HEINRICH, E. WM. (1948) Deposits of the sillimanite group of minerals south of Ennis, Madison County, with notes on other occurrences in Montana. *Mont. Bur. Mines Geol. Misc. Contrib.* **10.**

——— (1950) Sillimanite deposits of the Dillon region, Montana. *Mont. Bur. Mines Geol. Mem.* **30.**

——— AND A. A. LEVINSON (1955) Studies in the mica group; polymorphism among the high-silica sericites. *Am. Mineral.* **40,** 983–995.

———, A. A. LEVINSON, D. W. LEVANDOWSKI AND C. H. HEWITT (1953) Studies in the natural history of micas. *Univ. Mich. Eng. Res. Inst., Final Rpt. Project* **M 978.**

——— AND JOHN C. RABBITT (1960) Pre-Beltian geology of the Cherry Creek and Ruby Mountains areas, southwestern Montana. *Mont. Bur. Mines. Geol. Mem.* **38.**

LEO, G. W., H. J. ROSE, JR. AND J. J. WARR (1965) Chromian muscovite from the Serra de Jacobina, Bahia, Brazil. *Am. Mineral.* **50,** 392–402.

LEVANDOWSKI, DONALD W. (1956) Geology and mineral deposits of the Sheridan-Alder area, Madison County, Montana. Univ. Mich. Ph.D. Thesis.

WHITMORE, D. R. E., L. G. BERRY AND J. E. HAWLEY (1946) Chrome micas. *Am. Mineral.* **31,** 1–21.

THE AMERICAN MINERALOGIST, VOL. 50, MAY–JUNE, 1965

PHASES IN THE SPINEL REGION OF THE SYSTEM CuO_x-MnO_y-FeO_z

A. BERGSTEIN, J. ŠESTÁK, E. KITZINGER, *Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.*

The region of the quasiternary system CuO_x-MnO_y-FeO_z, in which the occurrence of phases with spinel structure is known (Weil *et al.* 1950; Toropov and Borisenko, 1950; Kordes and Röttig, 1951; Delorme, 1958; Goodenough, 1963), was investigated by means of thermogravimetric, dilatometric and *x*-ray measurements in air at temperatures between 20–1200° C. The samples were prepared from pro analysi (p.a.) pure oxides by mixing, preheating at 500° C., wet milling, and sintering at 1150° C. for five to six hours. The compositions investigated are listed in Fig. 1. The dilatometric measurements were repeated five times, the thermogravimetric measurements three times, in both directions, using the same sample. The *x*-ray powder patterns were exposed for 6 hours after the samples had been heated an adequate time for attaining equilibrium.

The following structures were found by *x*-ray to be formed at temperatures between 20 and 1200° C.: 1. cubic spinel in all samples, 2. tetragonally deformed spinel in all samples except samples 4 and 5; 3. hematite (αFe_2O_3) in samples 4 and 5, lying on the $CuFe_2O_x$-$MnFe_2O_x$ join and in sample 3, lying nearer to Fe_3O_x; 4. a monoclinic phase with the diffraction lines of tenorite (CuO) at higher manganese content, near the join $CuFe_2O_x$-$CuMn_2O_x$; 5. a hexagonal phase of the type of delafossite

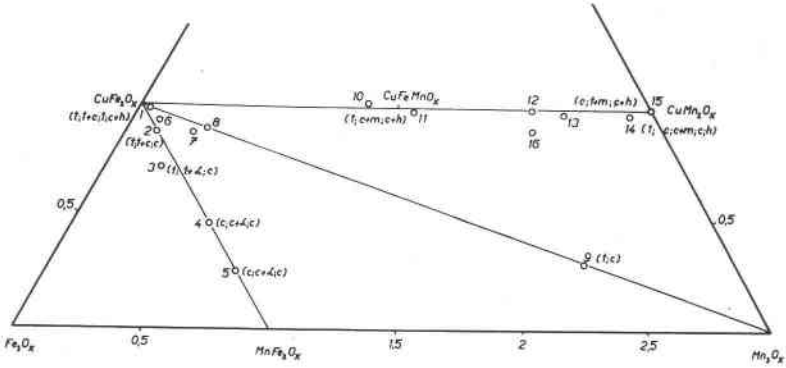

FIG. 1. Compositions under investigation and phases found (in the order of rising temperature). c cubic spinel; t tetragonally distorted spinel; m monoclinic phase, analogous to tenorite (CuO); h hexagonal phase, analogous to delafossite ($CuFeO_2$); α solid solutions with the structure of hematite (αFe_2O_3.

Nr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Cu	0.99	0.874	0.72	0.47	0.27	0.94	0.88	0.9	0.34	1.02	0.94	1.01	0.96	1.0	1.0	0.92
Mn	0.03	0.126	0.22	0.53	0.73	0.10	0.26	0.3	2.1	0.88	1.10	1.52	1.69	1.92	2.0	1.59
Fe	1.98	2.00	2.06	2.00	2.00	1.96	1.86	1.8	0.66	1.86	1.06	0.47	0.35	0.1		0.59

($CuFeO_2$) along and in the vicinity of the join $CuFe_2O_x$-$CuMn_2O_x$.

In Fig. 1 the phase compositions of the respective samples are given in the order of rising temperature.

There was no difficulty in coordinating the changes and transitions of the phases, found by *x*-ray analysis, with the decomposition and oxidation reactions shown by the thermogravimetric curves and with the changes of the coefficient of linear expansion found by dilatometry. The heating curves in Fig. 2 show some typical examples.

In Fig. 2, *1*, the precipitation of solid solutions with the structure of αFe_2O_3 at $\sim$650° C. is accompanied by an oxidation process (gain in weight) and by a constriction of the sample, and during the subsequent redissolution of the αFe_2O_3 phase an expansion on the dilatogram and a loss of oxygen on the thermogravimetric curve can be observed. In Fig. 2, *2a,b*, *3*, and *4a,b* the formation of the hexagonal delafossite type phase beginning at $\sim$1000 and 1100° C. respectively is accompanied by a sharp constriction and by a considerable loss of oxygen, apparently connected to the reduction of Cu^{2+} to Cu^{+} ions. Normally this hexagonal phase was found together with a cubic spinel phase, but in some instances, *e.g.* in sample 4, no diffraction lines of other phases were present on the *x*-ray patterns. From our results we may conclude that this structure does not belong to the composition of delafossite ($CuFeO_2$) alone;

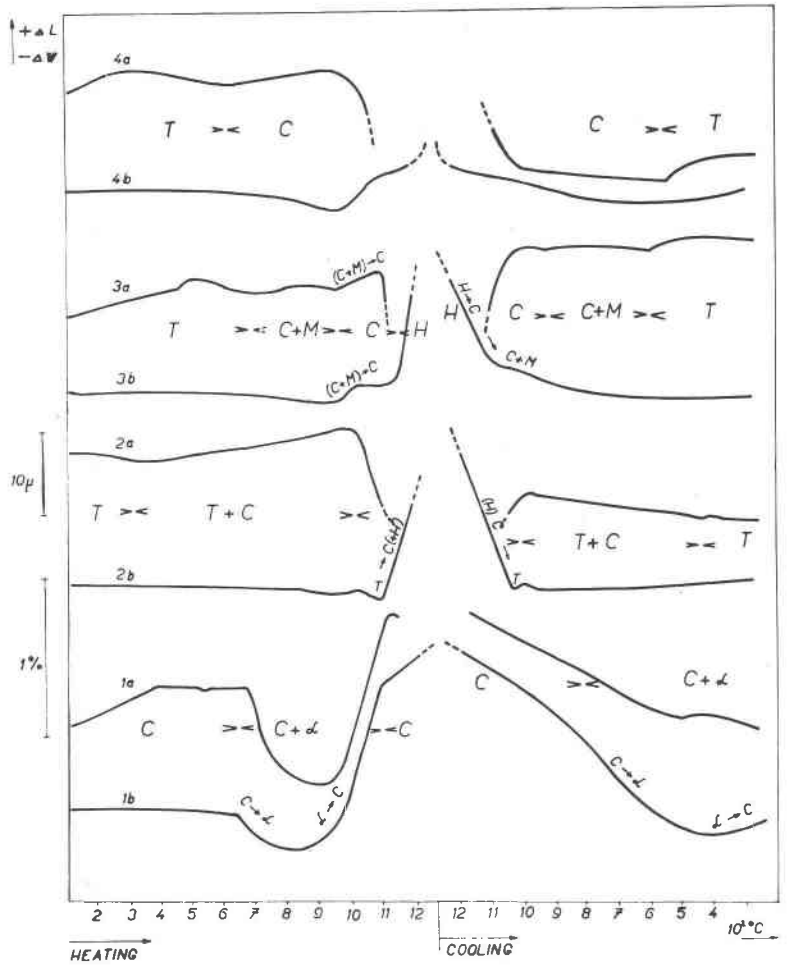

FIG. 2. Dilatometric (a) and thermogravimetric (b) curves for four Cu-Fe-Mn-oxide compositions, showing effects typical for the changes of the phases found. 1, sample 5; 2, sample 1; 3, sample 14; 4, sample 9. Phase symbols as in Fig. 1; ΔL increase of the difference between the length of the sample and of the sintered alumina sample holder in μ; −Δw weight loss in percent.

the iron ions may be partly or entirely substituted by manganese ions and the ratio of copper to the second metal may be less than 1:2.

Sample 1 (Fig. 2,*2*) is an example of the influence of oxygen nonstoichiometry on the tetragonal deformation of the spinel lattice (Bergstein, 1961). At a temperature as high as 1050° C. the small increase of the oxygen content, shown by the thermogravimetric curve (Fig. 2, *2b*) is

accompanied by a remarkable increase of the amount of tetragonally deformed spinel. During the following decomposition, the deformation vanishes and cubic spinel together with the hexagonal delafossite type phase are formed.

The transition from cubic to tetragonally deformed spinel appears on the dialatometric cooling curves as an expansion, beginning between 450–600° C. This effect is very pronounced for the samples with high manganese content (samples 9, 12, 14, in Fig. 1, curves *3a*, *4a* in Fig. 2). In other samples it is generally weak (Fig. 2, *2a*). On the heating curves the inverse process may be discerned, but in general the shape of the curves is not so obvious as during cooling. A weak effect of this type, pointing to a small tetragonal deformation, was observed near 500° C. also with $CuMn_2O_4$ (sample 15); according to literature (Kolomijec *et al.* 1957; Delorme, 1958) and to our own measurements, however, no tetragonal distortion could be found by *x*-ray analysis, and from 20–850° C. the samples were $CuMn_2O_4$ with a cubic spinel structure.

In the presence of the monoclinic tenorite-type phase a characteristic increase of the slope of the dilatometric curves is always observed at 950–1000° C. Fig. 2, *3a* is a typical example. The region of the steeper slope between 980–1100° C. is probably due to a decomposition process and the dissolution of the monoclinic phase in the cubic spinel phase.

Problems related to the mechanism, the reversibility, and the thermal hysteresis of the crystallographic transitions and the chemical reactions described were encountered and will be dealt with in further experimental work.

References

Bergstein, A. and L. Červinka (1961) Influence of manganese and oxygen content on tetragonal deformation of copper ferrite. *Czech. Jour. Phys.* **B11,** 584–594.

Delorme, C. (1958) L'asymétrie de l'ion cuivre bivalent dans des combinaisons du "type NaCl" et du "type spinelle." *Bull. Soc. franc. Minéral.* **81,** 79–102.

Goodenough J. B. (1963) *Magnetism and the Chemical Bond.* Interscience Publisher, New York—London, 144–149, 194–197.

Kolomijec B. T., I. T. Sheftel and E. V. Kurlina (1957) Elektriceskije svojstva nekotorich sloznich oxidnich poluprovodnikov. *Jour. Tech. Fiz.* **27,** 51–72.

Kordes, E. and I. E. Röttig (1951) Neue Mischoxyde mit Spinellstruktur. *Zeit. anorg. allg. Chem.* **264,** 34–47.

Rosenberg M., O. Nicolau, R. Manila and P. Pausescu (1962) Studiul proprietatilor electrice si al structurilor cristaline in sistemul $(CuO)_x(Mn_2O_3)_{1-x}$. *Stud. cercetari fiz.* **13,** 651–665.

Toropov N. A. and A. N. Borisenko (1950) Isledovanija ferritov medi. *Jour. prikl. chim.* **23,** 1165–1175.

Weil L., E. F. Bertaut and L. Bochirol (1950) Propriétés magnétiques et structure de la phase quadratique des ferrites de cuivre. *Jour. Phys. Radium* **11,** 208–212.

X-Ray Powder Data File (1959) *ASTM Tech. Publ.* **48 H.**