example, hydrothermal) event postdating metamictization. The chemical changes are quite similar to primary pseudomorphic alteration of complex Nb-Ta-Ti oxides (*5*) and the natural recrystallization of the metamict Nb-Ta-Ti oxide, pyrochlore (*6*). The formation of spherulites during primary alteration and recrystallization may be a temporary feature which becomes obscured as the recrystallization progresses and spherulites coalesce and themselves recrystallize. Their transitory nature may explain why spherulites have not been previously observed in altered metamict Nb-Ta-Ti oxides.

RODNEY CHARLES EWING
Department of Geology,
Stanford University,
Stanford, California 94305

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Monoclinic Sulfur: Heat Capacity Anomaly at 198°K Caused by Disordering of the Crystal Structure

Abstract. *The entropy of disorder of the idealized crystal structure of monoclinic sulfur at high temperatures is equal to the extra entropy change in the lambda-type (second order transformation type) heat capacity anomaly found at 198°K. The extrapolated entropy is zero at 0°K. The partially disordered crystal structure gradually becomes ordered as the temperature is lowered.*

The crystal structure of monoclinic sulfur (the form which is stable over a 20° temperature range just below the melting point at normal pressure) was found by Sands (*1*) to be partially disordered, in that one-third of the S_8 molecules which make up the structure can assume either of two orientations. The heat capacity measurements described below indicate that this disorder disappears as the temperature is lowered, resulting in a lambda-type (second order transformation type) heat capacity anomaly peaking at about 198°K.

The heat capacities of monoclinic and orthorhombic sulfur were measured separately from 12°K to the temperature T_e where they were in equilibrium with each other. In this temperature range, orthorhombic sulfur is the stable form at normal pressures. The heat of transformation (ΔH_e) was determined at T_e. A heat capacity anomaly was found at 198°K. The data are accurate enough to permit reliable calculations of entropy differences pertinent to the crystal structure.

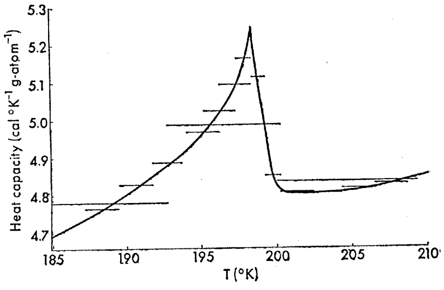

Fig. 1. Heat capacity of monoclinic sulfur near 198°K.

Orthorhombic sulfur has an ordered crystal structure and its entropy is conventionally defined as zero at 0°K. From a third-law calculation comparing orthorhombic and monoclinic sulfur, the entropy of the monoclinic form at 0°K is 0.007 ± 0.020 cal °K^{-1} g-atom^{-1}. This calculation was made with only the new heat capacity data obtained in the study reported here. If the disordered crystal structure determined by Sands (*1*) were maintained down to 0°K, the zero point entropy would be $(R/24)\ln 2$ per gram atom (R is the gas constant), or 0.057 cal °K^{-1} g-atom^{-1}, calculated according to statistical thermodynamics. This entropy is not present at 0°K and the crystal structure at very low temperatures is therefore ordered.

The obvious place to look for the missing entropy is in the lambda anomaly shown in Fig. 1. The experimental data (average heat capacities and temperature ranges) are shown by the horizontal bars; the solid curve was derived from them. Except for this anomaly, the heat capacities were smooth, monotonically increasing functions of temperature.

To find the extra entropy change in this anomaly, it was necessary to determine what the heat capacity would have been in the absence of an anomaly. Conveniently, the heat capacity difference between monoclinic and orthorhombic sulfur was the same linear function of temperature over ranges below and above the anomaly. This linear function could be used to interpolate the "normal" heat capacity through the anomalous region. A smooth interpolation of this type is reasonable because of the similarity between orthorhombic and monoclinic sulfur and the very slight effects to be expected from introducing complete ordering into the monoclinic structure.

Figure 2 shows the extra entropy, ΔS, calculated by integrating the difference between the actual and interpolated heat capacities of monoclinic sulfur between 70° and 300°K. The uncertainty of integration from 120° to 220°K is estimated as ± 0.005 cal °K^{-1} g-atom^{-1} in addition to any error of interpolation. The agreement between the data in Fig. 2 and the theoretical entropy of disorder of the high-temperature crystal structure is quite reasonable. The heat capacity anomaly is most likely caused by the gradual acquisition of disorder as the temperature is raised, and the data in Fig. 2 reflect the degree of this disorder at each temperature. The entropy at 0°K is not significantly different from zero within the experimental uncertainty, but it is worth noting that the total of this entropy and the maximum ΔS from Fig. 2 agrees almost perfectly with the entropy calculated by Sands (*1*).

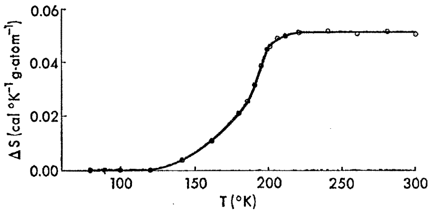

Fig. 2. Extra entropy in the heat capacity anomaly of monoclinic sulfur.

The entropy calculations described here thus support crystallographic data by confirming the existence of an entropy due to the disorder, and show a gradual change to an ordered structure as the temperature is lowered.

The uncertainties pertinent to the calculations are the precision uncertainties; additional uncertainties affecting the absolute values would be expected to cancel out almost completely. The precision uncertainty was taken as twice the estimated standard deviation (S.D.) of the measured heat capacities from the smoothed data. In most cases 2 S.D. was 0.003 to 0.004 cal $°K^{-1}$ g-atom^{-1}; 2 S.D. was highest (0.022) in the region shown in Fig. 1. In estimating uncertainties of integration, it was assumed that the errors of the smoothed heat capacity data were always 2 S.D. (that is, that absolute values of error were additive). However, it was assumed that the difference between the heat capacities of orthorhombic and monoclinic sulfur was random (that is, that errors added to form the square root of the sum of their squares). The errors of extrapolation to 0°K and of ΔH_e and T_e were considered too small to be significant in the presence of the errors already considered. The procedure used gives a conservative estimate of the uncertainty.

Measurements were made by adiabatic calorimetry. The main modification of the basic design (*2*) was the addition of an outer shield of copper (gold-plated on the outside) to the calorimeter. This was done to reduce the difference in surface temperature gradients between the empty and filled calorimeter. The system accuracy was checked by measuring the heat capacity of *n*-heptane. The largest deviations from selected values (*3*) were 0.2 percent. The results for solid sulfur below T_e agree with other determinations (*4*) within expected limits of accuracy. The sulfur measurements were made under a low pressure of helium (well below atmospheric pressure at the melting point of sulfur) and thus are essentially equal to constant-pressure measurements at a low pressure.

A small calorimeter filling tube made of Monel and soldered with tin (lightly alloyed to prevent "tin disease") was exposed to any sulfur that might have vaporized and migrated to it. The amount of tin exposed was minute. The amount of Monel exposed was small, and an experiment showed that Monel was attacked only very slowly, even by molten sulfur. Therefore, chemical reactions should not have affected the results.

The leak test performed at the beginning of the measurements could not be repeated afterward, because the calorimeter ruptured (apparently because of volume changes accompanying the transformation of solid sulfur near T_e) during later studies. The copper shield of the calorimeter acted as a "leak detector"; the heat effect of reaction between it and sulfur was immediately apparent. Between the low-temperature studies and the rupture, the calorimeter had been used at temperatures as high as 434°K. The heat exchange rates during this period were essentially the same as those observed with the empty calorimeter before it was filled with sulfur; they showed no evidence of any reaction between copper and sulfur. The calorimeter was cycled between temperatures around T_e and cryogenic temperatures during the low-temperature measurements without causing a large precision uncertainty. Therefore leakage was not a problem during the low-temperature measurements.

The sulfur was obtained from the National Bureau of Standards, and a study of the fraction melted versus temperature indicated that it contained 10^{-5} mole fraction of impurities soluble in the liquid and insoluble in the solid. No anomalous behavior was noted in the heat capacities near the boiling point of water, and water is not likely to have been present in a significant amount (*5*).

R. L. Montgomery
Boeing Company,
Wichita, Kansas 67210

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Electronic Structure and Catalytic Behavior of Tungsten Carbide

Abstract. *Tungsten carbide has been shown to be an effective catalyst for a number of reactions that are readily catalyzed by platinum, but not at all by tungsten, and it was speculated that this behavior is due to changes in the electron distribution when carbon is added to tungsten. A test of this hypothesis, made by measuring the valence band x-ray photoelectron spectrum of tungsten carbide and comparing it with the spectra of tungsten and platinum, shows that, near the Fermi level, the electronic density of states of tungsten carbide more nearly resembles that of platinum than that of tungsten.*

Tungsten carbide has been found (*1*) to be an effective catalyst for a number of chemical reactions (particularly the isomerization of 2,2-dimethylpropane) that are catalyzed readily by the scarce metal platinum, but not at all by tungsten. A growing body of experimental data (*2*) indicates a close relationship between catalytic activity and the density of *d*-like states at the Fermi level, the energy below which all the electronic states are occupied and above which they are empty. It is therefore of interest to investigate the state density of WC, and compare it to those of W and Pt. We have used x-ray photoelectron spectroscopy (XPS) to study the valence band and core levels of WC; our results show that this compound is more like Pt than it is like W.

The sample studied was a powder (−200 mesh), more than 99.9 percent pure (by flame spectroscopic analysis), and was single phase (x-ray diffraction showed sharp lines and no extra lines). A thick coating of the powder was pressed onto an annealed Au substrate. The powder layer was sufficiently thick and evenly distributed that the intense $4f$ lines of the Au substrate could not be detected. Nonmonochromatized Mg $K\alpha$ radiation was used for the measurement, at a base pres-