MINERALOGICAL NOTES

Force Constant For Be–O Stretching in Behoite and in Chrysoberyl

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Abstract

An absorption band near 780 cm⁻¹ in the infrared spectra of behoite [β-Be(OH)₂] and of
crysoberyl [Al₂BeO₄] was assigned to the vibration of a beryllium atom moving in a
tetrahedral cage of four fixed oxygen atoms. Using this simple model, a force constant of 2.4
mdyne/Å was calculated for Be–O stretching in behoite and chrysoberyl.

Introduction

The infrared spectrum of behoite [β-Be(OH)₂] was
given by Ehlmann and Mitchell (1970), and the in-
frared spectrum of β-Be(OH)₂ has been studied by
Funck (1964) and by Bear, Lukaszewski, and Turn-
bull (1965). The β-Be(OH)₂ crystal is composed of
tetrahedral Be(OH)₄ groups (Seitz, Rössler, and
Schubert, 1950).

The IR spectrum of chrysoberyl [Al₂BeO₄] has
been studied by Henning and Volke (1966), Povaren-
nykh and Gevorkyan (1971), Povarennik and Nefedov (1971), and Plyusnina (1963). Chrysoberyl
contains tetrahedral BeO₄ groups and octahedral
AlO₆ groups (Farrell, Fang, and Newnham, 1963).

For crystals having a small number of degrees of
freedom in the unit cell, an analysis using lattice
dynamics is feasible. Nusimovici (1969) has per-
formed a lattice dynamical calculation for beryllium
oxide, a crystal which contains tetrahedral BeO₄
groups. Using the Raman spectrum, he obtained a
value of 2.3 mdyne/Å for the Be–O stretching force
constant.

For crystals containing the BeO₄ group but having
a large number of degrees of freedom in the unit cell,
the infrared spectrum is often interpreted as arising
principally from the vibrations of the tetrahedral
BeO₄ group. A tetrahedral unit exhibits a non-
degenerate vibration of frequency ν₁, a doubly
degenerate vibration of frequency ν₂, and two triply
degenerate vibrations at ν₃ and ν₄ (Wilson, Decius,
and Cross, 1955). Generally, only ν₃ and ν₄ are
infrared active, but distortions of the tetrahedral
symmetry and couplings with other parts of the
crystal can result in ν₂ and ν₃ appearing in the infrared
and can break the degeneracy of the modes ν₂, ν₃, and
ν₄.

Funck (1964) has looked at ν₃ for several BeO₄-
containing molecules from the standpoint of a light
central atom surrounded by heavy ligands. Using ν ≈
800 cm⁻¹ for the BeO₄ group, he obtained a metal-
ligand force constant for Be–O of 1.79 mdyne/Å.

Model for the 780 cm⁻¹ Band

A simple model is proposed to account for the
band near 780 cm⁻¹ which occurs in the infrared
spectra of several BeO₄-containing minerals. This
band is interpreted as arising from the vibration of a
beryllium atom moving in a tetrahedron of fixed ox-
ygen atoms. The frequency, ν₃, of this vibration
would be triply degenerate for a perfect tetrahedron,
the degeneracy being broken by slight distortions of
the tetrahedron.

The same procedure that would be used to evaluate
the Einstein frequency of a crystal (Rice, 1967) is

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employed to express \( \nu_{\text{Be}} \) in terms of the Be-O stretching force constant \( K \). A situation is considered in which a beryllium atom experiences a displacement from equilibrium in the amount \( \tilde{r}_{\text{Be}} = \tilde{r}_i - \tilde{r}_{\text{Be}}^* \), where \( \tilde{r}_i \) is the instantaneous displacement of the beryllium atom from the \( i \)th neighboring oxygen atom, and \( \tilde{r}_{\text{Be}}^* \) is the corresponding equilibrium displacement. Neglecting all but central force interactions, the potential due to the displacement \( \tilde{r}_{\text{Be}} \) is given by this model as

\[
V = \frac{1}{2} K \sum_{i=1}^{4} (r_i - r_i^*)^2,
\]

where the sum extends over the four fixed oxygen atoms.

Upon expanding \( r_i = |\tilde{r}_i^* + \tilde{r}_{\text{Be}}| \) to first order in \( \tilde{r}_{\text{Be}} \) and writing the \( \tilde{r}_i^* \) in any convenient coordinate system, the simple expression

\[
V = \frac{1}{2} \left( \frac{4K}{3} \right) \nu_{\text{Be}}^2
\]

is obtained. Hence the beryllium atom behaves as a simple harmonic oscillator vibrating with a frequency

\[
\nu_{\text{Be}} = \frac{1}{2\pi} \left( \frac{4K}{3} \right)^{1/2},
\]

where \( m \) is the mass of a beryllium atom. This expression is similar in form to that of Funck (1964), except that \( \nu_{\text{Be}} \) above shows no dependence on the mass of the outer oxygen atoms. A value for \( K \) is obtained upon assignment of an infrared band to \( \nu_{\text{Be}} \).

Using the infrared spectrum of behoite reported by Ehlmann and Mitchell (1970), a band composed of peaks at 875, 780, 750, and 720 cm\(^{-1}\) was assigned to the vibration of the Be in a tetrahedron of fixed OH groups. The average frequency, 781 cm\(^{-1}\), was taken as \( \nu_{\text{Be}} \). These frequencies are similar to the assignments of \( \nu_{\text{Be}} = 875, 775, \) and 700 cm\(^{-1}\) given by Funck (1964) and close (somewhat similar) to the assignments of \( \nu_{\text{Be}} = 880, 875, 825, \) and 780 cm\(^{-1}\) made by Bear et al. (1965).

A band in the infrared spectrum of chrysoberyl with peaks at 750, 775, and 820 cm\(^{-1}\) was tentatively assigned to \( \nu_{\text{Be}} \) by Henning and Volke (1966). The average of these peaks, 782 cm\(^{-1}\), is close to the assignment of 780 cm\(^{-1}\) made for \( \nu_{\text{Be}} \) by Povarennykh and Nefedov (1971), and is not inconsistent with the assignment of \( \nu = 1000, 860 \) and 780 cm\(^{-1}\) given by Povarennykh and Gevorkyan (1971). A quite different assignment was given by Plyusnina (1963) who tentatively assigned to \( \nu \) a band having peaks ranging from 963 to 1161 cm\(^{-1}\).

Using the frequency 780 cm\(^{-1}\) for \( \nu_{\text{Be}} \) in both behoite and chrysoberyl, a Be–O stretching constant of \( K = 2.4 \) mdyne/Å is obtained, in good agreement with the Be–O stretching constant of 2.3 mdyne/Å obtained by Nusimovici (1969) for beryllium oxide.

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**References**


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