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The temperature-dependent optical activity of quartz: from Le Châtelier to chirality measures

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Abstract—Quartz, the most abundant mineral in Earth's crust, is a chiral crystal. It was the first material for which the phenomenon of the optical rotation was observed. In the late 19th century/beginning of the 20th, several researchers, the most famous of which is Le Châtelier, investigated how this optical rotation changes with temperature. By employing a modern analytical/computational tool for evaluating the degree of chirality on a continuous scale, we were able to show a remarkable agreement between the original optical rotation/temperature curve, and the chirality/temperature curve. We thus provide a direct interpretation of the early observations, as reflected in the dependence of the optical rotation of the degree of chirality, linking these two properties quantitatively.

1. Introduction

Herein, we report that the changes in the optical rotation of quartz with temperature are directly correlated with the quantitative degree of chirality of the SiO_4 helices that compose this material. In doing so, we provide a structural interpretation to the century-old quartz studies of Le Châtelier[1] (1850–1936; best known for his 'Le Châtelier's Principle') and of his contemporaries.[2] We also report the utility of quantifying chirality—classically treated as a 'yes/no' structural property—in identifying material property/structure correlations. In fact, quartz, the most abundant crystalline material in the Earth's crust and a key component in modern optoelectronics,[3] was the first crystal for which optical rotation was observed.[4] The combined optical rotation/temperature early studies are shown in the inset of Figure 1 (as originally presented by Lowry):[5] They cover a broad range of temperatures (−200-1000 °C; 98-1298 K), crossing also the phase transition from low-quartz—which is the commonly found form—to high quartz (around 848 K[6]).[7] Here we show a remarkable fit of this curve to the underlying structural chirality changes.

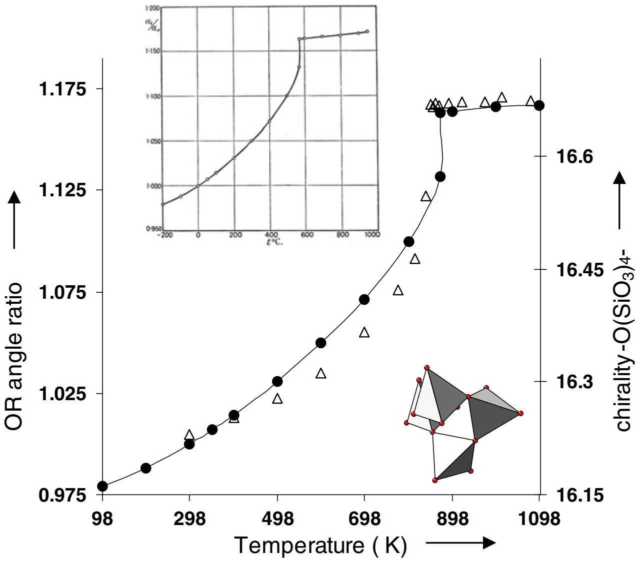

Figure 1. The optical rotation and the chirality of quartz—superposition of old and new: the temperature-dependent changes of the optical rotation (upper inset covering various studies in the years 1889–1909;[5] and dots, left axis); and in the degree of chirality (triangles, right axis) of the helical fragment –$O(SiO_3)_4$– (inset). The optical rotation measurements were taken along the optical axis (the 33-tensor). The phase transition from low to high quartz is clearly visible at 848 K.

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2. Results and discussion

The degree of optical rotation of a chiral crystal depends (amongst other parameters) on the structural details of the molecular units that form it, and as this structure changes with temperature, its ability to rotate circularly polarized light is affected as well. In other words, the 'degree of geometrical chirality' and the level of the interaction with the incident light should be correlated. For quartz, the molecular level chirality is mainly manifested by the beautiful helices of the oxygen-linked SiO_4 tetrahedra, which compose it, such as the helix, which is used as the crystallographic label for quartz ($P3_221$) (Fig. 1, inset).

We have just used the phrase 'degree of geometrical chirality'. The notion of treating chirality not in the dichotomic terms of either an existing property or not, but as a quantitative term on a continuous scale has developed quickly over the past two decades, and this modern approach has been used successfully for many chirality related problems (for recent reviews, including other approaches).[8,9] In brief, the approach has been to formulate a general measure of symmetry, which can be used for the quantitative evaluation of any symmetry point group (chirality, we recall, is characterized by the lack of improper elements of symmetry such as reflection and inversion). Thus, the evaluation of the degree of G-symmetry, $S(G)$, or of the degree of chirality, S_{ch}, by the continuous symmetry or chirality measures (the CSM and CCM) is based on finding the *minimal* distance that the atoms of the studied molecule (or a fragment of it) have to be shifted in order to reach the G-symmetry (any symmetry for the CSM; the nearest achiral symmetry for the CCM). If a structure has the desired G-symmetry or is achiral, then $S = 0$ and the measure increases (up to an upper bound, which is 100 or less[10]) as it deviates from the G-symmetry or becomes more chiral.[11] A relevant quantitative-chirality result for this report is the observation[12] that the chirality of the helix of quartz reaches its maximal value already after one turn and a third, namely in a fragment, which is composed of four tetradra, –$O(SiO_3)_4$– (Fig. 1, inset); we therefore focus on this fragment, and show that the early results are associated with the temperature-dependent changes in the degree of chirality of quartz.

For that purpose we use the temperature-dependent X-ray-derived structural data of Kihara[13] who covered the range of 298–1073 K. The changes in the degree of chirality of the helical fragment with temperature are shown in Figure 1 (triangles).[14] It can be seen that the degree of chirality increases with temperature, following practically the same curve-shape of the changes in optical rotation (reproduced as dots). The striking overlap of the two curves indicates that the relation between the optical rotation and the degree of chirality is nearly linear. Furthermore, since the CSM methodology is general,[15] it can be used for the determination of yet another important structural feature of the changing helix, namely its degree of helicity. Determining how helical, a helix is, can be carried out in a number of ways. The most straightforward one is the evaluation of the degree of the most characteristic symmetry of a helix, namely its degree of C_2-symmetry (the C_2 axis bisects the long helical axis). When one evaluates the degree of C_2-ness of the helix, the value is not zero (and this should come as no surprise, since the C_2-axes of the individual atom-helices do not coincide). We then used the temperature-affected changes in $S(C_2)$, with the results shown in Figure 2 (open circles). It can be seen that the behaviour of $S(C_2)$ mirrors that of the chirality change: as the temperature increases and with it also the optical rotation, the $S(C_2)$ decreases. Note again the fit to the optical rotation changes (Fig. 2, dots), reciprocal in this case. In terms of helicity we would say that it *improves* with temperature (becomes closer to being C_2-symmetric); improvement in helicity and enhancement in chirality thus go hand in hand, confirming the expectation of the relation between the two symmetry elements.

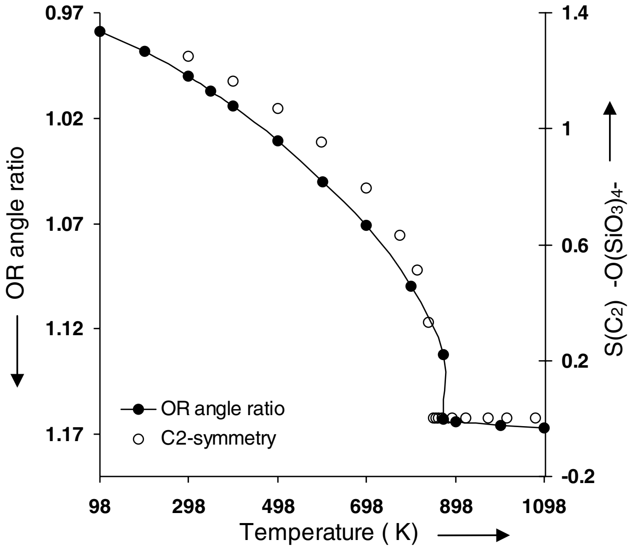

Figure 2. The dependence of the degree of C_2-symmetry (representing the degree of helicity; right axis, open circles) of the helical fragment –$O(SiO_3)_4$– on temperature. Note the 'mirror' behaviour compared to the chirality changes in Figure 1 (triangles); and the reciprocal superposition with the changes in the optical rotation (left; dots).

3. Conclusion

In conclusion, we have been able to link the 19th century optical rotation observations of Le Châtelier and his contemporaries to quantitative changes of chirality. We have shown that the increase in optical rotation with temperature is associated with an increase in the degree of chirality and a decrease in the degree of helicity of its helical molecular building blocks. In doing so, we have also shown that the continuous symmetry and chirality measures approach translate chirality changes in realistic way. It should be noted, however that for such correlations to emerge, a homologous series of structures is needed, such as the gradually changing –$O(SiO_3)_4$– fragment used here. Indeed, other examples for correlations between the degree of chirality in a homologous series of structures or molecules and chemical/physical properties exist,[8] and some examples include the enantioselective chromatographic separation of helicenes,[16] the deactivation of enzymes with chiral inhibitors,[17] and the enantiomeric excess of the chiral product obtained with a series of chiral catalysts.[18] The computational programs of the symmetry and chirality measures described herein can be used freely at http://www.csm.huji.ac.il, or by writing to the authors.

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$$S(G) = \min\left[\frac{\sum_{i=1}^{N}|Q_i - P_i|^2}{\sum_{i=1}^{N}|Q_i - Q_0|^2}\right] \times 100$$

   where N is the number of vertices. The denominator is a mean square size normalization factor. The main computational task is to find P_i. Several methods have been developed towards this goal, and are described in Refs. 8–10. Finally, $S(G)$ values, regardless of G or of the structure, are on the same scale and therefore comparable.
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