SUPPLEMENTARY MATERIAL

PARAMETERS AND ASSIGNMENTS OF WATER-RELATED MODES OBSERVED IN BERYL FOR POLARIZATIONS E⊥c AND E||c AT T = 5 K.

TABLE I. Parameters and assignments of water-related modes observed in beryl for polarization ***E***⊥*c* at *T* = 5 K: *E* – energy, ν_0 – eigenfrequency, *f* – oscillator strength (intensity), γ – damping. Stars mark the values obtained using the model of coupled Lorentzians (expression 2).

Terahertz band					
E (meV)	**ν_0 (cm^{-1})**	**f (cm^{-2})**	**γ (cm^{-1})**	**(G,m)-(G,m)**	**Assignment**
1.33	10.7*	106 *	12 *	(G,0)-(G,1)	Water-I. Intra-ground (G) band
3.21	25.9*	1 770 *	25 *	(G,1)-(G,2)	Water-I. Intra-ground (G) band
5.21	42	74	1.5	?	Water-II
5.82	47	134	6	?	Water-II
Far-infrared translation band					
E (meV)	**ν_0 (cm^{-1})**	**f (cm^{-2})**	**γ (cm^{-1})**	**(G,m)-(T,m)**	**Assignment**
14.01	113	3 320	43	(G,1)-(T,0)	Water-I. T-band: transitions between ground band (G) and translation band (T)
14.51	117 *	2 960 *	8 *	(G,2)-(T,1)	
18.35	148 *	1 860 *	34 *	(G,0)-(T,1)	
21.33	172	900	19	(G,3)-(T,2)	
23.44	189	780	15	(G,1)-(T,2)	
27	218	1300	42	(G,2)-(T,3)	
Far-infrared libration band					
E (meV)	**ν_0 (cm^{-1})**	**f (cm^{-2})**	**γ (cm^{-1})**	**(G,m)-(L,m)**	**Assignment**
36.21	292	2 020	34	(G,1)-(L,0)	Water-I. L-band: transitions between ground band (G) and libration band (L)
46.38	374	13 220	15	(G,2)-(L,1)	
53.32	430	10 750	14	(G,0)-(L,1)	
56.05	452	26 600	8	(G,3)-(L,2)	
56.92	459	10 110	5.9	(G,1)-(L,2)	
58.53	472	42 870	9	(G,2)-(L,3)	

TABLE II Parameters and assignments of water-related modes observed in beryl for polarization ***E***⊥*c* at *T* = 5 K: *E* – energy, ν_0 – eigenfrequency, *f* – oscillator strength (intensity), γ – damping. Bold numbers correspond to intramolecular H_2O modes; numbers in the brackets show how much the intramolecular H_2O modes in beryl have softened or hardened relative to their positions in free water molecule. Differences between positions of ν_1, ν_2 and ν_3 intramolecular water vibrations and of the observed modes are presented.

Infrared modes around internal ν_2 (1595 cm^{-1}) mode of free H_2O molecule				
E (meV)	**ν_0 (cm$_{-1}$)**	**f (cm^{-2})**	**γ (cm$_{-1}$)**	**| $\nu_{2water-I}$ - ν_0| (cm^{-1})**
197.3	**1 591**	**695**	**7.4**	**ν_2, Water-I (4 cm^{-1} hardened)**
197.7	1 594	84	2.6	3
198.0	1 597	215	5	6
199.9	1 612	857	29	21

202.7	1 634	190	25	43
212.0	1 710	29	12	119

Infrared modes around internal ν_1 (3657 cm^{-1}) and ν_3 (3756 cm^{-1}) modes of free H_2O molecule

E (meV)	ν_0 (cm^{-1})	f (cm^{-2})	γ (cm^{-1})	$\lvert\nu_{1water\text{-}I} - \nu_0\rvert$ (cm^{-1})	$\lvert\nu_{3water\text{-}II} - \nu_0\rvert$ (cm^{-1})
389.9	3 144	32	14	461	528
446.2	3 598	80	12	7	74
446.9	**3 604**	**277**	**0.8**	**ν_1, Water-I (53 cm^{-1} softened)**	
449.5	3 625	70	52	20	47
453.7	3 659	57	4	54	13
454.3	3 664	270	8	59	8
454.8	3 668	70	4.4	63	4
455.1	3 670	15	1.8	65	2
455.3	**3 672**	**342**	**6.6**	**ν_3, Water-II (84 cm^{-1} softened)**	
455.7	3 675	36	3	71	3
456.0	3 677	225	5.5	73	5
457.1	3 686	136	5	82	14
458.7	3 699	20	3	95	27
461.8	3 724	144	20	120	52
463.9	3 741	4	7	137	69
465.4	3 753	183	22	149	81
479.4	3 866	40	13	262	194
483.0	3 895	250	30	291	223
486.1	3 920	60	15	316	248
653.5	5 270	50	7	1 665	1 598

TABLE III. Parameters and assignments of water-related modes observed in beryl for polarization ***E***||*c* at $T = 5$ K: *E* – energy, ν_0 – eigenfrequency, f – oscillator strength (intensity), γ – damping. Bold numbers show parameters of intramolecular H_2O modes. For infrared range, differences are presented between positions of ν_1, ν_2 and ν_3 intramolecular water vibrations and of the observed modes.

Terahertz band

E (meV)	ν_0 (cm^{-1})	f (cm^{-2})	γ (cm^{-1})	Assignment
10.91	88	200	4	Translation mode of Water-I
19.6	158	2 780	22	Librational mode of Water-I

Infrared modes around ν_2 (1595 cm^{-1}) of free H_2O molecule

E (meV)	ν_0 (cm^{-1})	f (cm^{-2})	γ (cm^{-1})	$\lvert\nu_{2water\text{-}II} - \nu_0\rvert$ (cm^{-1})
197.2	1 590	21	1.7	32
201.1	**1 622**	**12 450**	**0.7**	**ν2, Water-II (27 cm^{-1} hardened)**
220.7	1 780	82	37	158

Infrared modes around ν_1 (3657 cm^{-1}) and ν_3 (3756 cm^{-1}) of free molecule mode

E (meV)	ν_0 (cm^{-1})	f (cm^{-2})	γ (cm^{-1})	Assignment
446.3	**3 599**	**955**	**5.5**	**ν_1, Water-II (58 cm^{-1} softened)**
458.3	**3 696**	**490**	**5.6**	**ν_3, Water-I (60 cm^{-1} softened)**
653.4	5 269	95	2.9	$\nu_1 + \nu_2$ (= 5 221 cm^{-1}), Water-II

Temperature behavior of water related resonances

In Figs. 1 - 4 we present in detail the temperature dependences of the parameters obtained from the water-related absorption resonances which correspond to transitions from the ground band to the translation and libration bands for the polarization $\boldsymbol{E}\perp c$. In addition, Fig. 1 shows the similar dependences for the other polarization, $\boldsymbol{E}\|c$. Only weak changes of the damping constants are observed for these essential modes in the broad range of temperature from 290 K to 100 K; this implies that the damping mechanism is mostly determined by impurities.

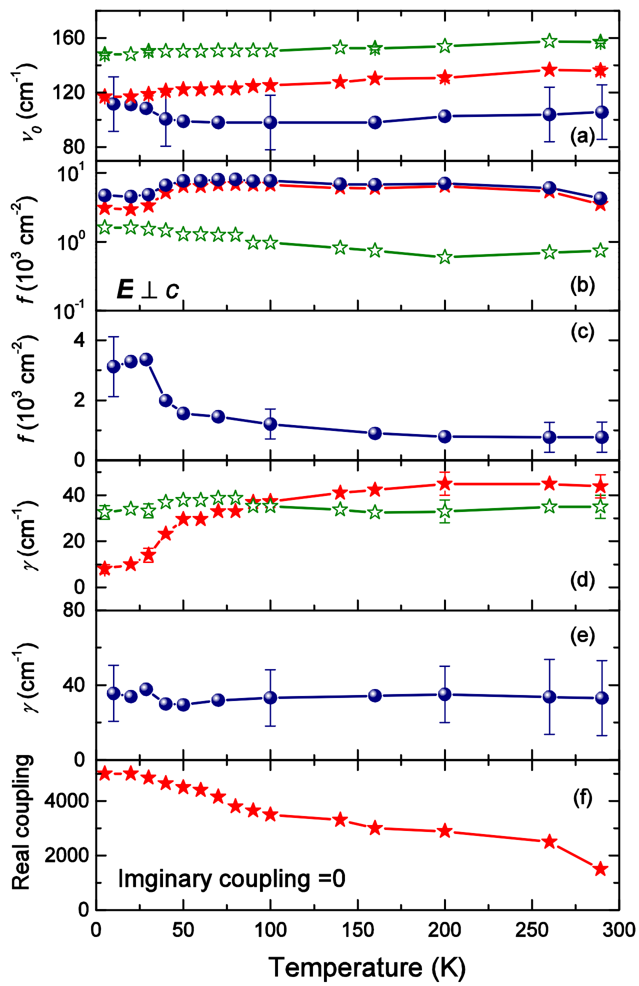

FIG. 1. (Color online). Detailed temperature dependences of parameters of the water-related absorption lines in beryl observed in the far-infrared range for polarizations $\boldsymbol{E}\perp c$: eigenfrequencies ν_0, oscillator strengths f, damping factors γ and coupling constant.

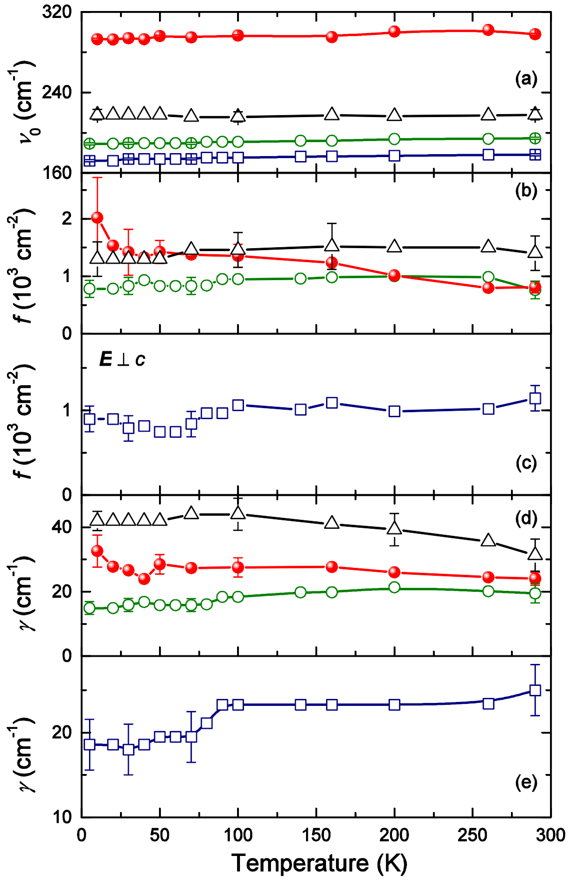

FIG. 2. (Color online). Detailed temperature dependences of parameters of the water-related absorption lines in beryl observed in the far-infrared range for polarizations $\boldsymbol{E} \perp c$: eigenfrequencies ν_0, oscillator strengths f, damping factors γ and coupling constant.

Fig. 6 displays the heat capacities, in $C_p(T)/T$ and $\Delta C_p(T)/T$ representations, of a beryl crystal and of a crystal measured after depletion of the crystal water, together with the literature data collected on a crystal with 0.36 H_2O per formula unit.[1] There is a clear difference between the data obtained on the water-containing and the dehydrated samples. The difference between the two data sets reaches its maximum value around 40 K – 50 K, i.e. at temperatures where oscillator strengths and dampings of some optical resonances reveal anomalous behavior, see main text. The dependence $\Delta C_p(T)/T$ was fitted to the sum of the heat capacities of four Bose-Einstein oscillators according to

$$C_V(T) = 3R\sum_{i=1}^{4} W_i \left(\frac{E_i}{k_B T}\right)^2 \frac{\exp(E_i/k_B T)}{\left[\exp(E_i/k_B T)-1\right]^2}\ , \qquad (1)$$

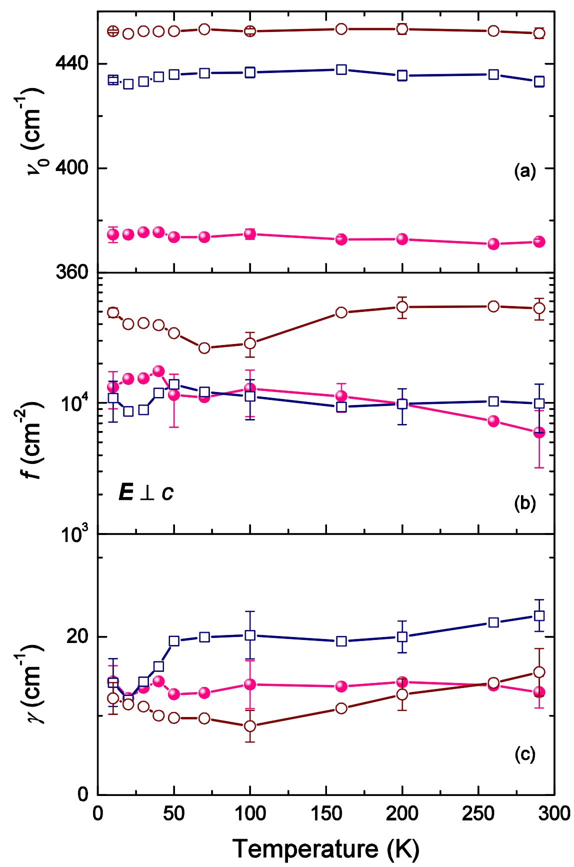

FIG. 3. (Color online). Detailed temperature dependences of parameters of the water-related absorption lines in beryl observed in the far-infrared range for polarizations $\boldsymbol{E}\perp c$: eigenfrequencies ν_0, oscillator strengths f, damping factors γ and coupling constant.

where E_i are the energies of the individual oscillators, W_i are the weights and R is the molar gas constant. Above ~10 K the Eq. (1) describes well the experimental data with energies and weights of the Bose-Einstein oscillators listed in the inset of Fig. 6. The energies of the oscillators compare well with characteristic low-energy terahertz-infrared absorption bands associated with water in beryl. Especially the sharp absorption band at ~117 cm^{-1} is well reproduced and accounts for the lower temperature contributions to the heat capacity of the crystal water. Below ~10 K, the approach with four Bose-Einstein oscillators is not fully adequate to describe the heat capacity completely. The difference $\delta C_p(T)/T$ between the calculated (on the basis of four oscillators) and the experimental data is plotted in the lower inset in Fig. 6. This difference is reminiscent of the heat capacity of a two-level *Schottky* anomaly with the two levels at an energy distance of ~10 K. Such an anomaly indicates excitations of very low energy. The weight, however, is very small and corresponds to ~2% of such two-level systems per formula unit of beryl also leaving extrinsic effects like lattice defects or imperfections which are modified by the annealing process as a possible origin.

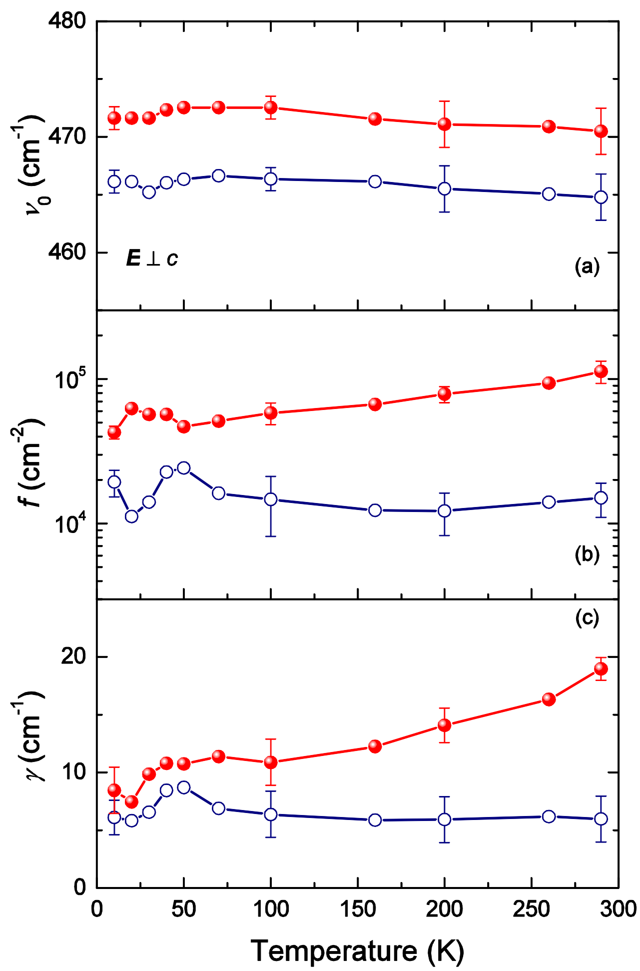

FIG. 4. (Color online). Detailed temperature dependences of parameters of the water-related absorption lines in beryl observed in the far-infrared range for polarizations $\boldsymbol{E}\perp c$: eigenfrequencies ν_0, oscillator strengths f, damping factors γ and coupling constant.

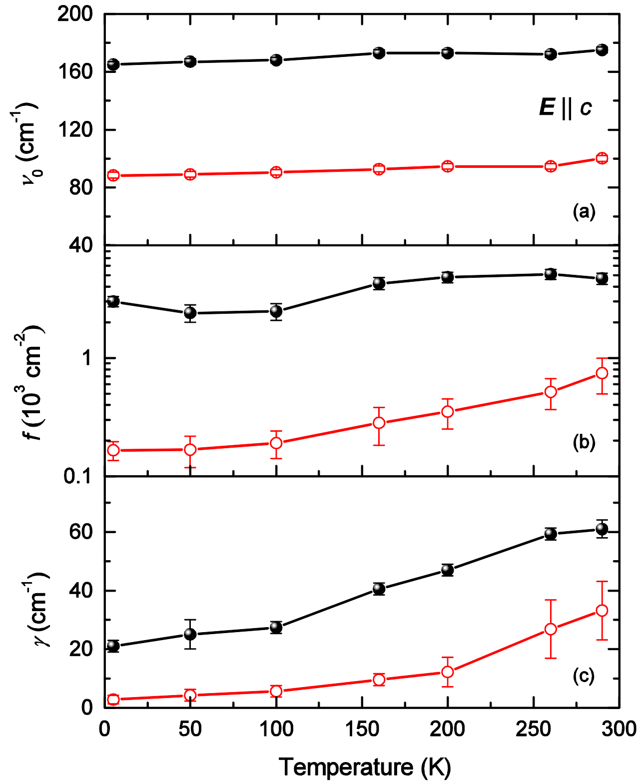

FIG. 5. (Color online). Detailed temperature dependences of parameters of the water-related absorption lines in beryl observed in the far-infrared range for polarizations E||c: eigenfrequencies ν_0, oscillator strengths f, damping factors γ and coupling constant.

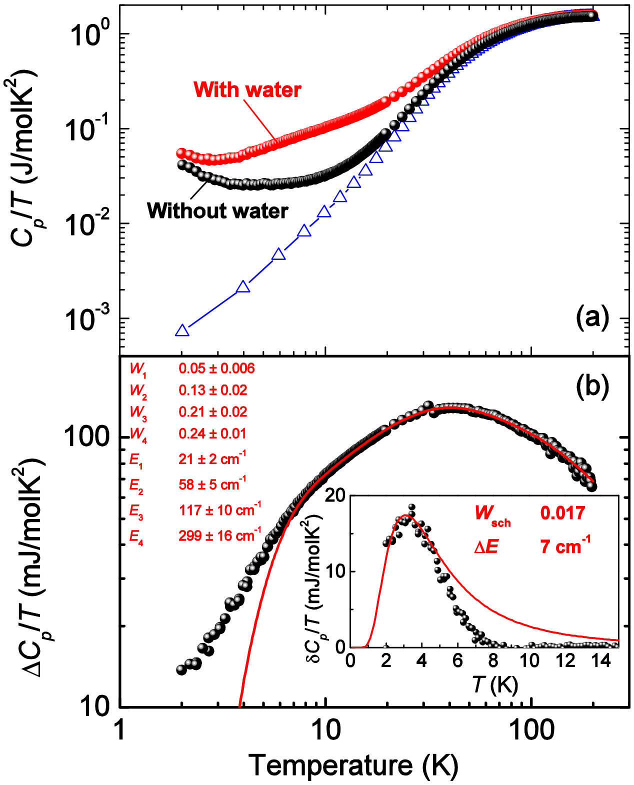

FIG. 6. (Color online). (a) Heat capacity of beryl with (red circles) and without (black circles) crystal water. Literature data by Hemingway et al. [1] for a beryl crystal with $0.36H_2O$ per formula unit are presented by blue triangles. (b) Difference of the heat capacities, ΔCp(T)/T, of a beryl crystal with and without crystal water. The solid (red) line shows the fit of the data with the heat capacity of four Bose-Einstein oscillators (expression (1)) with energies E (in wavenumbers) and weight factors W. The difference δCp(T)/T between the fit and the experimental data is shown by open symbols in the inset together with the heat capacity of a two-level Schottky anomaly (red line in the inset) with level distance of $\Delta E = 7$ cm^{-1} and with the weight $W_{Sch} = 0.017$.

[1] B. S. Hemingway, M. D. Barton, R. A. Robie, and H. T. Haselton Jr., Am. Mineral. **71**, 557 (1986).