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The anilite/low-digenite transition[1]

FREDRIK GRØNVOLD

Department of Chemistry, University of Oslo, Oslo 3, Norway

AND EDGAR F. WESTRUM, JR.

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Abstract

Transition from the anilite phase ($Cu_{1.75}S$) to low-digenite was detected calorimetrically near 310K and confirmed by X-ray powder diffraction. The reverse transition is more sluggish and appears to be initiated at about 290K; the transition, which might serve as a geological thermometer, has a transitional enthalpy ≃790J mol^{-1}.

In the course of a thermodynamic study of copper(I) sulfide by Grønvold *et al.* (in preparation), copper(II) sulfide by Westrum and Grønvold (in preparation), and intermediate phases, we have found an interesting thermal effect near 310K with maximum transitional enthalpy for compositions near $Cu_{1.75}S$. The transition is separate and distinct from the previously reported one around 350K which is ascribed to the low-/high-digenite transition by Morimoto and Kullerud (1963) and by Roseboom (1966).

A copper sulfide mineral with composition $Cu_{1.75}S$ found in the Ani mine in Japan was characterized by Morimoto *et al.* (1969). The crystal structure of this phase (which they designated anilite) was determined by Koto and Morimoto (1970) as an ordered orthorhombic relative of digenite with composition Cu_7S_4. The upper stability limit was given as (343±3)K by Morimoto and Koto (1970) and (348±3)K by Potter (1977), coinciding with the low-/high-digenite transition temperature.

We have been studying a synthetic $Cu_{1.75}S$ sample in our adiabatic-shield calorimeters (Grønvold, 1967; Westrum *et al.*, 1968), which allow the detection of minor relatively slow transitions. A lambda-shaped heat capacity maximum in the 350K region was readily reproduced, and we also ascribe it to the low-/high-digenite transition.[2] A pronounced endothermic effect was observed around 310K, with a transitional enthalpy of 790J mol^{-1} for $Cu_{1.75}S$. Repeated determinations through the transition yielded successively smaller values. The behavior in the region 320 to 340K was also not quite reproducible and depended to some extent on previous thermal history.

X-ray powder photographs of the sample that had been held at 290K for more than two years showed the presence of anilite, but with somewhat diffuse lines. After refrigeration at 275K for 15 hours, Guinier photographs produced very sharp lines and the resulting lattice constants (in Å) $a = 7.887$ *esd* 0.010, $b = 7.826$ *esd* 0.007, $c = 11.08$ *esd* 0.02 agreed well with those by Morimoto *et al.* (1969) and by Potter and Evans (1976). Heating the sample to 325K resulted in disappearance of many lines characteristic of anilite, but some lines in addition to those of face-centered-cubic high-digenite (111, 200, 220, 311, *etc.*) remained, see Table 1. The additional lines (which presumably signalize the presence of low-digenite) appear also on photographs of samples quenched from 375K, in accordance with the observation by Morimoto and Kullerud (1963) that high-digenite cannot be retained by quenching. The cubic subcell lattice constant is $a = 5.556$ *esd* 0.003Å. The observed lines occur at angles so close to those of some of the anilite lines that we are not yet sure that we obtained pure anilite (without admixture of low-digenite) in the cooling experiments.

The transition of anilite to low-digenite (possibly differing slightly in composition) occurs within minutes at 310K, or about 40K lower than the low-/high-digenite transition. Characteristic anilite diffraction lines which are diffuse or absent in low-dige-

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[2] Low-digenite is used here to designate digenites of varying structures and compositions existing below the ~350K transition.

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Table 1. Low-angle reflections on Guinier photographs of $Cu_{1.75}S$ taken at about 295K with $CuK\alpha_1$ radiation. (a) Anilite as obtained after cooling to 275K for 15 hours. (b) Low-digenite as obtained after subsequent heating to 325K for 1 day. The samples were not crushed after having been annealed initially at 675K for 3 weeks.

a			b		
I_{obs}	$\sin^2\theta_{obs}$	hkl	I_{obs}	$\sin^2\theta_{obs}$	hkl
w	0.0143	011			
vw	0.0329	?			
w	0.0514	211	w	0.0516	
w	0.0521	103	w	0.0527	
w	0.0533	121			
m	0.0553	202	w	0.0555	
s	0.0578	022	s*	0.0577	111
m	0.0638	113	m	0.0642	
s	0.0769	220	s*	0.0767	200
w	0.0781	004			
m	0.0823	221	w	0.0825	
vw	0.0830	203 ?			
vw	0.0874	104			
w	0.0917	301			
w	0.0923	031			
m	0.0945	114 ?	w	0.0934	
m	0.1016	131	w	0.1010	
w	0.1168	?			
s	0.1254	124	m	0.1265	
w	0.1260	321			
w	0.1390	313			
w	0.1402	133			
w	0.1437	?			
w	0.1476	?			
vs	0.1542	224	vs*	0.1539	220

* Broad reflection

nite can easily be detected, and the transition might serve as a mineralogical thermometer. The possibility of impurity stabilization by low-digenite would need further investigation. The low-digenite to anilite transition is more sluggish and typically undercools about 20K.

A definitive paper on the thermodynamics of synthetic anilite and digenite is in preparation by Grønvold *et al.*

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