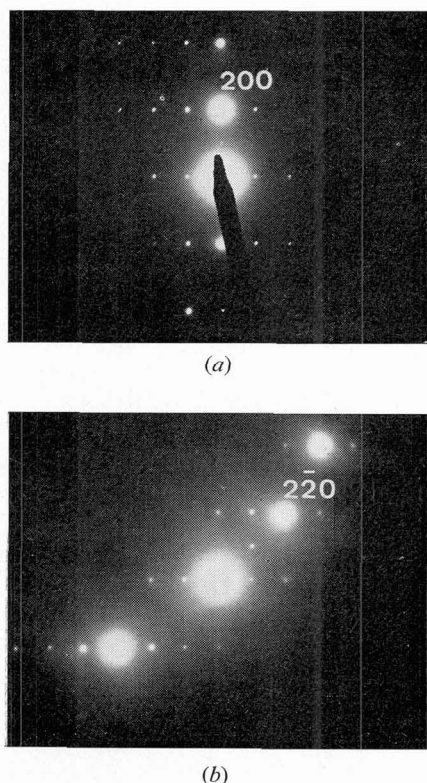


FIG. 6. — $(001)^*$ section of the low temperature phase of CuS_2 .

We ascertain that $[100]^*$ and $[\bar{1}\bar{1}0]^*$ reflections are not due to double diffraction effects by careful examination of the $(001)^*$ section of reciprocal space, in which $[100]^*$ and $[\bar{1}\bar{1}0]^*$ reflections of the pyrite structure cannot appear by double diffraction (Fig. 3a, b). Therefore the appearance of very weak $[100]^*$ and $[\bar{1}\bar{1}0]^*$ spots (Fig. 6) in this section proves they are due to a new phase. Notice that the intensity of these reflections is very weak and they appear only when the corresponding $[200]^*$ or $[2\bar{2}0]^*$ reflection is strongly excited.

The problem is now to determine more precisely the crystal structure of the low temperature phase. Because of the very low intensity of superstructure spots, it has not been possible to see by dark field imaging if there are or not domains in the crystal and therefore it has not been possible to determine if

the crystal symmetry of the low temperature phase is actually lower than that one of the pyrite. But we can affirm that at least one of the four body diagonals in the pyrite unit cell becomes twice as long due to the transition. This might stem from periodic lattice distortion connected with the formation of charge density waves $[\bar{4}]$. It can be argued, however, that the crystal system of the superstructure is quite probably no longer cubic: From the occurrence of reflections with reciprocal lattice vectors $\langle 100 \rangle^*$, $\langle 110 \rangle^*$ and $\frac{1}{2} \langle 2m+1, 2n+1, 2p+1 \rangle^*$, the lattice might be face-centred cubic with a parameter twice as long as the pyrite parameter. However, since the « ordered » phase must have a symmetry not higher than the « disordered » phase, the only compatible space groups would be $Fm\bar{3}$, $F23$ or $Fd\bar{3}$ (point group $m\bar{3}$). But the atomic positions in these groups are not simply related to atomic positions in the pyrite space group $Pa\bar{3}$. Therefore this superstructure has a lower symmetry and the four $\langle 111 \rangle$ directions in the pyrite cell are no longer equivalent. In terms of the packing of (111) planes normal to one particular $[111]$ threefold axis of pyrite ... $A\gamma B\alpha C\beta A\gamma$... (see section 2), it could be viewed as an alternate elongation, contraction or translation of the $[111]$ S_2 pairs every two sulphur planes, the $[111]$ pair axis being unchanged, giving rise to a new stacking sequence of twelve planes ... $A\gamma' B\alpha C\beta' A\gamma B\alpha' C\beta A\gamma'$...

4.2 NICKEL DISULFIDE. — A possible explanation of the changes of the properties of the compounds NiS_x ($1.91 \leq x \leq 2.1$) was given by the assumption [2] of the existence of a macroscopic two phase mixture, an insulating and a metallic one, with different magnetic properties. However we have not found any influence of stoichiometry and temperature (down to ~ 130 K) on the structure of these compounds. All the observed diffraction patterns belong to the same pyrite phase. We conclude therefore that there is no observable modification of the crystal structure, i. e. that Ni vacancies are not long range ordered. Notice that the results of a recent Mössbauer spectroscopy investigation contradicts as well the hypothesis of a two phase mixture. It is proposed instead a model of local inhomogeneities at an atomic scale, associated with vacancies on the nickel sublattice [10].

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