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HIGH PRESSURE POLYMORPHISM OF SPINEL COMPOUNDS

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By means of high pressure-high temperature techniques polymorphs of $FeCr_2S_4$ and of some other spinel compounds have been synthesized. β-$FeCr_2S_4$ has a structure related to the common hexagonal nickel-arsenide type. It is about 9 per cent more dense than the normal spinel structure. A P-T diagram of the phase transformation is given.

IN THE SERIES OF COMPOUNDS $FeCr_2X_4$, with X respectively O, S, Se and Te, structures of the spinel type as well as derivatives of the NiAs type occur (see Table 1).

TABLE 1

Compound	Structure type	Lattice constants
$FeCr_2O_4$	spinel	a = 8.377 Å [1]
$FeCr_2S_4$	spinel	a = 9.998 Å [2]
$FeCr_2Se_4$	nickel-arsenide derivative (Cr_3S_4 structure)	a = 6.72 Å, b = 3.62 Å c = 11.85 Å, $\beta = 90^\circ 49'$ [3]
$FeCr_2Te_4$	nickel-arsenide derivative	a = 3.938 Å, c = 6.018 Å *,[4]

*$FeCr_2Te_4$ possibly has a rather broad existence region; a and c may be dependent on the exact composition.

Using the opposed-anvil apparatus described earlier,[5] a high pressure polymorph of $FeCr_2S_4$ has been obtained with a structure related to the nickel-arsenide type.

From the data of Table 2 it will be clear that the adoption by $FeCr_2S_4$ of a structure related to the nickel-arsenide type may result in a density increase of about 8 per cent.

The fact that the high pressure polymorph of spinel has the nickel-arsenide type of structure is in accordance with the general rule for ionic compounds, that the increase in density is accompanied by an enhancement of the cation coordination number (from 4.6.6 to 6.6.6).

The results of the high pressure-high temperature experiments are set out graphically in Fig. 1.

The observed, rather broad, X-ray reflections of the high pressure polymorph can be indexed in the hexagonal unit cell of the nickel-arsenide structure with a = 3.4 Å and c = 5.7 Å. (The number of unit formulas per unit cell is Z = 1/2.) Ordering effects could not be observed. Treating this multicomponent system as a quasi-unary one, which may be justified for kinetic reasons, the transition entropy ΔS of the first-order phase transformation can be calculated from the curve of Fig. 1 using the Clausius Clapeyron equation. The value is $\Delta S = 5.5 \pm 2$ cal mol^{-1} deg^{-1}.

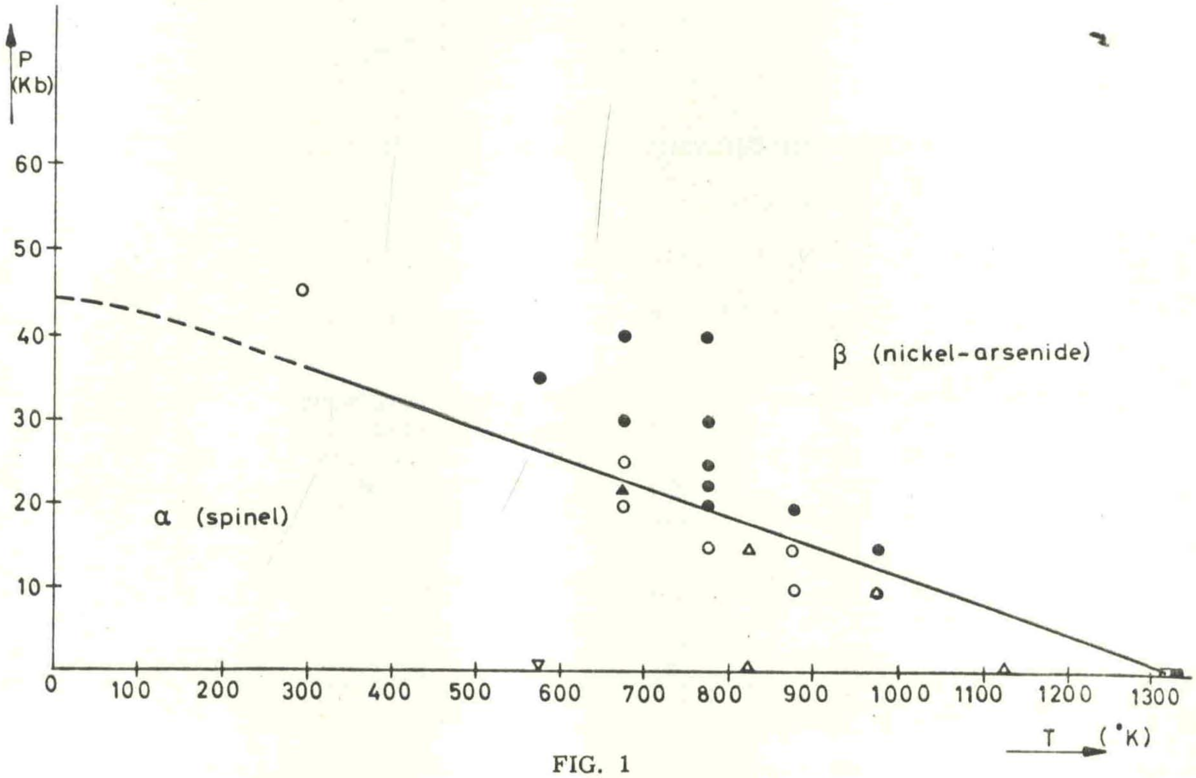

FIG. 1

● Presence of β phase, starting from α , in opposed anvil apparatus. X-ray diagram taken after release of pressure.

O α phase, unchanged; technique as above.

△ Presence of α phase, starting from β (prepared at 40 Kb; 500°C); technique as above.

▲ β phase unchanged, starting from β (prepared at 40 Kb; 500°C); technique as above.

▽ Presence of α phase, starting from β (prepared at 40 Kb; 400°C); after hydrothermal treatment.

◧ Transition point as indicated by D. T. A.

TABLE 2

Compound	Structure type*	Density*
Fe_3S_4	nickel-arsenide derivative (smythite)	4.09
$FeCr_2S_4$	spinel	3.84
Cr_3S_4	nickel-arsenide derivative (Cr_3S_4-type)	4.16

*Data from A. S. T. M. index.

This value, and also the intersection point of the P-T curve with the horizontal axis, are in reasonable agreement with preliminary differential thermal analysis measurements.

This is the first time to our knowledge that a high pressure polymorph of a substance, having a spinel lattice at atmospheric pressure has been observed. So far we have been able to prepare also high pressure polymorphs of the same type from the spinels $CuCr_2Se_4$, $CuCr_2Te_4$, $CoCr_2S_4$ and the cation-deficient spinel In_2S_3.[6] In nature Fe_3S_4 is known to occur as smythite,[7] but also, as has been found recently, as a mineral with spinel structure (greigite).[8]

The transformation found here for the ternary chalcogenides could have important implications for the structural composition of the deeper layers of the earth, as the oxides could possibly undergo a similar transformation at more extreme conditions.

It is also interesting to note that the spinel $FeCr_2S_4$ has been found in meteorites and is known as the mineral daubréelite. Careful observation has made it clear that this mineral behaves as if it had originally been hexagonal.[9] The polymorphism now observed in the laboratory might therefore give a new clue to the origin and history of meteorites. A more extensive publication on the spinel-nickel-arsenide transformation is in preparation and will be published in due course.

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References

1. WHIPPLE E. and WOLD A., J. Inorg. Nucl. Chem. 24, 23 (1962).
2. LOTGERING F.K., Philips Research Reports 11, 190 (1956).
3. CHEVRETON M., Thèse, Lyon (1964).
4. ALBERS W. and RINZEMA G., to be published.
5. ROOYMANS C.J.M., Reactivity of Solids, Proceedings 5th I.S.R.S., Munchen, 1964. Elsevier, Amsterdam (1965).
6. ROOYMANS C.J.M., to be published.
7. ERD R.C., EVANS H.T. and RICHTER D.H., Amer. Miner. 42, 309 (1957).
8. SKINNER B.J., ERD R.C. and GRIMALDI F.S., Amer. Miner. 49, 543 (1964).
9. RAMDOHR P.J., Geophys. Res. 68, 2011 (1963).

Mit Hilfe von Hochdruck-Hochtemperatur Techniken konnte ein Polymorph von $FeCr_2S_4$, und von einigen anderen Spinellen synthetisch hergestellt werden. β-$FeCr_2S_4$ hat hexagonale Struktur vom Nickel-Arsen Typus. Seine Dichte ist etwa um 9 prozent höher als die der Spinellmodifikation. Ein P-T Diagram der Phasentransformation wird gegeben.

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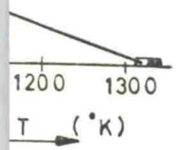

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