THERMODYNAMIC PROPERTIES AND ORIGIN OF METEORITIC MINERAL. III. HEIDEITE, FeTi$_2$S$_4$. M.I. Petaev (1), K.S. Gavrichev (2), V.M. Gurevich (1), E.G. Osadchij (3), T.A. Stolyarova (3), V.E. Gorbunov (2), I.I. Khodakovskii (1); (1) Vernadsky Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences, Moscow, USSR; (2) Kurnakov Institute of Chemistry of the USSR Academy of Sciences, Moscow, USSR; (3) Institute of Experimental Mineralogy of the USSR Academy of Sciences, Chernogolovka, USSR.

Physico-chemical study of meteoritic minerals provides useful information on origin of meteoritic mineral assemblages, i.e. a meteorite as a whole. The most valuable data may be obtained from the investigations of exotic accessory meteoritic minerals, i.e. nitrides and sulfides of Si, Ti, Cr, etc.

To these minerals also belongs heideite found only in aubrite Bustee. According to Keil and Brett [1], the Bustee enstatite achondrite consists predominantly of enstatite and diopside with minor amounts of other silicate minerals. Small quantities of metallic nickel-iron, osbornite, troilite, ferroan alabandite and daubreelite are also present. Heideite occurs as rare, discrete, anhedral grains at the grain boundaries of silicate minerals. Grains range in diameter up to 100μm, but most are of the order of 40μm in diameter. Heideite is nowhere in contact with any other opaque mineral in the sections examined.

The Bustee meteorite contains several Ti and Fe-bearing minerals while these are not in contact with each other. This may be used for estimates of gas fugacities equilibrated with these minerals. These estimates are derived from the analysis of phase relations in the Ti-Fe-S-N-O system. Though oxides of Ti and Fe are not found in Bustee, the minerals, i.e. ilmenite and rutile are observed in other meteoritic types[2]. To carry out this investigation we determined the thermodynamic properties of synthetic FeTi$_2$S$_4$.

Synthetic FeTi$_2$S$_4$ is a powder with the grain size of 50-100 μm. The phase was prepared by dry synthesis at 850°C from elements in evacuated silica tubes. X-ray analysis was used for identification of synthetic FeTi$_2$S$_4$. Impurities in synthetic FeTi$_2$S$_4$ were determined by semiquantitative spectral analysis: Ni<n*100 ppm, Mn, Cu, Zn, Mg, Si, Al, Cr, Ca<n*10ppm.

Using the adiabatic calorimeter the low temperature heat capacity of synthetic FeTi$_2$S$_4$ was measured over the 4.75-345K temperature range. Heat capacity curve has 2 anomalous regions. One region is observed over the 90-155K temperature range. This anomaly corresponds to magnetic transition [3]. Its energetic characteristics are: $T_{\text{max}} = 135\pm2K$, $\Delta S_{135} = 1.4\times10^{-3} \text{J mol}^{-1} \text{K}^{-1}$, $\Delta H_{135} = 170\pm10\text{J mol}^{-1}$. The second anomaly is observed over the 2-14K temperature range. It has a complex configuration. The λ-form peaks are observed at the beginning and at the end of anomalous region. Maximums of peaks correspond to 8.3K and 12.8K. Its energetic characteristics are: $\Delta S_{8.3} = 0.41\times10^{-3} \text{J mol}^{-1} \text{K}^{-1}$, $\Delta H_{8.3} = 2.29\times10^{-3} \text{J mol}^{-1}$, $\Delta S_{12.8} = 0.05\times10^{-3} \text{J mol}^{-1} \text{K}^{-1}$, $\Delta H_{12.8} = 0.73\times10^{-3} \text{J mol}^{-1}$.

The standard thermodynamic properties at 298.15K are: $C_{p,298} = 208.62\pm0.12\times10^{-3} \text{J mol}^{-1} \text{K}^{-1}$, $S_{298} = 226.97\pm0.40\times10^{-3} \text{J mol}^{-1} \text{K}^{-1}$, $H_{298} - H_0 = 35890\pm30\text{J mol}^{-1}$. The coefficients of Mayer-Kelley equation were computed by least squares analysis using heat capacity data over the 250-345K temperature range: $C = 68.68 +453.99\times10^{-3}T -3.998\times10^{-5}T^2$. 

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The reaction \( \text{FeTi}_2\text{S}_4(s) + 4\text{Zn}(s) = 4\text{ZnS}(s) + \text{Fe}(s) + 2\text{Ti}(s) \) (1) was chosen for determination of the standard enthalpy of heideite formation. This reaction proceeds completely at ca. 10000 in evacuated (10⁻⁴ torr) silica tubes during 5–6 minutes. According to X-ray analysis the products of the reaction are: \( \beta\)-\text{ZnS} (wurtzite) and metallic \text{Fe} and \text{Ti}. The calorimetric investigation of the possibility of the reaction between \text{Fe} and \text{Ti}(\text{Fe}+2\text{Ti}) under conditions similar to those for the reaction (1) was also carried out. According to X-ray analysis and due to the absence of thermal effect the initial state of the mixture remains unchanged throughout the experiment. Using a vacuum-block calorimeter [4] the heat of the reaction (1) was measured. The inner space of calorimetric bomb is filled with argon (P=30 atm). During the experiment the thermostat temperature was 25.00±0.01°C. The completeness of the reaction is tested by reheating of tubes. No additional thermal effect is observed. The enthalpy change of the reaction (1) is \(-112.7±3.8\text{kJ/mol}\). This value and the standard formation enthalpy of wurtzite [5] was used for the calculation of the standard formation enthalpy of heideite. \( \Delta H^{\circ}_{298}(\text{FeTi}_2\text{S}_4) = -666.7±3.8\text{kJ/mol} \).

Thermodynamic properties of \( \text{FeTi}_2\text{S}_4 \) and other meteoritic minerals [6, 7] were used for estimation of heideite origin conditions. The analysis of phase relations in the Ti-Fe-S-N-O system was made. The sulfur fugacities were calculated from the Fe-FeS buffer. The results are shown in Fig. 1. As seen in Fig. 1, the heideite formation is promoted by high temperatures and low nitrogen fugacities. Here the equilibrium temperature of osbornite-heideite assemblage is reciprocal in respect to nitrogen fugacity value. Taking into consideration the breccia structure of Bustee and discrete grains at the grain boundaries of silicates we may suggest that heideite and osbornite were formed at a different time. Furthermore, they resulted from different formation processes. If so, Bustee in its further evolution was not heated to temperatures higher than the osbornite decomposition temperature and did not contact with the gases of relatively high nitrogen fugacities (Fig. 1).