Low-temperature heat capacity of heulandite: comparison with clinoptilolite

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Abstract

Low-temperature heat capacity of heulandite $Na_{0.365}K_{0.059}Ca_{0.861}Al_{2.138}Si_{6.860}O_{18} \cdot 6.17H_2O$ was measured in an adiabatic vacuum calorimeter. The results obtained were compared with those for heulandite and clinoptilolite from literature. The errors in measurements of the water content are shown to be the main reason of discrepancies among the data on heat capacities for the zeolites. The random error can be as high as 1.1%. The greatest systematic error of 2.5% was shown to be in the heat capacities of clinoptilolite. Unusual temperature dependence has been recognized in published data on heat capacity of clinoptilolite, as if free electrons are there in a silicate. Heat capacity of four different species of heulandite–clinoptilolite series are known. However, the data published do not enable one to recognize the relationship between heat capacity and a composition. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heat capacity; Zeolites; Heulandite; Clinoptilolite; Water content

1. Introduction

Zeolites heulandite and clinoptilolite are identical in structure [1]. By mineral classification, heulandite and clinoptilolite form the continuous series [2]. Thermodynamic properties of substances in series are the functions of chemical composition.

Low-temperature heat capacity of clinoptilolite was first published in [3]. The sample investigated was obtained from the tuff. The final results were corrected to the formula $(Na_{0.56}K_{0.98}Ca_{1.50}Mg_{1.23})(Al_{6.7}Fe_{0.3})Si_{29}O_{72} \cdot 22H_2O$.

Low-temperature heat capacity of heulandite was published in [4]. The sample investigated was crystals of the composition $(Ba_{0.065}Sr_{0.175}Ca_{0.585}K_{0.132}Na_{0.383})Al_{2.165}Si_{6.835}O_{18} \cdot 6.00H_2O$.

Low-temperature heat capacity of clinoptilolite was published in [5]. The sample investigated was crystals separated under a microscope. The composition $Sr_{0.036}Mg_{0.124}Ca_{0.585}Mn_{0.002}Ba_{0.062}K_{0.543}Na_{0.954}Al_{3.450}Fe_{0.017}Si_{14.533}O_{36.000} \cdot 10.922H_2O$ was defined. The results were found out to differ from those of [3] by about 3%. The discrepancies

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were explained by differences in the compositions or in the configurational entropies. However, the latter were not evaluated. Differences between heat capacities of clinoptilolite and heulandite were not discussed.

We have found that the distinctions in heat capacity between heulandite and clinoptilolite below 14 K are too large. It induces us to publish our own data on heat capacity of heulandite and to discuss the differences between heulandite and clinoptilolite. The second objective of the work was to check whether the data published are enough to recognize the relationship between heat capacity of these zeolites and their composition.

2. Experimental

Natural white semitransparent crystals of heulandite (Nidym river, Siberia) 1–3 mm across were investigated. Total sample weight is 6.024 g. According to chemical analysis, the sample contains (in wt.%): SiO_2 — 59.73, Al_2O_3 — 15.80, CaO — 7.00, K_2O — 0.40, Na_2O — 1.64, H_2O — 16.12; total — 100.69. The formula of the heulandite is $Na_{0.365}K_{0.059}Ca_{0.861}Al_{2.138}Si_{6.860}O_{18} \cdot 6.17H_2O$.

A schematic diagram of the cryostat is shown in Fig. 1. The cryostat has up to three stages of cooling when operates at minimal temperature of 1.7 K. External Dewar flask with liquid nitrogen (the first stage) has inside another Dewar flask with liquid helium (the second stage). The latter contains vacuum jacket with another vessel inside. The vessel is filled with liquid helium which is pumped out to cool it down (the third stage). Internal vacuum chamber with a calorimeter is attached to the vessel. To provide adiabatic conditions, the temperature of adiabatic shield is maintained equal to that of the calorimeter. Two series thermocouples compare the temperatures and a wire heater on the shield equalizes them.

Low-temperature heat capacity was measured using the calorimeter shown in Fig. 2. The calorimeter was made of copper, then was covered by silver and polished. The thickness of the walls ranges from 0.15 to 0.20 mm. The body and the bottom are welded together by solder which has no phase transitions above 1 K (50% Sn, 32% Pb, 18% Cd). The top is tied up with the bottom by means of a nut. There are
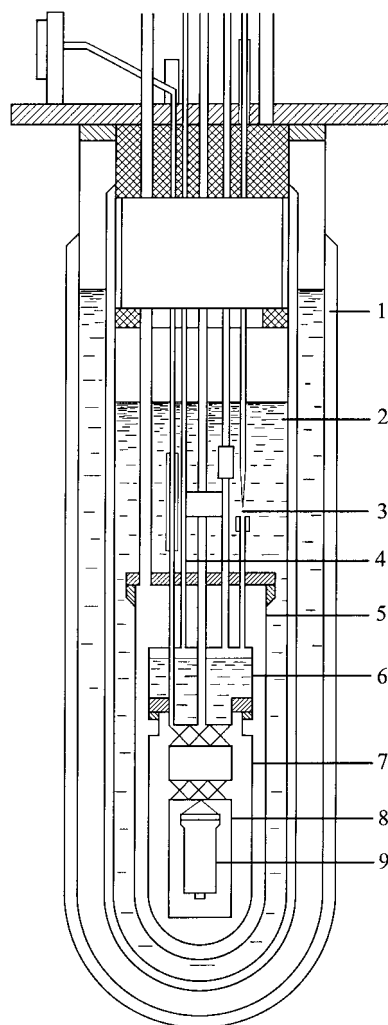

Fig. 1. *Cryostat*: 1 — Dewar flask with liquid nitrogen; 2 — Dewar flask with liquid helium; 3 — needle valve for the filling of vessel 6 with helium; 4 — tube to pump out helium of vessel 6; 5 — internal vacuum chamber; 6 — vessel for pumping helium out; 7 — external vacuum jacket; 8 — adiabatic shield; 9 — calorimeter.

cylindrical seats for a wrench in the top. The calorimeter is 65 mm in height, 15 mm in outside diameter, total mass 44 g, internal volume 6.5 cm³. The calorimeter is sealed by Teflon ring (mass 3 mg, thickness 0.04 mm) that is clamped with ridge (0.9 mm in thickness) on the top. The heater (650 Ω) was made from wire (0.05 mm in diameter). The temperature is measured by means of two thermometers. Both thermometers were made and calibrated in the Physico-
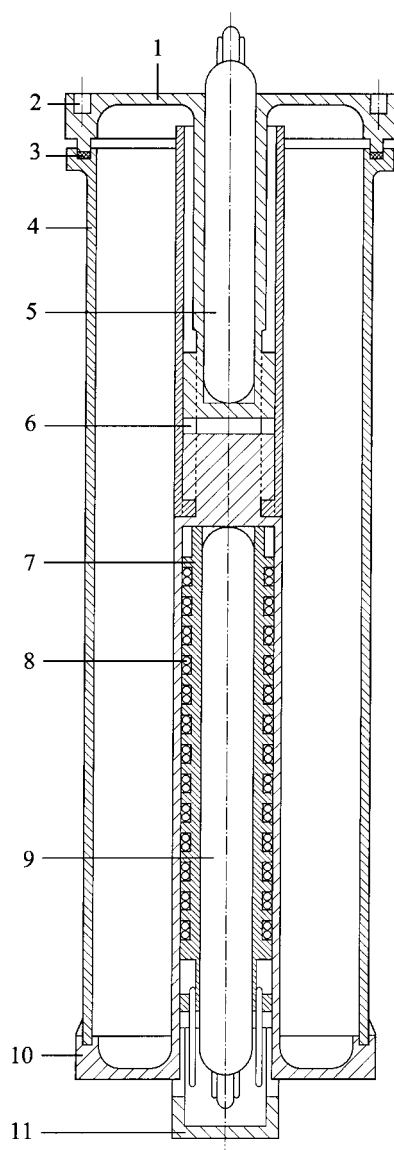
Fig. 2. Calorimeter: 1 — calorimeter top; 2 — the seats for a wrench; 3 — Teflon gasket; 4 — calorimeter body; 5 — germanium resistance thermometer; 6 — nut; 7 — heater body; 8 — heater's wire; 9 — platinum resistance thermometer; 10 — calorimeter bottom; 11 — radiation trap on the heater.

Technical and Radio-Technical Measurements Institute (PRMI, Moscow, Russia). The germanium resistance thermometer is used in the temperature range from 2 to 20 K [6], the platinum resistance thermometer is used above 13.81 K [7].
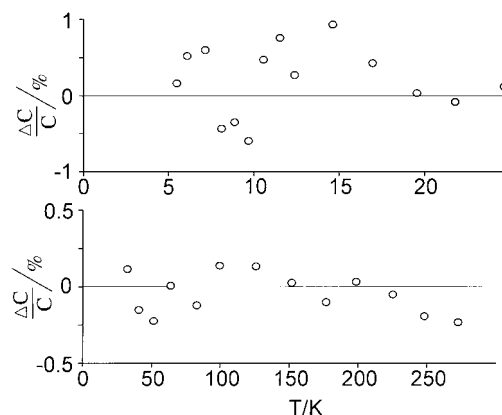

Fig. 3. The deviations of experimental heat capacities for copper from smoothed relationship.

The performance of the calorimeter and the accuracy of the results were tested in measurements of heat capacity of high purity copper specimen. Difference between measured and smoothed values of the heat capacity is shown in Fig. 3. The smoothed heat capacity, in turn, was compared with published data. The differences are within the limits of 1% for the temperature range from 5 to 50 K and of 0.25% from 50 to 320 K.

The calorimeter with the sample was hermetically encapsulated by screwing at room temperature under atmospheric pressure with helium impurity. The latter promotes rapid thermal equilibration at low temperatures. The mass of air in the calorimeter was 5.3×10^{-3} g, helium 1×10^{-6} g. The measurements were carried out in the temperature range of 6–320 K.

3. Results

The measured values were corrected for heat capacity of solid air (6–28 K), melting (28–34 K), and boiling (59–68 K) of air. The corrections do not exceed 5% for the temperature range of 6–28 K, 2% for 28–34 K, and 5% for 59–68 K. The corrected experimental data are given in Table 1. The derived thermodynamic functions are in Table 2. At 298.15 K, the accuracy was estimated on the assumption that the main reason of the uncertainty in the thermodynamic functions derived is the error in the water content (see Section 4).

Table 1
Experimental heat capacities for heulandite $Na_{0.365}K_{0.059}$-$Ca_{0.861}Al_{2.138}Si_{6.860}O_{18}\cdot6.17H_2O$ (molar mass: 694.724 g)

T (K)	C_p (J mol^{-1} K^{-1})
6.89	0.626
7.47	0.799
8.10	1.091
8.88	1.501
9.74	2.070
10.62	2.807
11.64	3.821
12.91	5.273
14.84	8.267
15.85	10.004
16.88	12.088
18.09	14.589
19.59	18.152
21.26	22.301
23.00	26.886
24.68	31.749
26.38	36.959
28.58	43.56
30.96	51.48
33.22	59.54
35.61	67.81
38.26	77.11
41.30	86.84
44.56	98.65
47.83	109.77
51.13	121.58
54.68	134.08
55.58	139.64
58.29	145.89
59.08	148.67
63.01	161.18
67.34	176.46
71.33	189.66
75.65	203.55
80.28	218.14
84.82	233.43
88.46	244.54
92.89	259.13
97.74	273.72
102.69	289.70
107.59	304.29
112.33	318.88
117.36	334.16
122.70	350.84
127.87	366.12
133.33	381.40
139.06	398.08
144.65	412.36
150.12	428.64
155.67	443.23
161.41	458.52
167.16	473.11

Table 1 (*Continued*)

T (K)	C_p (J mol^{-1} K^{-1})
172.98	487.70
178.86	502.98
184.65	516.18
190.36	530.07
196.00	543.27
201.84	557.17
207.88	571.06
213.85	584.26
219.75	597.46
221.94	601.63
228.27	616.22
234.53	630.12
240.72	643.31
246.85	655.82
252.92	668.32
258.94	680.14
264.91	691.95
270.83	703.06
277.07	714.87
282.89	725.29
306.02	767.67
310.39	771.14
314.74	778.09

4. Discussion

4.1. Heulandite–clinoptilolite series

Low-temperature heat capacity data for four (including this work) species of heulandite–clinoptilolite series are available now. It seems to be enough to solve the problem of recognizing thermodynamic properties of these minerals. However, this is not the case. First of all, let us make sure that the minerals investigated were really heulandites and clinoptilolites. In Ref. [3], the sample used was named ''clinoptilolite'' after [8]. In Ref. [4], the sample was termed as ''heulandite'' without explanations. In Ref. [5], the sample was identified as clinoptilolite because ''the X-ray diffraction pattern . . . agreed with that given by Boles [9]''. However, heulandite and clinoptilolite are identical in structure. These cannot be distinguished by X-ray diffraction. In Ref. [9], the way to distinguish them was suggested. Another way was suggested in [10]. Both papers stated that there are three (not two) minerals: heulandite (I), intermediate species (II), and clinoptilolite (III). Two parameters are necessary to

Table 2
Molar thermodynamic properties of heulandite (molar mass: 694.724 g)

T (K)	$C_{p,m}^{o}(T)$ (J mol^{-1} K^{-1})	$S_{m}^{o}(T) - S_{m}^{o}(0)$ (J mol^{-1} K^{-1})	$H_{m}^{o}(T) - H_{m}^{o}(0)$ (J mol^{-1})	$\Phi_{m}^{o}(T)$[a] (J mol^{-1} K^{-1})
(5)	(0.237)	(0.079)	(0.297)	(0.020)
10	2.274	0.680	5.176	0.163
15	8.510	2.621	30.13	0.612
20	19.10	6.431	97.62	1.550
25	32.68	12.10	226.0	3.064
30	48.38	19.42	427.9	5.159
35	65.52	28.16	712.3	7.805
40	82.79	38.04	1083	10.96
45	100.1	48.79	1540	14.56
50	117.5	60.23	2084	18.55
60	151.7	84.71	3432	27.51
70	185.1	110.6	5116	37.52
80	217.6	137.4	7130	48.32
90	249.6	164.9	9466	59.75
100	281.0	192.9	12120	71.66
120	342.4	249.5	18360	96.57
140	400.6	306.7	25790	122.5
160	454.7	363.8	34350	149.1
180	505.2	420.3	43960	176.1
200	552.8	476.0	54540	203.3
220	598.1	530.9	66050	230.6
240	641.5	584.8	78450	257.9
260	682.3	637.8	91700	285.1
280	720.1	689.7	105700	312.1
300	755.2	740.6	120500	339.0
315	781.6	778.1	131990	359.1
298.15	752±8	736±8	119100±1300	336.5±3.7

[a] $\Phi_{m}^{o}(T) = S_{m}^{o}(T) - S_{m}^{o}(0) - \{H_{m}^{o}(T) - H_{m}^{o}(0)\}/T$.

identify what mineral the sample under the question refers to. These are Si/Al and $\sum M^{++} / \sum M^{+}$. Here $\sum M^{++}$ is the sum of divalent cations and $\sum M^{+}$ the sum of univalent cations. The parameters enable us to identify the samples used in calorimetric measurements (see Table 3). The results are unexpected: only heulandite and intermediate species were investigated but not clinoptilolite.

The subcommittee on zeolites of the International Mineralogical Association recommends to distinguish two species: heulandite (Si/Al<4) and clinoptilolite (Si/Al>4) [2].

One should resume that the problem of recognizing differences in properties between heulandite and clinoptilolite has nothing to do with thermodynamics. This is the objective of mineral classification. To recognize thermodynamic functions of heulandite and clinoptilolite, only variations in chemical composition will be considered below.

4.2. Comparison of data on heat capacity

To compare the heat capacities, we used average gram atom ($\bar{M}$). Fig. 4 shows the relative differences in heat capacities of the zeolites published, as compared to ours: $Y = (C_{p}(T_i) - C_{ev}(T_i))/C_{ev}(T_i) \times 100\%$. Here $C_{p}(T_i)$ is the heat capacity at temperature T_i, and $C_{ev}(T_i)$ the heat capacity evaluated at T_i, using polynomial for the smoothing of our data. Two temperature regions in Fig. 4 are of interest. The first one is above 50 K. All heat capacities for various samples are within the limits ±3%. The second one is below 50 K where heat capacities differ significantly (up to 200%).

Table 3
Identification of the minerals for calorimetric measurements[a]

Sample	[9]		[10]	
	Si/Al	$\sum M^{++}/\sum M^+$	Si/Al	$\sum M^{++}/\sum M^+$
Mineral classification				
1 — Heulandite	2.90–3.52	10.31–1.61	2.85–3.73	3.69–0.88
2 — Intermediate	3.57–4.31	2.20–0.43	3.45–4.35	2.06–0.73
3 — Clinoptilolite	4.12–5.10	0.60–0.09	5.10–5.20	0.37–0.16
Investigated samples				
Ref. [3]	4.33 (3)	1.77 (1 or 2)	4.33 (2)	1.77 (1 or 2)
Ref. [4]	3.16 (1)	1.60 (2)	3.16 (1)	1.60 (1 or 2)
Ref. [5]	4.21 (2 or 3)	0.54 (2 or 3)	4.21 (2)	0.54 (?)
This work	3.21 (1)	2.04 (1 or 2)	3.21 (1)	2.04 (1 or 2)

[a] Classification by [9,10].

In calculating average gram atom, we use formula that consists of two parts: water and the rest (or dehydrated zeolite):

$$\bar{M} = \frac{\sum M_i k_i + n M_{H_2O}}{\sum k_i + 3n} \qquad (1)$$

Here k_i is the number of atoms of sort "i" in the formula of zeolite, M_i the atomic mass of these atoms, n the number of water molecules, and M_{H_2O} the molecular mass of water. The error in chemical analysis yields the error in the $\bar{M}$ evaluated. Main atoms in dehydrated zeolites are O, Si, Al, Na, Ca, K, Mg. These are measured quite precisely. Other cations (Sr, Ba, Fe, Li, etc.) are in amounts of as much as a fraction of percent. These cannot change $\bar{M}$ significantly. Water contributes atomic mass of 6 (=18:3) to the average gram atom and is as much as 15 wt.%. It can produce significant error in $\bar{M}$.

Let Δn be an error in the n determined. Then the relative error of the average gram atom is

$$\frac{\Delta \bar{M}}{\bar{M}} = \frac{\Delta n \cdot M_{H_2O}}{\sum M_i k_i + n \cdot M_{H_2O}} - \frac{3\Delta n}{\sum k_i + 3n} \qquad (2)$$

Given the zeolite formula with 72 oxygen atoms, the sum of k_i is close to 113 for heulandites and clinoptilolites studied. The molecular mass of zeolites is about 2750. Taking $n=24$, one can derive

$$\frac{\Delta \bar{M}}{\bar{M}} \approx \frac{\Delta n}{100} \qquad (3)$$

4.3. Systematic error

Water content in considered zeolites was measured in different ways. Certain of the procedures can produce a systematic error. For example, water content in heulandite was determined by heating a sample to 873 K for 24 h and measuring the weight loss [4]. There is no certainty that heulandite was dehydrated completely. Equilibrium water content for heulandite was investigated as a function of temperature in [11], for clinoptilolite in [12]. The results were represented graphically. Here, the data are given in Table 4. Our heulandite contains 0.3 water molecules at 863 K. The water content in clinoptilolite was determined by
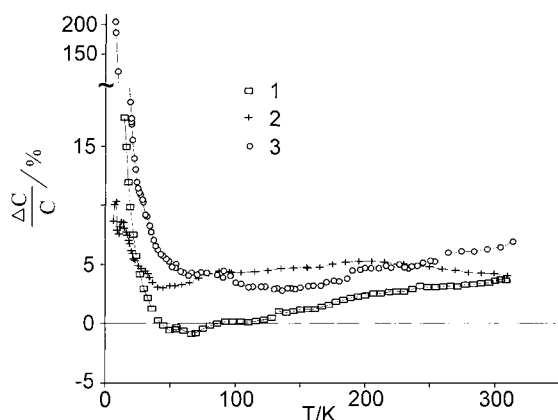

Fig. 4. Relative differences in heat capacity of the zeolites published as compared to our smoothed data: 1 — clinoptilolite [3], 2 — heulandite [4], 3 — clinoptilolite [5].

Table 4
Equilibrium number of water molecules (n) in the unit cell of heulandite [11] and clinoptilolite [12] at elevated temperatures

T (K)	Mass loss (%)	n
Heulandite		
308	0.69	22.9
323	1.34	21.9
335	1.91	21.1
348	2.56	20.1
360	3.33	18.9
373	4.16	17.6
380	4.29	17.4
398	5.52	15.5
423	6.58	13.9
443	7.09	13.1
448	7.26	12.8
473	8.25	11.3
485	8.64	10.7
498	9.12	10.0
503	9.15	9.9
513	9.06	10.1
513	8.97	10.2
523	10.96	7.2
533	11.24	6.7
583	12.27	5.2
653	13.44	3.4
653	13.50	3.3
723	14.73	1.4
793	15.07	0.8
863	15.42	0.3
Clinoptilolite		
347	3.90	15.0
380	5.42	12.7
380	5.28	12.9
408	7.32	9.9
443	7.90	9.0
478	9.18	7.1
513	9.54	6.6
548	10.75	4.8
583	11.10	4.3
618	11.98	3.0
653	12.28	2.5
688	12.80	1.7
723	13.02	1.4
758	13.26	1.1
793	13.41	0.9
828	13.61	0.6
863	13.75	0.3
898	13.83	0.2

heating a sample to 650 K [5]. At that temperature, clinoptilolite was accepted as dehydrated. Chemical analysis (without water) yielded the sum 97.385%. Such a value is hard to be accepted as a result of correct measurements. Our clinoptilolite in Table 4 (crystals, not tuff) with the composition $Na_{2.61}K_{0.48}Ca_{1.60}Al_{l6.64}Si_{29.45}O_{72} \cdot 20.76H_2O$ contains 2.5 water molecules at 653 K. According to Eq. (3), this value is equivalent to the systematic error in heat capacity as much as 2.5%.

According to Eq. (1), the greater water content, the less the average gram atom. Water content in our heulandite is shown to be the largest among others, and heat capacity is the least.

4.4. Random error

Heulandite and clinoptilolite readily change the water content according to temperature and humidity. Our heulandite was found to change the water content at room temperature as $(1/m_0)(dm/dt)=4\times10^{-4}\,K^{-1}$, where m is the mass of the sample [12]. Setting the random changes in room temperature as ±3 K, one can estimate random changes in zeolite mass as high as $\pm0.12\%$. The total mass loss of 15% is equivalent to approximately 24 water molecules per 72 oxygen atoms in the framework, and the number of water molecules can change at random with temperature within the limits ±0.2.

The relationship between relative humidity and water content in heulandite and clinoptilolite in tuffs was investigated at room temperature by one of the authors (V.A.D., unpublished). When relative humidity changes from 44% (saturated water solution of K_2CO_3) to 79% (NH_4Cl), the mass of pure zeolite changes by $1.1\pm0.1\%$. It is equivalent to ±0.9 water molecules per 72 oxygen atoms. The overall random error in $\bar{M}$ is estimated to be as high as $\pm1.1\%$.

4.5. Relationship between heat capacity and composition

Above 50 K, heat capacities for four zeolites are within the limits of $\pm3\%$. A significant part of the differences is caused by experimental error: 1.1% due to a sample (random error in the water content of zeolites) and 0.25% due to experimental technique (accuracy derived from data for the reference copper, the estimation is valid at least for our data).

The rest differences in the heat capacities, about 1.5%, are to be compared with differences in composition. The zeolites differ both in types of cations
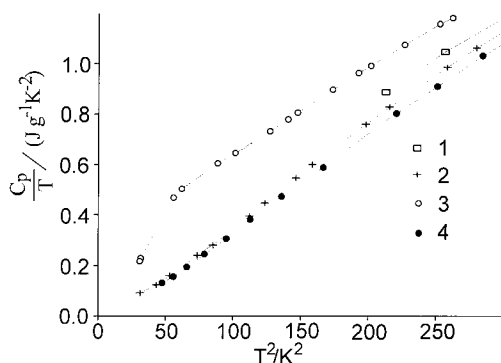
Fig. 5. Low-temperature heat capacity of heulandites and clinoptilolites: 1 — clinoptilolite [3], 2 — heulandite [4], 3 — clinoptilolite [5], 4 — this work. The Debye model does not hold for data from Ref. [5].

(Ba+Sr+Ca+K+Na and Ca+K+Na) and in their amounts. We failed to construct the reliable mathematical model for heat capacity as a function of the composition even not considering errors in chemical analysis. Too many variables. We think this problem can be solved only after measurements of cation-exchanged forms of one initial sample.

Below 50 K, the heat capacities differ drastically. Unfortunately, clinoptylolite tuff was measured at temperatures above 13 K. Fig. 5 shows heat capacity in coordinates C_p/T vs. T^2. According to the Debye model, heat capacity of non-metal solids at low temperatures (much less than the Debye temperature) tends to $C_p \sim a \times T^3$. It is valid for both heulandites but not for clinoptilolite in [5]. Heat capacity of the latter depends on temperature in a strange way. Either there is an unusual phenomenon in thermal properties of the clinoptilolite investigated or the results are wrong. The data cannot be used in recognizing the

relationship we are interested in as long as the problem of unusual temperature dependence is not solved.

5. Conclusion

The heat capacity of heulandite crystals was measured in the temperature range from 6 to 315 K. Now the experimental data for four zeolites of series heulandite–clinoptilolite are available. All the differences in heat capacity between the references are within the limits of experimental error (systematic and random) for temperatures above 50 K. Below 50 K, the temperature dependence of heat capacity of clinoptilolite published in [5] is not typical of silicates and the values exceed other data as high as three times.

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