

INTERPRETING HIGH TEMPERATURE AND PRESSURE VENUS-ANALOG SPECTRA: CONSIDERATIONS FROM CRYSTAL FIELD THEORY. M. D. Dyar¹ and J. Helbert², ¹Mount Holyoke College, Dept. of Astronomy, South Hadley, MA, 01075, USA, mdyar@mtholyoke.edu, ²Institute for Planetary Research, DLR, Rutherfordstrasse 2, 12489 Berlin, Germany.

Introduction: Past and proposed measurements of the surface composition of Venus are hampered by the dense CO₂-rich atmosphere and the extreme conditions on the surface: 460°C and 93 bars. Fortunately there are several windows in the CO₂ spectrum in the visible region that permit acquisition of several channels of information where most Fe-bearing minerals have absorption bands. Also, laboratory measurements capable of acquiring visible region spectra at high temperatures are now possible, as implemented in the Planetary Emissivity Laboratory in the Institute for Planetary Research, DLR.

However, the time-consuming nature of the *in situ* Venus-analog measurements means that extensive databases under Venus conditions are going to be slow in development. A more feasible plan for understanding current (from VIRTIS) and proposed spectral data from Venus's surface should rely on those hard-won laboratory data to validate our theoretical understanding of the effects of pressure (P) and temperature (T) on well-understood bands in common rock-forming minerals. Thus a combination of badly-needed Venus-condition lab data and theory will facilitate expansion of the foundational databases for Venus surface exploration. Crystal field theory [1] provides an excellent starting point for these comparisons.

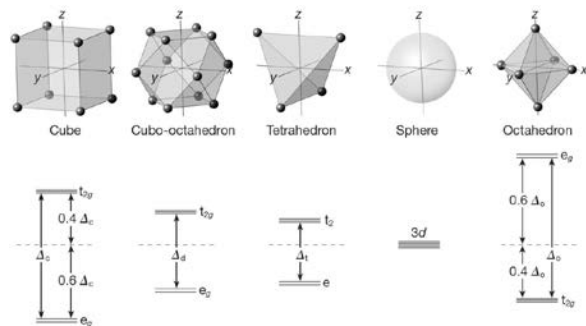


Figure 1. Crystal field splitting of 3d orbitals in cubic (Δ_c), dodecahedral (Δ_d), tetrahedral (Δ_t), spherical, and octahedral (Δ_o) coordination polyhedra. From [2] adapted from [1].

Background: Crystal field splitting (Δ or $10Dq$) describes the difference in energy between the lowest and highest orbital in the electron cloud surrounding (generally) a transition metal (**Figure 1**). The energies of Δ vary according to several factors including 1) the symmetry and coordination number of the coordination polyhedra, 2) the valence state of the cation, 3) the strength of its bond with the surrounding anions, 4) the

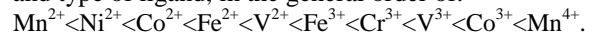
distance between the cation and the surrounding anions, 5) pressure, and 6) temperature. Of interest to Venus exploration is the question of the relative magnitudes of these different variables on spectra.

In general, the largest factor affecting Δ values is coordination number, as shown in Figure 1. The amount of separation, or Δ , between energy levels can be expressed mathematically as:

$$\Delta_o : \Delta_c : \Delta_d : \Delta_t = 1 : \frac{8}{9} : \frac{-1}{2} : \frac{-4}{9}.$$

These ratios correspond to the magnitude of the splitting between t_{2g} or t_g orbitals and e_g or e orbitals. The minus sign implies that the relative stabilities of the two orbitals are reversed for octahedral vs. the other types of coordination polyhedra. In other words, the e_g orbitals are highest in energy in octahedral coordination, while in tetrahedral (Δ_t), cubic, or dodecahedral coordination (Δ_d , where the metal atom is at the center of a dodecahedron with 12 oxygens at its corners), the t_{2g} or t_g orbitals are higher in energy. The Δ values also represent the amount of energy that will be needed to move an electron from the low energy orbitals to the high energy ones, and thus they correspond to the energies of bands seen in spectra.

The Δ values are also a function of valence state and type of ligand, in the general order of:



However, coordination number, valence state, and bond strength rarely change with pressure and temperature. On the other hand, bond length is directly related to Δ . Pressure effects on Δ are described by the relation [1]:

$$\frac{\Delta_P}{\Delta_0} = \left(\frac{R_0}{R_P} \right)^5,$$

where Δ_0 and R_0 are the splitting and typical cation to anion distance under ambient conditions and Δ_P and R_P represent splitting and bond distance, which shortens at high pressures. **High P thus increases Δ and moves absorption bands to lower λ** [1]. Similarly the temperature variation of Δ is expressed [1] as:

$$\frac{\Delta_0}{\Delta_T} = \left(\frac{\Delta_0}{\Delta_T} \right)^{-5/3} = [1 - \alpha(T - T_0)]^{-5/3}$$

where α is the volume coefficient of thermal expansion, T is elevated temperature, T_0 is ambient, and V and V_0 represent molar volumes. **The net effect is that Δ decreases (λ gets longer) as T increases.** Higher temperatures also increase the amplitude of vibrational motions and broaden the bands. Thus in locations where pressure is very high (i.e., the Earth's mantle,

where $P = 140$ GPa), the effects of high P and high T tend to cancel each other out, though there will be intensification and broadening of bands due to increased covalency and vibronic coupling [1]. Some of the background for this work was laid by classic early studies [3-5] but many additional measurements are needed, particularly on rocks and meteorites (e.g., [6,7]) instead of minerals.

Venus Mineralogy: Estimates for Venus' surface mineralogy come from normative calculations based on compositions from the *Venera 13*, *14*, and *Vega 2* landing sites, such as those given in [8]. Primary mineralogy includes Ca and low Ca pyroxene, olivine, plagioclase and alkali feldspars, and iron oxides including ilmenite and possible hematite, with the addition of various reaction products such as pyrite [9-11]. Thus, band shifts as a function of high temperature in all these minerals are of particular interest.

Existing Optical Spectral Data at High P,T: Much of what is known about changes in olivine and pyroxene spectra with T and P comes from the literature on mantle petrology, where pressures up to tens of GPa have been studied, and asteroids, where the focus has been in lower temperature effects. By comparison, the increased pressure on the Venus surface relative to ambient P is minor (93 bars = 0.0093 GPa). Thus under Venus conditions the effects of the increased P on spectra are comparatively benign, and the primary spectral changes will result from T . A few examples of high- T studies of possible Venus surface materials serve to illustrate these phenomena.

Olivine: The dominant olivine absorption band at 1.04-1.08 μm has been shown to shift $130 \text{ cm}^{-1}/\text{GPa}$ to lower λ as P increases [12] – this change would be undiscernible at Venus P . Analogous shifts have been observed for the other olivine bands at 1.2 and 0.9 μm [13]. High T produces only a small shift to longer λ [14]. The main effect of T and P on Venus would be expected to be the above-noted broadening and strengthening of the absorption bands.

Pyroxene: Small shifts to lower λ at high P have been reported for the M1 site bands in pyroxenes [15] but high T has little effect on the 1 μm band [3]. The 2 μm pyroxene band, however, has a diagnostic shift to longer λ in opx and shorter λ in cpx that is predictable in terms of the site distortion of the M2 site, [3] but this region will be masked in Venus spectra by CO_2 .

Ilmenite/Hematite: Although silicates do not show significant changes in band positions in the 1 μm region, the same cannot be said for oxides, which tend to have a variety of charge transfer absorptions near that energy. High- T studies of hematite [16,17] show that features ca. 620 nm and 750 nm become indistinct at 800K. Ilmenite has a similar broad absorption between 600-700 nm [18], but there are no known high- T spectral data. It seems likely that oxides, sulfides, and re-

lated phases might be indistinguishable by reflectance spectroscopy on Venus due to the high temperatures.

Rocks and Mineral Mixtures: One of the key observations of [6] is that band broadening occurs with increasing T , which will make it difficult to discern the differences in pyroxene and olivine contributions around 1.1 μm .

Discussion: Much of the literature on the temperature dependence of mineral and rock spectra is focused on applications to lower- T environments on objects such as asteroids. In those circumstances, narrowing of absorption bands and major changes in band shapes require that T be carefully characterized and accounted for in spectral interpretations. On Venus, this problem is less troublesome because the temperature is constant. However, laboratory mineral spectra at 740K are comparatively rare in the literature. Most studies top out at ca. 450K, well short of the Venus conditions, so band shapes at Venus temperatures are poorly understood. For this reason, new work on rocks and minerals at Venus temperatures is absolutely required for interpretation of VIRTIS and future Venus surface spectra. Our expectation is that silicate features will show no wavelength change in the 1 μm region where the CO_2 windows exist but that changes in magnitude and band width will likely be observed. Further measurements are needed to extend preceding work to Venus surface conditions.

Conclusions: There are no substitutes for actual *in situ* measurements of minerals acquired at Venus-specific temperatures [19]. Although theory predicts the general trends, those predictions *must always be validated by laboratory data*.

References: [1] Burns R. G. (1993) *Mineralogical Applications of Crystal Field Theory*, 2nd ed., Cambridge Univ. Press. [2] Dyar M. D. and Gunter, M. E. (2008) *Mineralogy and Optical Mineralogy*, MSA. [3] Singer R. B. and Roush, T. L. (1985) *JGR*, 90, 12434-12444. [4] Roush T. L. and Singer R. B. (1986) *JGR*, 91, 10301-10308. [5] Roush T. L. and Singer R. B. (1987) *Icarus*, 69, 571-574. [6] Hinrichs J. L. et al. (1999) *GRL*, 26, 1661-1665. [7] Hinrichs J. L. and Lucey P. (2002) *Icarus*, 155, 169-180. [8] Klingelhöfer G. and Fegley B. Jr. (2000) *Icarus*, 147, 1-10. [9] Fegley B. et al. (1995) *Icarus*, 118, 373-383. [10] Fegley B. et al. (1997) *Venus II*, 591-636. [11] Fegley B. et al. (1997) *Icarus*, 125, 416-439. [12] Shankland T. J. et al. (1974) *JGR*, 79, 3273-3282. [13] Bell P. M. and Mao H.-K. (1969) *Geophys. Lab. Yrbk.*, 68, 253-256. [14] Fukao Y. et al. (1968) *Phys. Earth Planet Interiors*, 1, 57-62. [15] Shankland, T. J. et al. (1974) *JGR*, 79, 3273-3282. [16] Yamanoi Y. et al. (2009) *Amer. Mineral.*, 94, 90-97. [17] Mussella et al. (2002) *Intl. J. Thermophysics*, 23, 1303-1310. [18] Isaacson, P. J. et al. (2011) *LPS XLII*, Abstract #2130. [19] Helbert J. et al. (2016) *LPS XLVII*, Abstract #1947.