

## A Note on the Bonding, Optical Spectrum and Composition of Tetrahedrite

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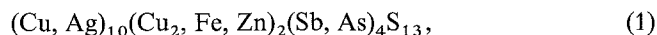
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**Abstract.** Tetrahedrites of composition  $(\text{Cu, Ag})_{10}(\text{Cu}_2, \text{Fe, Zn})_2(\text{Sb, As})_4\text{S}_{13}$  or  $\text{Cu}_{12}\text{Sb}_{14/3}\text{S}_{13}$  have 208 valence electrons per unit cell and are expected to be semiconductors. The bands are full in these cases, whereas compositions towards the classical formula  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (204 valence electrons per unit cell) have only partially filled bands and are therefore expected to be metallic. These predictions are supported by new optical absorption spectra of tetrahedrites with 205 and 208 valence electrons per unit cell. The gap between valence and conduction bands of the semiconductor is about 1.7 ( $\pm 0.2$ ) eV. A further prediction based on a nearly-free electron model is that 208 valence electrons per unit cell represent a compositional limit for tetrahedrites, and that the stability increases as compositions approach this limit. Existing data indicate an exponential increase in the number of occurrences as the limit is approached.

### Introduction

The tetrahedrite-tennantite series is an important family of ore minerals with a broad range of compositions. Natural and synthetic samples occur with compositions of approximately



and further substitutions in the cubic tetrahedrite structure include (Hg, Cd, Pb) for (Fe, Zn), Bi for (Sb, As) and Se for S. A long standing problem has been to determine the compositional stability limits for tetrahedrites.

Recently, Johnson and Jeanloz (1983) have suggested that a simple approach based on the nearly-free electron model can be used to explain both the observed range and the relative frequency of tetrahedrite compositions. In short, they proposed that the stability of tetrahedrite is governed by the number of valence electrons available for each composition. As composition varies from the classical formula



(Pauling and Neumann 1934) to the formula of Equation 1, the number of valence electrons per unit cell increases from

204 to 208. At a value of 208, the 52<sup>nd</sup> Brillouin zone is completely filled and that composition of tetrahedrite (Eq. 1) should be a semiconductor. Varying composition such that additional valence electrons are available requires a large increase in energy because the electrons must be promoted across the energy gap before the next Brillouin zone can be filled. Therefore, tetrahedrites with 208 valence electrons per unit cell were proposed as a limit for the range of compositions that would normally be observed. Other than Equation 1, such limiting compositions include  $\text{Cu}_{12}\text{Sb}_{14/3}\text{S}_{13}$  and  $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$  (Johnson and Jeanloz 1983).

Tetrahedrites with compositions between formulas (1) and (2) were proposed to be metallic because between 204 and 208 valence electrons would be available per unit cell, and the 52<sup>nd</sup> Brillouin zone would therefore only be partially filled. Preliminary electrical resistivity data were found to be consistent with this model, but it was not possible to conclusively prove that compositions with 208 valence electrons are semiconductors (i.e., have a filled Brillouin zone). Furthermore, no conclusive data are available on the magnitude of the band gap in tetrahedrite (Shuey 1975).

In this study, we show that the optical absorption spectrum of a tetrahedrite with 208 valence electrons per unit cell is consistent with that of a large-gap semiconductor. A sample with composition between (1) and (2) appears to be metallic, and we find that the predictions of Johnson and Jeanloz (1983) are borne out.

### Optical Absorption Experiments

Polished thin sections of two samples were investigated: a natural sample of composition  $\text{Cu}_{9.94}\text{Ag}_{0.01}\text{Fe}_{0.18}\text{Zn}_{1.77}\text{Sb}_{3.97}\text{As}_{0.11}\text{S}_{13.0}$  (208 valence electrons per unit cell) and a synthetic sample of composition  $\text{Cu}_{12.12}\text{Sb}_{4.09}\text{S}_{13}$  (205 valence electrons per unit cell). These were cut from the samples used by Johnson and Jeanloz (1983) for electrical resistivity measurements, and they were polished to a thickness of about 5  $\mu\text{m}$ . Both samples appear opaque in thin section, but light of a deep red color is transmitted through the first sample at the edges (estimated to be  $\leq 1 \mu\text{m}$  thick). The samples contain inclusions and apparent impurities; however, in both cases it was possible to locate clean areas to fill out the 215  $\mu\text{m}$  diameter field of view used in the spectroscopic measurements. The sample thickness is uncer-

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tain at the exact location of the optical measurement, and it could differ by as much as a factor of two from the average value of 5  $\mu\text{m}$ .

Optical spectra were collected at room temperature using a holographic-grating monochromator attached to a petrographic microscope. A 100 W tungsten-halogen lamp was used as a source (unpolarized), along with a silicon detector, and the spectral resolution of the system is  $\leq 10$  nm. This microspectrophotometer was developed for other purposes, and details are given elsewhere (Knittle and Jeanloz 1984).

The results for the natural tetrahedrite indicate that an optical absorption edge occurs at about 720 nm (Fig. 1). The absorption coefficient decreases from values in excess of  $10^4$   $\text{cm}^{-1}$  in the visible to about  $2 \times 10^3$   $\text{cm}^{-1}$  in the near infrared. These are typical values for semiconductors (e.g., Pankove 1971), but they are uncertain in absolute value by a factor of two (mainly due to the uncertainty in sample thickness). In contrast with the results shown in Figure 1, the synthetic sample exhibits no transmission (absorption coefficient exceeding  $10^4$   $\text{cm}^{-1}$ ), consistent with its low electrical resistivity ( $\rho_e \lesssim 3 \times 10^5$  ohm-meters). With 205 valence electrons per unit cell, this sample would be expected to be metallic as we observe.

Little is known about the electronic structure of tetrahedrite (Shuey 1975). Earlier work (Wernick and Benson 1957) had suggested that the energy gap between the valence and conduction bands of tetrahedrite is less than 1.0 eV. Our results, however, demonstrate that the band gap for semiconducting tetrahedrite is approximately 1.72 eV in magnitude (corresponding to the absorption edge centered at 720 nm). The absorption edge energy may be an underestimate of the true value of the band gap because of the possible presence of impurity states and excitons (Pankove 1971). The onset of transmission (640 nm) corresponds to 1.94 eV, so that our value of the gap energy is uncertain by at least 0.2 eV. More detailed absorption and reflection spectra would be required (along with theoretical calculations) to derive a refined estimate. Nevertheless, our determination of the energy gap is sufficient for the present application, which consisted mainly in showing that tetrahedrite with 208 valence electrons per unit cell is a semiconductor.

### Tetrahedrite Compositions

If the simple model of band filling is correct as proposed, the total electron contribution to the energy is determined by the free electron model. As the number of valence electrons per unit cell increases from 204 to 208, the band fills in the 52<sup>nd</sup> Brillouin zone and the energy increase per valence electron decreases by the amount.

$$\mu_e \sim \frac{1}{D(\epsilon)} \propto \epsilon_F / N^{1/3}(\epsilon), \quad (3)$$

where  $D(\epsilon)$  is the free electron density of states,  $\epsilon_F$  is the Fermi energy and  $N(\epsilon)$  is the number of electrons up to energy  $\epsilon$ . As pointed out by Johnson and Jeanloz (1983), Equation 3 suggests that tetrahedrites become stabilized as the number of valence electrons (i.e., the composition) is changed from 204 towards 208 per unit cell. Because the gap energy is found to be quite large, thermal excitation of electrons across the band gap is negligible up to the melting temperature.

In the present approach, only the free electron contribu-

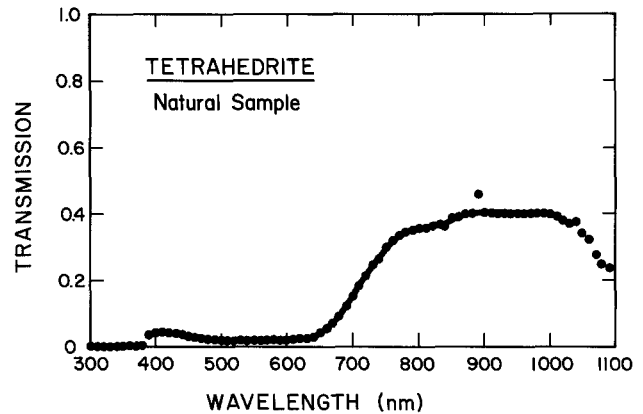


Fig. 1. Optical absorption spectrum of a natural tetrahedrite with composition corresponding to 208 valence electrons per unit cell (see text). The absorption edge centered at about 720 nm indicates that this sample is a semiconductor. In contrast, no transmission is observed through a synthetic sample with 205 valence electrons per unit cell. Because of the detector response and absorption by the microscope optics, the signal/noise ratio exceeds one only between 400 and 1,000 nm

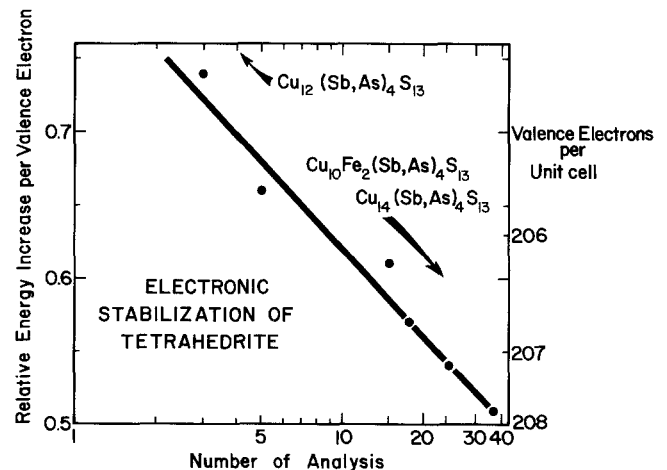


Fig. 2. Test of Equations 3 and 4: relative energy increase per valence electron,  $\mu_e$ , versus the number of analyses (see Johnson and Jeanloz 1983). The electronic stabilization energy  $\mu_e$  is given in units of the Fermi Energy  $\epsilon_F$  (normalized so that  $\mu_e = \epsilon_F/2$  for a full band), and the corresponding number of valence electrons per unit cell is shown on the right-hand axis. A straight-line relationship is expected on this semilog plot, and the largest number of samples should occur near the most stable value of 208 valence electrons per unit cell. Scatter increases as the number of analyses decreases, but both expectations are met

tion to the stability is being considered. Thus,  $\mu_e$  can be viewed as an electronic analog of the chemical potential, and the relative stability of a given composition can be described as the likelihood of its occurrence:

$$P \sim P_0 \exp\left(\frac{E - \mu_e}{kT}\right), \quad (4)$$

with  $P_0$  being a constant,  $E$  includes all nonelectronic contributions to the stabilization energy, and  $k$  is Boltzmann's constant. Equation 4 correctly predicts the relative occurrences of different compositions of tetrahedrites. That is, as the number of valence electrons approaches 208 per unit cell the number of sample occurrences increases exponentially (Fig. 2). Thus, the range and the relative occurrences of tetrahedrite compositions appears to be well explained

by a Brillouin-zone model based on the nearly-free electron theory.

*Acknowledgements.* We thank E. Knittle for assistance with the experiments and M.S.T. Bukowski for helpful discussions. This work was supported by the National Science Foundation.

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Received November 7, 1983