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MICROWAVE ACOUSTIC RELAXATION ABSORPTION IN IRON TOURMALINE

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Résumé. — On a mesuré l’absorption de microondes acoustiques dans de la tourmaline schörlite vert foncé à 580 MHz et 1,03 GHz et en fonction de la température entre 1,5 K et 300 K. On trouve, en plus de l’atténuation due aux phonons thermiques, deux grands pics à basse température. Ces pics sont plus prononcés pour des ondes transverses, et apparaissent ensemble ou séparément selon la nature du mode que l’on propage.

On analyse les résultats avec un simple modèle de relaxation et on déduit de la forme des deux pics d’absorption des séparations d’énergie entre niveaux de 14,4 ± 0,2 cm⁻¹ et 42,2 ± 0,6 cm⁻¹ respectivement. Ces chiffres sont confirmés par la spectroscopie infra-rouge lointaine.

On suggère que les pics peuvent être dus à des ions Fe²⁺ sur des sites octaédriques distordus.

Abstract. — Microwave acoustic absorption measurements have been made on dark green schörlite tourmaline at 580 MHz and 1.03 GHz and as a function of temperature between 1.5 K and 300 K. In addition to thermal-phonon attenuation, two large low temperature peaks are found. These peaks are most pronounced for transverse wave propagation and are found together or individually, depending on the mode propagated.

The data has been analysed on a simple relaxation model and energy level separations of 14.4 ± 0.2 cm⁻¹ and 42.2 ± 0.6 cm⁻¹ have been deduced from the form of the two absorption peaks. These figures are confirmed by far-infrared spectroscopy.

It is tentatively suggested that the peaks may be caused by Fe²⁺ ions on distorted octahedral sites.

1. Introduction. — The tourmalines are a group of piezoelectric minerals of space group R3m which have a wide range of chemical compositions [1], but a general chemical formula,

$$(\text{Na, Ca})_3\text{Al}_6(\text{SiO}_3)_6(\text{BO}_3)_3(\text{OH}, \text{F})_4$$ [2, 3].

The end members of the group are, schörl with $R = \text{Fe}^{2+}$, Mn, dravite with $R = \text{Mg}$, elbaite with $R = \text{Li}$, Al and buergerite with $R = \text{Fe}^{3+}$. The microwave ultrasonic properties of tourmalines are of interest because of their high Debye temperature ($\sim 800$ K) and the large number of atoms per unit cell ($\sim 150$), a combination which is predicted to give very low thermal phonon attenuation [4]. The attenuation of longitudinal waves propagating along the threefold axis of a dravite has been measured by Lewis and Patterson [5] and found to be sufficiently low to make the material of interest for device applications in the giga-hertz range [6].

Because tourmaline has proved hard to grow in the laboratory [7] and since naturally occurring specimens of sufficient size and perfection for use in ultrasonic absorption measurements tend to occur near the schörl end of the schörl-elbaite, schörl-dravite range of compositions, these iron rich tourmalines were investigated in some detail. Two samples of single crystal schörl, of essentially identical composition and both originating from the Mines Gerais in Brazil, were supplied by Roditi International and GEC Ltd.

2. Analysis of the schörl samples. — The schörl specimens used in the attenuation measurements had a density in the range 3.15 ± 0.01 g cm⁻³. Similar specimens were given a partial analysis by wet chemical methods to characterize the material and to determine the concentration of paramagnetic species. Table I shows the average of the results obtained from the two crystal samples, compared with an average of four
TABLE I

A comparison of the structural formulae of the present tourmalines with those of typical schörls presented in terms of number of ions in a molecular unit. There are three molecular units in each unit cell.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Average of samples from GEC and Roditi International</th>
<th>Average of previously reported schörl samples [19], [20], [21], [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>(5.8 ± 0.1)</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>Be</td>
<td>(2.8 ± 0.3)</td>
<td>2.8 ± 0.3</td>
</tr>
<tr>
<td>Al</td>
<td>(4.6 ± 0.4)</td>
<td>6.55 ± 0.15</td>
</tr>
<tr>
<td>Li</td>
<td>(0.77 ± 0.06)</td>
<td>0.77 ± 0.11</td>
</tr>
<tr>
<td>Mg</td>
<td>(0.07 ± 0.02)</td>
<td>0.73 ± 0.07</td>
</tr>
<tr>
<td>Ti</td>
<td>(0.034 ± 0.010)</td>
<td>0.052 ± 0.015</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>1.28 ± 0.02</td>
<td>0.14 ± 0.14</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>1.8 ± 0.2</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.08 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.14 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.026 ± 0.002</td>
<td>0.14 ± 0.14</td>
</tr>
<tr>
<td>Na</td>
<td>1.24 ± 0.04</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>0.080 ± 0.008</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>K</td>
<td>&lt; 0.02</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>OH</td>
<td>(3.4 ± 0.6)</td>
<td>3.4 ± 0.6</td>
</tr>
<tr>
<td>F</td>
<td>(0.25 ± 0.25)</td>
<td>0.25 ± 0.25</td>
</tr>
<tr>
<td>O</td>
<td>27.4 ± 0.8</td>
<td>27.4 ± 0.8</td>
</tr>
</tbody>
</table>

Total number of atoms in a unit cell: 143.7 ± 5.4, 150 ± 7.2

( ) No analysis of this ion in our samples are made. The number of ions in the structural formula is assumed to be the same as that given in column three.

Published analyses of schörl crystals. The method of obtaining the solution of tourmaline was by dissolving it in a solution of perchloric acid and hydrofluoric acid in a teflon pressure bomb [8]. This procedure almost certainly changed the oxidation state of the iron. Therefore it is only possible to quote the total iron content. The unit cell dimensions of our schörlite samples were found from X-ray analyses. The samples from GEC have unit cell dimensions of $a = 15.89$ Å, $c = 7.12$ Å and the Roditi samples gave values of $a = 15.85$ Å, $c = 7.13$ Å. These results confirm that our samples have the character of tourmalines in the schörl-elbaite range of compositions [9].

3. Experimental method and attenuation results. — Cylindrical specimens of tourmaline were cut, oriented along the orthogonal $a$, $b$ and $c$ crystallographic axes. The ends of these rods were polished flat and parallel to optical tolerances and standard pulse-echo and cryogenic techniques were then used to measure the microwave ultrasonic attenuation. Measurements were made with both longitudinal and transverse modes at 580 MHz and 1.03 GHz and between 1.5 K and 300 K. It should be noted that the slow (S) and fast (F) transverse modes which are not exactly pure. Here the polarization of the longitudinal mode lies $1.5^\circ$ out of the basal plane. The natural piezoelectric properties of tourmaline were used for generation and detection, where this was possible. Cadmium sulphide thin film transducers, overlaid on aluminium thin films, were used for the modes which did not couple to an external electric field, in particular for the fast transverse modes in the basal plane. The aluminium coating was used both as a ground plane for the transducer and to give greater adhesion of the cadmium sulphide films to their substrates.

Measurements of ultrasonic attenuation were made by recording the echo patterns on an X-Y plotter and comparing pairs of echoes at different temperatures. Above about 100 K, however, the attenuation obtained had a dependence on the pair of echoes selected for comparison and the measurements become less reliable. This effect has been previously observed in other dielectrics containing magnetic ions, and is thought to be due to inhomogeneous ionic concentrations and consequent buckling of the acoustic wave front during propagation.

The measurements made on longitudinal modes are shown in figure 1. It can be seen that in each case the attenuation exhibits a plateau like high temperature region and falls rapidly below 20 K, a behaviour typical of the losses in a dielectric material [10]. There is little evidence for strong peaks. The measurements made on the $c$ axis degenerate shear mode and the slow shear modes propagating in the basal plane are so similar both in magnitude and form that for clarity
only the 580 MHz and 1.03 GHz measurements made for b axis propagation are shown in figure 2. In addition to the thermal phonon attenuation plateau there is a strong low temperature peak which increases in magnitude and moves to higher temperatures as the frequency is increased. A typical result for a basal plane fast shear mode is shown in figure 3. Two low temperature peaks can be observed, one in a similar position to the peak on the slow shear attenuation and one higher in temperature. The results are summarized in table II, where the peak heights, corrected for an estimated phonon-phonon contribution, are given for the various modes measured. The transverse mode propagating along the c-axis of an almost iron free dravite was also investigated at 580 MHz and no peaks in the attenuation were detected to 0.02 dB cm\(^{-1}\).

![Graph showing attenuation versus temperature for different frequencies and propagation directions.](image)

**FIG. 2.** — Experimental slow transverse wave attenuation in tourmaline as a function of temperature : Curve 1, 1.03 GHz, b axis ; Curve 2, 0.58 GHz, b axis.

**FIG. 3.** — 0.58 GHz, b axis, fast transverse wave attenuation in tourmaline as a function of temperature.

**TABLE II**

*The heights of the observed relaxation peaks (in dB cm\(^{-1}\))*

<table>
<thead>
<tr>
<th>Propagation, direction and polarization</th>
<th>0.58 GHz</th>
<th>1.03 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low temperature peak</td>
<td>High temperature peak</td>
</tr>
<tr>
<td>c L ((^1))</td>
<td>&lt; 0.01</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>T ((^1))</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>a L ((^1))</td>
<td>&lt; 0.01</td>
<td>0.25 ± 0.1</td>
</tr>
<tr>
<td>F ((^1))</td>
<td>0.45 ± 0.1</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>S ((^1,2))</td>
<td>3.4 ± 0.2</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>b L ((^2))</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>F</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S ((^2))</td>
<td>3.5 ± 0.2</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

Key to Table :

L : Longitudinal waves.
F : Fast transverse waves.
S : Slow transverse waves.
(\(^1\)) Crystal samples obtained from Roditi International.
(\(^2\)) Crystal samples obtained from the General Electric Co.
4. Analysis of results. — The lower temperature peaks found in the schörl samples have the characteristics of typical relaxation phenomena. The peaks are broad, the heights are close to being linearly proportional to the frequency of measurement and the peak positions move upwards in temperature as the frequency is raised.

In its simplest form, the relaxation model considers that the absorption is due to a collection of identical systems each of which can exist in one of two originally degenerate or nearly degenerate ground states. The presence of a strain ε, causes one of the levels to be raised in energy by an amount $\Delta E$ and the other to be depressed by the same amount, where $\Delta E$ is the strain coupling coefficient. If the strain is provided by an ultrasonic wave, there will be a sinusoidal time dependence of frequency $\omega$. If there is a relaxation between the levels, then an attenuation of the ultrasound results which is given by

$$\alpha = 4.343 \frac{\bar{V}^2 N}{\rho k T^3} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \text{dB/unit length} \quad (1)$$

where $N$ is the number of absorbing systems per unit volume, $\tau$ is the relaxation time between the levels, $\rho$ is the density of the medium and $\bar{V}$ is the ultrasonic velocity. This expression has been used to derive the dependence of $\tau$ on temperature and propagation mode, from the shape of the individual peaks.

The lower temperature peak occurs at temperatures where the phonon-phonon connection is small and uncertainties in its estimation cause little error. The resulting form of $\tau(T)$ is shown in figure 4. The data obtained from the different measurements of the low temperature peak are substantially in agreement. The higher temperature peak was obtained by subtracting the lower temperature peak and the phonon-phonon contribution, both of which were estimated from the measured attenuations. From the resulting relaxation peak, and using equation (1), $\tau(T)$ was calculated and is shown in figure 4.

A possible source of these peaks could be relaxation between the energy levels of paramagnetic ions. At the temperatures considered in this work, only direct and Orbach relaxation processes are of significance. The relaxation rate associated with these two processes is

$$\frac{1}{\tau} = AT + \sum \frac{B_i}{\tau} \exp \{ -\Delta_i/kT \} - 1 \quad (2)$$

where $A$ and $B$ are constants and $\Delta/k$ is the separation of higher levels from the strain split lower energy levels. Two peaks may be produced either from two distinct ion species or from the energy levels of a single ion which have been effectively uncoupled into two distinct groups by their symmetry and the phonon selection rules [12]. Figure 4 shows a best fit to $\tau(T)$ derived from the low temperature peak and calculated from equation (2), using a single Orbach term. The coefficients have values

$$A = 4.2 \pm 1.3 \times 10^6 \text{ s}^{-1} \text{ K}^{-1}$$
$$B = 1.00 \pm 0.05 \times 10^{10} \text{ s}^{-1}$$
$$\Delta/k = 20.7 \pm 0.3 \text{ K} \equiv 14.4 \pm 0.2 \text{ cm}^{-1}. \quad (3)$$

Within experimental error a good fit is obtained to the experimental data. The higher temperature peak was treated in a similar way and again a good fit to the experimental relaxation rate data was obtained using equation (2). This fit is also shown in figure 4 and uses:

$$A = 2.9 \pm 0.9 \times 10^6 \text{ s}^{-1} \text{ K}^{-1}$$
$$B = 6.3 \pm 0.3 \times 10^6 \text{ s}^{-1}$$
$$\Delta/k = 60.6 \pm 0.8 \text{ K} \equiv 42.2 \pm 0.6 \text{ cm}^{-1}. \quad (4)$$

In the above analysis it was assumed that $N$ was temperature independent. King and Oates [12] have found that the difference between $\Delta/k$ calculated using temperature dependent and temperature independent values of $N$ is very small. Therefore the values of $\Delta/k$
5. The infrared and optical absorption spectrum of tourmaline. — A study was made of the far infra-red absorption of schörl and rubellite, an elbaite which is extremely weak in iron. The transmission of thin slides of these materials was measured at room temperature using a Fourier spectrometer. Two broad absorption bands were found in the schörl centred at 15 ± 4 cm⁻¹ and 42 ± 4 cm⁻¹ which are in good agreement with 14.4 ± 0.2 cm⁻¹ and 42.2 ± 0.6 cm⁻¹ respectively which are given in equation (3) and equation (4). No absorption bands were found in rubellite in this region. However reducing the amplitudes of the observed infrared absorption bands seen in schörl by the ratio of the concentration of Fe²⁺, Ti, Mg or K ions in our schörl samples to that in rubellite would reduce the bands to a magnitude of less than the error on the spectrum of rubellite. Therefore any of these ions could be responsible for the two infrared absorption bands and the ultrasonic attenuation peaks.

No absorption peaks larger than 0.02 dB cm⁻¹ were observed in a dravite, low in iron for transverse waves propagating along the c-axis, whereas an 8.2 dB cm⁻¹ peak was observed in schörl for a similar mode and propagation direction. Comparing the chemical composition of dravite with that of our schörl samples (Table I) and assuming that the ion responsible for the attenuation peaks is in a similar environment in both schörl and dravite, then Fe ions are the most likely source of the ultrasonic attenuation peaks. However because there is no published analysis of Cr or Ni in dravite no conclusion can be made on the role of these ions in the absorption process.

Absorption spectra of our schörl samples were also obtained between 4 000 cm⁻¹ and 50 000 cm⁻¹. Absorption bands were observed at 9 200 cm⁻¹, 14 000 cm⁻¹, 18 000 cm⁻¹ and 23 000 cm⁻¹. Similar absorption bands were reported by Wilkins et al. [13] and Manning [14] for a black schörl. They attributed the 9 200 cm⁻¹ and 14 000 cm⁻¹ bands to ¹T₂ → ⁵E transitions involving Fe²⁺ ions in distorted octahedral sites with the ⁵E state split by about 5 000 cm⁻¹. From the tourmaline crystal structure given by Ito, Sadas, and Doonay [3] and Doonay, Buerger [15] the Fe²⁺ sites are each of distorted octahedral symmetry and are arranged so that three sites from an equilateral triangle in the basal plane. The explanation put forward by Manning [14] is therefore not unreasonable one. Wilkins et al. [13] have suggested that the absorption bands at 18 000 cm⁻¹ and 23 000 cm⁻¹ are due to Fe³⁺ ions, which have replaced some of the Fe²⁺ in the distorted octahedral sites, undergoing ⁶A → ⁴T₂ and ⁶A₁ → ⁴A₁ type transitions.

6. Discussion. — Although it is possible for dislocation movements [16] to produce attenuation peaks, the temperature dependences observed here and the agreement of our calculated energy level separations with the infrared data and the magnitude of the separations make it extremely likely that the peaks are due to magnetic ions. We have at present inadequate evidence to clearly identify the ion or ions responsible but Fe²⁺ is a most likely candidate. Not only is it the most abundant paramagnetic species but Fe²⁺ on octahedral sites is known to give relaxation peaks in other materials.

If as a first approximation it is assumed that the Fe²⁺ ions are in regular octahedral sites, then only ultrasound with an irreducible representation (ir) of E (tetragonal) can couple with the ions [17]. Therefore because the Fe²⁺ ions are situated at the corners of equilateral triangles in the basal plane, only transverse modes have an E type ir and exhibit relaxation absorption for propagation along the c axis. This is in agreement with experimental results. For ultrasound propagating along the a- or b-axis group theory predicts that both the longitudinal and transverse modes will couple to some degree to the Fe²⁺ ions. From experiment, the transverse modes are more strongly coupled to the Fe²⁺ ions than the longitudinal modes to a degree which suggests the model may be in error, but introducing a tetragonal distortion to the octahedral sites does not remove the problem. At the concentration of iron in schörl many of the triangular sites have more than one Fe²⁺ ion and the possibility exists for exchange interactions to occur between the ions of a triangle [18]. This would require further modifications to the simplified model of the Fe²⁺ sites proposed above.

7. Conclusion. — Broad peaks in the attenuation of ultrasound in tourmaline have been observed. These peaks are most pronounced for transverse wave propagation, and depending on the ultrasonic mode, two peaks are observed, one at ~ 11 K and the other at 45 K. These peaks in some cases extend to room temperature and would adversely affect the performance of tourmaline as a low loss device material. From the available X-ray, chemical, spectroscopic and ultrasonic data, it appears probable that Fe²⁺ in distorted octahedral sites in our samples may cause relaxation absorption of ultrasound propagating in this material. It is proposed that the relaxation absorption occurs via Orbach and direct processes. A good fit to experimental data is obtained when the energy separation between the energy levels is 14.4 ± 0.2 cm⁻¹ and 42.2 ± 0.6 cm⁻¹ for the low temperature and high temperature peaks respectively. When Fe²⁺ is not present, or is in low concentration, the only significant attenuation is that due to phonon-phonon interactions, and is among the lowest values observed for any crystal [6].
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References