Temperature dependent absorption spectra of biotites and olivines reinvestigated: on the distinction of polaron and exciton excitations

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Excitons are electron-hole paired states related to the lowest lying excited states of insulating and semiconducting crystals, whereas small polarons are crystal ground states of "self trapped" conduction band carriers. A distinction between polaron and exciton states in minerals could be interesting on one hand related to existing temperature dependent optical absorption spectra for biotites (Rüscher and Schrader 1996) and olvines (Ullrich et al. 2002, 2004) and on the other hand to the discussion whether or not small polarons in olivines could be important for the better understanding of the variation of electrical conductivity and temperature with depth in the mantel (Hirsch et al. 1993, Farla et al. 2010).
The line shape of the optical absorption (α) according to photon assisted hopping (PAH) of small polarons is given by:

$$\alpha \approx \exp(-(w-2E_P)^2/(8E_PkT)) \quad \text{(eq. 1)}$$

(w, E_P, kT in cm^{-1}, 1 eV = 8066 cm^{-1}, k = Boltzmann factor, T = temperature, E_P = polaron binding energy). Eq. 1 becomes modified by density of states contributions and disorder effects mainly only for $w > 2E_P$ (Böttger and Bryksin, 1985). Therefore, taking d(ln(eq.1))/dw reveal a linear relation with intercepts $(2kT)^{-1}$ and 2Ep. Following Rüscher and Schrader (1996) the optical absorption of biotites in the range between 4000 and 8000 cm^{-1} is described by eq. 1 for temperatures between 150 and 800 K. Taking d(ln(α)/dw of the spectra reveal the expected intercepts $(2kT)^{-1}$ and $E_P \approx 4500$ cm^{-1}. The PAH effect dominates in intensity over Fe dd transitions and intervalence charge transfer also observed.
Contrary to the observation for biotites there is no evidence for PAH in the available optical spectra of olivines. Ullrich et al. (2002, 2004) have investigated the temperature dependence of the absorption spectra of fayalite (Fe-olivine) and Co-olivines between 290 and 1270 K and in the range between 4000 and 32000 cm-1. These authors assigned the observed absorption peaks to Fe dd transitions and Co dd transitions. Above about 25000 cm^{-1} a strong increase in absorption has been noted, which shows a strong variation with increasing temperature. We have analyzed this effect further for excitation of excitons following the expressions (e.g. Tang et al. 1995):

$$\alpha = \alpha_0\exp(\sigma_T(w-E_u)/kT) \quad \text{(eq. 2) and} \quad \sigma_T = \sigma_0(2kT/w_{ph})\tanh(w_{ph}/2kT) \quad \text{(eq. 3).}$$

Reasonable values for the exciton energy (E_u), phonon energy (w_{ph}) and exciton formation parameter (σ_0) are obtained, e.g. for Co-olivine $E_u \approx 34600$ cm^{-1}, $w_{ph} \approx 1100$ cm^{-1} and $\sigma_0 \approx 0.37$ (pleochroism neglected). In particular a clear distinction between the temperature effect due to polarons and excitons is achieved observing that d(ln(eq. 2)/dw = const(T). Whether or not the variation in oxygen partial pressure could turn over valence band states or defect levels into a conduction band as could be expected following the discussion of Hirsch et al (1993) requires further investigations.

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