

LOW-TEMPERATURE REACTIONS USING POTASSIUM IRON DISULFIDE AS A PRECURSOR

N. ALLALI^a, J.F. FAVARD^a, M. RAMBAUD^b, A. GOLOUB^{a*}, and M. DANOT^a,

^a Laboratoire de Chimie des Solides, IMN, Unité Mixte CNRS-Université de Nantes, UMR 110, 2, rue de la Houssinière, 44072 Nantes-Cédex 03, France.

^b IUT de Lannion, Université de Rennes I, Rue Edouard Branly, BP 150, 22302 Lannion-Cédex, France.

* Permanent address : Institute of Organo-Element Compounds, 117813, Vavilov st. 28, Moscow, Russia.

(Received November 17, 1993; Communicated by P. Hagenmuller)

ABSTRACT

The chain structure of KFeS₂ allows exchange reactions to be performed. If potassium is replaced by calcium, the $[FeS_2]$ structural framework is retained so that this reaction can be considered as a Soft Chemistry process. It is not the case of the silver exchange which induces a change to a chalcopyrite structure. Potassium can be extracted from KFeS₂ but the obtained FeS₂ is pyrite. This drastic structural change precludes this reaction to be considered as a Soft Chemistry process.

MATERIALS INDEX : Potassium, Iron, Sulfides

Soft Chemistry, also known as "Chimie Douce", consists in low-temperature processes, in contrast with classical solid state chemistry for which high temperatures are required. These low-temperature processes allow new compounds to be obtained, which usually retain the structural framework of the precursor (1). Such a phenomenon can be illustrated by lithium intercalation into titanium disulfide (2). In this case, the intercalation proceeds without any structural modification of the host-structure : the [S-Ti-S] slabs and their stacking are kept unchanged since the $(AB)_n$ hexagonal close-packing is retained. If now the case of sodium intercalation into TiS₂ is considered, the [S-Ti-S] slabs still remain unchanged, but their packing is modified. Depending on the sodium amount, cubic close-packing $(ABC)_n$ or non-compact

136

N. ALLALI et al.

arrangement $(AABBCC)_n$ are so obtained (2). Despite these changes, the usual definition of Soft Chemistry is still obeyed, because the structural units of the host-structure, i.e. the [S-Ti-S] slabs, remain unchanged. A lot of similar examples could be found in intercalation, deintercalation, and ionic-exchange reactions. However, the structural framework of the precursor can sometimes be drastically changed through low-temperature processes such as deintercalation and cationic exchange, as it will here be shown on the example of potassium iron sulfide KFeS₂.

The historical background and the present study

1°) KFeS2

Potassium iron sulfide was first prepared in the late sixties by R. Schneider (3). The synthesis was performed by making red-hot the following mixture : sulfur, iron powder, and potassium carbonate, in the massic proportions 6/1/6. After washing with water, violet needles with the formula KFeS₂ were obtained.

The structure of KFeS₂ was established in 1942 by J.W. Boon and C.H. Mac Gillavry (4). Iron is tetrahedrally surrounded by sulfur, and every tetrahedron shares two opposite edges with its two neighbors so that $[FeS_2]_{\infty}$ chains are formed which run along the c-axis (fig. 1), according to a SiS₂ structural model (5). Potassium ions are located in large spaces between these chains. KFeS₂ can so be considered as a potassium-intercalated SiS₂-like structure and then, according to this picture, it appears to offer a good opportunity for deintercalation and ionic-exchange properties to be observed.



FIG. 1

Perspective view of the structure of KFeS₂ along the c-axis. Small, medium-sized, and large circles respectively represent iron, potassium, and sulfur.

2°) Exchange reactions using KFeS₂ as a precursor

In 1888 R. Schneider of course knew nothing whatever about this structural arrangement. However, he tried, and performed, some exchange reactions. For instance, with silver, he obtained a compound with the formula $AgFeS_2$ (6). Later, in 1944, J.W. Boon performed the same exchange reaction (7) on KFeS₂ single crystals. The needle-like shape of the

Vol. 29, No. 2

SULFIDES

crystals was retained through the exchange process which allowed a single-crystal diffraction study to be performed (rotation diagrams). From his diffraction data, J.W. Boon (7) deduced that $AgFeS_2$ likely belongs to the chalcopyrite (8) structural type. If starting from the $KFeS_2$ framework the chalcopyrite structure is obtained, it means that an important structural change has occured, especially concerning the iron positions (4, 7). In such a case this exchange reaction would not obey the usual definition of Soft Chemistry.

More recently H. Boller (9), also using KFeS₂ as the starting material, exchanged potassium with alkaline earth cations. For example, with calcium, he obtained a phase with the formula $(Ca_{0.50},xH_2O)FeS_2$. From the conservation of the *c* periodicity, he deduced that the [FeS₂] framework is retained. In that case the exchange reaction could be considered as a Soft Chemistry process.

3°) The present work

Due to the one-dimensionnal character of KFeS₂, its X-Ray diffraction-diagrams are far from being excellent. Moreover, the crystallites are severely damaged during the exchange reactions. The structural conclusions of J.W. Boon (7) and H. Boller (9) were thus drawn from poor-quality spectra. Mössbauer spectroscopy appears as a convenient technique for additional structural information to be obtained concerning exchanged compounds prepared from KFeS₂. Here is the reason for which the present Mössbauer study was undertaken, on AgFeS₂ and $(Ca_{0.50},xH_2O)FeS_2$.

To our knowledge, nothing has been reported about the deintercalation of potassium from KFeS₂. We attempted to do it with the hope of a new FeS_2 to be obtained, with the SiS_2 structure i.e. without the KFeS₂ chain arrangement to be broken.

Experimental

For the present work, KFeS₂ was prepared nearly in the same way as indicated by R. Schneider (3), but starting from a slightly different mixture : sulfur, iron powder, potassium carbonate, and sodium carbonate, in the massic proportions 6/1/5/1. The reaction was performed at 900°C, under an inert atmosphere, according to ref.(10). X-Ray diagrams were obtained from an INEL curved detector and CuK α 1 radiation. The observed lines are consistent with the reported unit-cell (4), but they are not very numerous due to the poor-quality of the diffraction patterns. Elemental X-Ray microanalysis gives atomic percents in good agreement with the expected formula (K : 25.0%, Fe : 25.5%, S : 49.5%).

The exchange reaction with silver was carried out as previously reported (6, 7), by reaction of a silver nitrate solution (0.4 M) on the KFeS₂ powder. Due to the oxidizing character of the nitrate ion, the reaction time was chosen short (half an hour) to limit the risk of an oxidation of the solid.

As for the Ca²⁺ exchange it was performed, as indicated by H. Boller (9), allowing KFeS₂ to react with a calcium chloride solution (0.3 M), at 45°C, for 12 hours.

After these reactions, the extracted potassium-amount was determined in the solution, using atomic absorption spectrophotometry. In both cases, it was found to correspond within 1-2% to the quantity of potassium initially present in the powder.

N. ALLALI et al.

Attempts to deintercalate potassium were made using classical oxidizing treatments, with iodine or ferric chloride solutions in acetonitrile.

For reasons which will be indicated below, we tried to perform exchange reactions with the ammonium ion. For that purpose, we first used ammonium chloride solutions, and then we heated $KFeS_2 + NH_4Cl$ mixtures in evacuated pyrex tubes, at temperatures ranging from 100°C to 350°C.

⁵⁷Fe Mössbauer measurements were performed at room and liquid nitrogen temperatures with a INEL spectrometer using a symmetrical saw-tooth vibrator. The 14.4 keV gamma-rays were supplied by a 10 mCi ⁵⁷Co/Rh source. The hyperfine parameters were refined with the aid of a least-square program written by F. Varret and J. Teillet (Université du Maine, Le Mans) and adapted by J.M. Barbet for a PC use. This program uses lorentzian line-shapes and constrains the intensities of a magnetic spectrum to be proportional to 3/2/1/1/2/3. Metallic iron spectra at room temperature were used for the velocity scale calibration. For these spectra, the half-width at half-height (Γ) refines to 0.12 mm/s, which will be considered as the experimental line-width of the device. The isomer shift values will refer to metallic iron at 300 K.

The Mössbauer parameters of our KFeS₂ starting compound are in good agreement with what previously reported (isomer shift $\delta = 0.19$ mm/s, quadrupole splitting $\Delta = 0.49$ mm/s (11)). Effectively our refined values are as follows :

 $\delta = 0.18 \pm 0.02$ mm/s, and $\Delta = 0.50 \pm 0.02$ mm/s.

No important line-broadening can be detected ($\Gamma = 0.14 \pm 0.01$ mm/s).

The silver and calcium Exchanges

1°) The silver exchange

The obtained silver-exchanged compound allows only poor-quality X-ray diffraction diagrams to be recorded because, as indicated above, the crystallites are severely damaged by the exchange reaction. Only some weak and broad lines can be observed, which are consistent with the cell-parameters (a = 5.66 Å and c = 10.30 Å) reported by J.W. Boon (7) for a chalcopyrite-like structure.

The Mössbauer spectrum (fig. 2) exhibits two components : a quadrupolar doublet and a magnetic sextuplet with slightly asymmetric lines. Despite the non-exactly lorentzian line-shape, the magnetic diagram can be correctly reproduced, with the following hyperfine parameters :

 $\delta = 0.21 \pm 0.02$ mm/s, $\Delta = 0.00 \pm 0.02$ mm/s, H = 37.2 ± 0.5 T.

The line-width refines to 0.17 mm/s, which is slightly larger than the experimental value (0.12 mm/s). This observation, along with the slight line asymmetry, can be related to the structural damages occuring during the exchange.

As for the central doublet, it can be due to the smallest particles resulting from the splitting of the crystallites during reaction. Some oxidized small particles (12) could also contribute to this part of the spectrum.



For both spectra, the experimental and calculated spectra are respectively represented by the crosses and the line.

2°) The calcium exchange

As in the case of the silver compound, the diffraction diagram is of poor quality. The (few) observed lines are in agreement with the tetragonal unit-cell (a = 11.31 Å, c = 5.46 Å) reported by H. Boller (9).

The Mössbauer spectrum (fig. 3) is a paramagnetic doublet with $\delta = 0.16 \pm 0.02$ mm/s, $\Delta = 0.43 \pm 0.02$ mm/s, and $\Gamma = 0.12 \pm 0.02$ mm/s. No magnetic component can be detected.

140

N. ALLALI et al.

3°) Discussion

- In KFeS₂ the intrachain Fe-Fe distance is 2.70 Å while the interchain one amounts to 6.43 Å which indicates that essentially one-dimensional Fe-Fe spin interactions (13) can be expected. Effectively, KFeS₂ exhibits magnetic properties typical of a one-dimensional behavior (14). The Mössbauer results are consistent with this 1-D character : the room-temperature spectrum is non-magnetic (15), due to the low ordering-temperature, and the saturation hyperfine field (16) is rather weak (23.7 T).

- On the contrary, for natural or synthetic chalcopyrites $CuFeS_2$, the Mössbauer spectrum is magnetic at room temperature. The reported values for the RT field range from 32.5 to 35.6 T depending on the considered sample. For a sample we prepared from the elements, we found 35.2 T. The RT hyperfine field at the iron nucleus can be considered to represent nearly the saturation value due to the high (>700 K) ordering-temperature (17,18). It means that the saturation field is much higher than in the case of KFeS₂. The values of the ordering-temperature and of the saturation field denote for CuFeS₂ the existence of strong three-dimensional magnetic interactions as it can be expected considering the structural 3-D character.

- For the calcium-exchanged compound, the RT Mössbauer spectrum is nonmagnetic (and closely resembles that of KFeS₂). This is in agreement with the conservation of the 1-D iron arrangement, which was suggested by the reported 5.46 Å periodicity (9) similar to the 5.40 Å c parameter of KFeS₂ (4). The calcium exchange-reaction retains the structural framework of the initial compound and thus obeys the definition of Soft Chemistry.

- For our AgFeS₂ compound obtained from KFeS₂ by cationic exchange, the hyperfine field is 37.2 T at room temperature and 38.6 T at 78 K. The closeness of these two values indicates that the ordering-temperature is high. Besides, these fields are close by that of chalcopyrite CuFeS₂. For that two reasons it clearly appears that J.W. Boon (7) was right : AgFeS₂ effectively belongs to the chalcopyrite structural type.

- The Ag/K exchange induces an important change of the pristine structural framework since the KFeS₂--> chalcopyrite transformation requires the migration of every second iron atom (7), which means that the chain arrangement of iron is not retained. Despite the fact that this exchange is performed at room-temperature it cannot be considered as a Soft Chemistry process.

- The so-obtained AgFeS₂ is not thermally stable. Under vacuum, annealing at only 150°C is sufficient for the exchanged compound to decompose, as indicated by the presence of the diffraction lines of Ag_2S in the X-ray patterns. For that reason, it is impossible to measure the magnetic-ordering temperature, since the compound decomposes before the magnetic order vanishes. For the same reason, the diffraction diagram quality cannot be improved by annealing which prevents unambiguous evidence for the chalcopyrite structure to be obtained from diffraction data. However, the Mössbauer results are clear enough about that.

Potassium deintercalation

Attempts to deintercalate potasssium from $KFeS_2$ were performed with the aim to obtain a new FeS_2 variety with the SiS_2 chain-structure. Such a compound should be of interest because of the original magnetic properties to be expected. However the oxidizing agents we

Vol. 29, No. 2

SULFIDES

used (iodine and ferric chloride, both in acetonitrile solutions) did not allow any deintercalation reaction to be evidenced.

We then imagined another route for our aim to be reached. The first step was an ammonium-potassium exchange for $(NH_4)FeS_2$ to be obtained. Such a compound should not be thermally very stable, and should be decomposed (second step) by a gentle heating with possibly formation of the SiS₂-like FeS₂ we wished to prepare. We first tried to perform the NH₄+/K⁺ exchange at room temperature using ammonium chloride solutions, but whatever their concentration no significant exchange occured. We then increased the temperature up to 200°C, using a high pressure vessel. In these conditions, after 12 hours, a reaction is observed and FeS₂ is obtained but not with the KFeS₂ structural framework : the prepared compound is unambiguously pyrite, as shown by the X-Ray pattern and Mössbauer spectrum. Another attempt was done : KFeS₂ and NH₄Cl powder were introduced (without water) in a pyrex tube which was evacuated and sealed. After heating 12 hours at 150°C, pyrite formation was also evidenced. A lot of other experiments were carried out, using as the reactant anhydrous ammonium chloride or aqueous solutions of various concentrations, and varying the temperature and the duration of the treatment, but never could be isolated the expected intermediate NH₄FeS₂. When a reaction occurs, it results in the formation of pyrite.

Such a reaction could be considered as a deintercalation because potassium is removed. However, despite the low-temperature reaction (150°C), the transition from KFeS₂ to pyrite FeS₂ does not obey the definition of Soft Chemistry since no simple relation exists between the two structures : the sulfur surrounding geometries are different and the iron arrangement shifts from uni-dimensional (1-D KFeS₂) to three-dimensional (3-D pyrite).

Besides, the electronic mechanism of this "deintercalation" is rather unusual. The removal of an alkali ion results in the oxidation of the host-structure, which is usually realized by oxidation of the cation, or the anion, or both. In the present case, the oxidation of iron to the +IV state does not occur, which is not surprizing in a sulfide, and as could be expected, the anion is oxidized to the -I state, as sulfur pairs $(S_2)^{-II}$. This oxidation could have concerned every second sulfur atom, so that the +III state of iron in KFeS₂ could have been retained in the obtained FeS₂. However, a better stability is reached with complete oxidation of sulfur to the -I state and concomitant reduction of iron to the ferrous state. Per formula unit, one sulfur is oxidized due to potassium removal and the other due to iron reduction. What is unusual in this mechanism is that the global oxidation of the matrix involves the reduction of the cation, which results from an internal electron transfer.

Conclusion

The three studied reactions could at first sight be considered as Soft Chemistry processes.

- It is effectively the case for the calcium exchange, for which the structural framework can be retained because the sulfur-sulfur inter-chain repulsions remain weak due to the presence of large $[Ca^{2+},xH_2O]$ species between the chains.

- It is not the case for potassium removal because it results in the obtention of a completely different structure. For that reason, the expression "potassium removal" has to be preferred to "potassium deintercalation". If real deintercalation had been obtained, sulfur-sulfur

N. ALLALI et al.

inter-chain repulsions would have been very important due to the absence of screening. Here can be found a reason for the structural rearrangement we observed.

- Lastly it is neither the case for the silver exchange because every second iron atom is displaced to a new position. Moreover, for this reaction, the denomination "*ionic* exchange" is questionable because it is not a purely ionic process. Effectively, the potassium ion is replaced in the solid lattice by silver which establishes essentially covalent bonds with its tetrahedral sulfur surrounding.

If no change had occured concerning the iron sublattice, two types of tetrahedra chains would have been obtained, half of them containing only iron and the others only silver. Such an arrangement would have resulted in structural strains due to the size difference between the two metal atoms. In fact, another kind of order is preferred with an alternate distribution of the two metals in each of the chains, which allows these strains to be reduced.

References

- 1. A.R. West, in Solid State Chemistry and its Applications, John Wiley and sons Ed., 1986, p.30.
- 2. J. Bichon, M. Danot, et J. Rouxel, C. R. Acad. Sc. 276, 1283 (1973)
- 3. R. Schneider, Ann. Physik, 136, 460 (1869).
- 4. J.W. Boon and C.H. Mac Gillavry, Rec. Trav. Chim., 61, 910 (1942).
- 5. W. Büssem, H. Fischer, and E. Grüner, Naturwissenschaften, 23, 740 (1935).
- 6. R. Schneider, J. Prakt. Chem., 38 (2), 569 (1888).
- 7. J.W. Boon, Rec. Trav. Chim., 63, 69 (1944).
- 8. L. Pauling and L.O. Brockway, Z. Krist., 82, 188 (1932).
- 9. H. Boller, Monatsch. Chem., 109, 975 (1978).
- 10. G. Brauer, in Handbook of Preparative Inorganic Chemistry, N.Y., 1965, p. 1507.
- 11. D. Raj and S.P. Puri, J. Chem. Phys., 50 (8), 3184 (1969).
- 12. W. Kündig, H. Bömmel, G. Constabaris, and R.H. Lindquist, Phys. Rev., 142 (2), 327 (1966).
- 13. M. Nishi and Y. Ito, Solid State Commun., 30, 571 (1979).
- A. Mauger, M. Escorne, C.A. Taft, N.C. Furtado, Z.P. Arguello, T.P. Arsenio, Phys. Rev. B, 30 (9), 5300 (1984).
- 15. W. Kerler, W. Neuwirth, E. Fluck, P. Kuhn, and B. Zimmermann, Z. Physik, **173**, 321 (1963).
- 16. J. Zink and K. Nagorny, J. Phys. Chem. Solids, 49 (12), 1429 (1988).
- 17. H.N. Ok and C.S. Kim, Il Nuovo Cimento, 28, (1), 138 (1975).
- 18. J.B. Goodenough and G.A. Fatseas, J. Solid State Chem., 41, 1 (1982).