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The Low-Temperature Solubility of Helium in Quartz

A. V. Koromyslov* and A. Ya. Kupryazhkin
Ural Federal University, Yekaterinburg, 620002 Russia
** e-mail: a.v.koromyslov@gmail.com*

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Abstract—The solubility of helium in α- and β-quartz single crystals, optical quartz crystals, and Pyrex glass has been studied by the method of thermal desorption of helium from crystals preliminarily saturated in the gaseous phase in the temperature range $T = 323–1123$ K and saturated vapor pressure $P = 0.6–31$ MPa. It has been shown that the behavior of the solubility of helium in quartz crystals is described by exponential dependences on the reciprocal temperature. The solubility of helium in quartz single crystals is almost independent of temperature. For all kinds of samples, the solubility varies in proportion to the saturated vapor pressure and attains values of $(6.2 \pm 0.3) \times 10^{15}$ cm^{-3} in single crystals for $P = 25.5$ MPa, $T = 873$ K, and $(8.64 \pm 0.04) \times 10^{19}$ cm^{-3} in optical quartz for $P = 31$ MPa and $T = 373$ K. It has been shown that the solubility of helium in quartz single crystals can increase upon an increase in the concentration of defects in the crystal as a result of multiple thermal cycling of samples in the course of measurements. Possible mechanisms of the dissolution of helium in quartz have been studied, and the results have been compared with those obtained by other authors.

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INTRODUCTION

Interest in the study of the solubility of helium in quartz, as well as its diffusion, has been aroused in connection with the refinement of the geochronological methods [1] and helium defectoscopy of crystals [2] and the development of the methods of obtaining highly concentrated solutions of helium isotopes.

Investigations in quartz are hampered due to the presence of large number of its phases in a wide range of temperatures and pressures [3], the presence of water on the surface, grain boundaries and dislocations [4], and the low solubility of helium in quartz single crystals [5]. As a rule, the main studies of the solubility are carried out in quartz single crystals by the penetrability technique [6], including studies in a small temperature interval [7], as well as the method of thermal desorption for powdered samples of quartz phases with high concentrations of defects [3], which exhibit high solubility in quartz. The change in the solution energy at 550 K was observed in [6], while the possibility of obtaining different values for helium solubility in quartz was demonstrated in [7] using the methods of penetrability and thermal desorption due to different contributions of bulk and surface defects on the quantities being measured in the investigated quartz samples. The values of the solution energy obtained in [7] for helium have rather high values.

The most consistent study of the interaction of helium with defects in the region of existence of the α-phase in quartz single crystals was carried out in [5]; however, the authors did not investigate the dependence of the solubility of helium on temperature and saturated vapor pressure. It would be interesting to carry out a comparative study of the low-temperature solubility of helium in quartz glass and α- and β-quartz single crystal to determine the potentialities of helium defectoscopy for the analysis of these samples.

1. EXPERIMENTAL TECHNIQUE

Experiments were carried out on optical quartz and Pyrex glass samples, as well as samples of synthetic quartz cut from various parts of a piezoquartz single crystal. The characteristic size of the samples used in the experiments did not exceed 2 mm.

A chemical analysis of the original samples (wt %) was carried out using inductively coupled plasma mass spectrometry (ICP-MS). The concentration of the main impurities (Fe) in the optical quartz sample and in single crystals did not exceed 0.009%, while the total concentration of the remaining impurities did not exceed 0.001%. The basic material SiO_2 in Pyrex sample had a concentration of 80.5%, while the concentration of the main impurities was 4.823% B, 6.348% Na, 0.044% K, 0.104% Ca, 0.014% Ti, 0.024% Fe, and 0.035% Zr. The rest of the impurities had a concentration that did not exceed 0.001%.

Solubility of helium in quartz was studied by the method of thermal desorption of the gas from samples preliminarily saturated in the saturation chamber at preset temperature and pressure of helium in samples

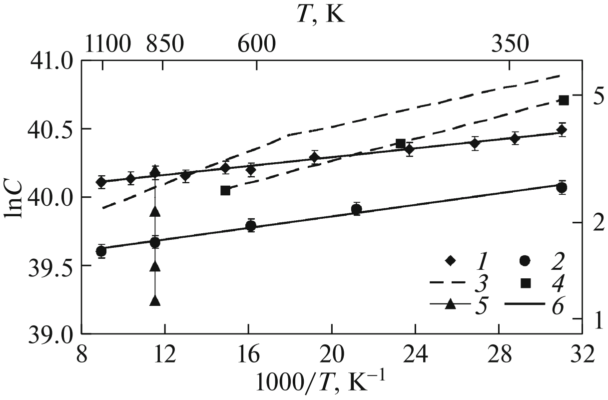

Fig. 1. Solubility of helium in quartz crystals, $P = 1 \times 10^5$ Pa; (*1*) optical quartz; (*2*) Pyrex; (*3*) results obtained in [6]; (*4*) results obtained in [8]; (*5*) results on the solubility of helium in optical quartz ($T = 873$ K) after four successive saturation–degassing cycles (see text); (*6*) approximation of the data obtained in the present work.

annealed to room temperature after saturation and loaded into the measuring chamber for degassing at a high temperature (1200 K). Degassing of single crystals at a temperature lower than the melting point of quartz allowed, on the one hand, the exclusion from the obtained solubility of the contribution from possible deep traps that bind helium up to the melting point [5] and, on the other hand, the repeated use of the same crystals over a wider range of temperatures and pressures.

The amount of released helium was measured with the help of a modernized mass spectrometer MI-1201 operating in the quasi-static (helium) pumping mode with a getter pump. The calibration of the mass spectrometer was carried out by the method of the dual expansion of a known amount of helium from a calibrated volume to a preliminarily measured volume of the mass-spectrometer measuring chamber with pressure measurements in a calibrated volume as in [2]. The saturation time for the investigated samples was selected experimentally after verifying the reproducibility of results for saturation times that differ by a factor of no less than three.

2. DISCUSSION OF EXPERIMENTAL RESULTS

Figure 1 shows the results of measurements of the temperature dependence of the solubility of helium in optical quartz (curves *1*) and Pyrex glass (curves *2*), which were carried out in the temperature interval $T = 323–1123$ K and saturated vapor pressure $P = 1 \times 10^{-5}$ Pa. For comparison, the figure also shows (curves *3*, *4*) the results obtained in [6, 8] for the investigated temperature range for determining the solubility of helium from the optical quartz penetrability. Figure 2 shows the results of measurements of the dependence of solubility of helium on saturated vapor pressure for

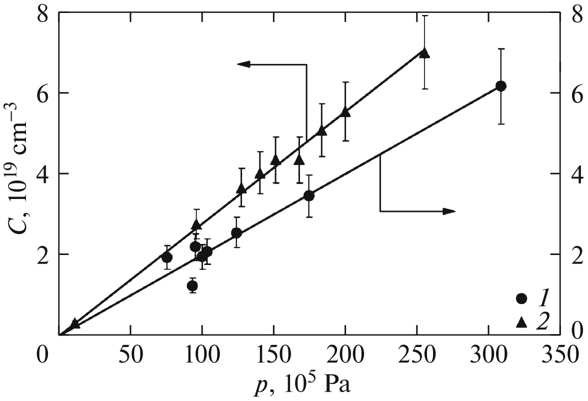

Fig. 2. Dependence of the solubility of helium on the saturation pressure: (*1*) quartz single crystals, $T = 873$ K; (*2*) optical quartz, $T = 373$ K.

optical quartz and one of the single crystal samples, which were obtained in this research. Comparison shows that, in contrast to the results obtained in [6], the behavior of the solubility of helium as a function of saturation temperature, $\ln C = f(1/T)$, is described quite well by a single exponential dependence (Fig. 1, curves *1* and *2*). The dependences of the solubility of helium on saturation vapor pressure in optical quartz and quartz single crystal (Fig. 2, curves *1* and *2*) follow Henry's law

$$C = \Gamma(T)P, \tag{1}$$

where $\Gamma(T)$ is a constant.

Analyzing the equilibrium conditions in the gas–imperfect crystal system, we can easily obtain the following expression for the dependence of the solubility of helium atoms occupying certain energy positions in the crystal at a given temperature T and a low saturation vapor pressure P (see, e.g., [9]):

$$C = C^*LP\exp(-\Delta E/kT), \tag{2}$$

where C^* and ΔE define the concentration of the positions and the helium solution energy at these positions, respectively; L is a constant that depends weakly on temperature; and $C^*LP = C_0$ is the exponential factor in expression (2).

The Table 1 describes the results of comparison of dependence (2) with the results obtained by other authors [6, 8]. In accordance with the experimental results presented in Fig. 2, the values of constant $\Gamma(T)$ for relation (1) are $\Gamma(373\text{ K}) = (2.7 \pm 0.1) \times 10^{17}$ cm^{-3} 10^{-5} Pa^{-1} for optical quartz and $\Gamma(873\text{ K}) = (2.0 \pm 0.2) \times 10^{13}$ cm^{-3} 10^{-5} Pa^{-1} for optical quartz.

The temperature dependences of the solubility of helium in optical quartz (Fig. 1, curve *1*) and Pyrex glass (Fig. 1, curve *2*) are nearly parallel on the semilogarithmic scale and have the same solution energy to within the experimental error. It can be assumed that the investigated glasses have an identical structure. Hence, according to the solubility data (2), the num-

Table 1. Parameters of temperature dependence of helium solubility in quartz

No.	Notation	T, K	C_{i0}, cm^{-3} 10^{-5} Pa^{-1}	ΔE_i, eV
		Glass (notation of Fig. 1)		
1	1	323–1123	$(2.24 \pm 0.04) \times 10^{17}$	-0.015 ± 0.001
2	2	323–1123	$(1.34 \pm 0.04) \times 10^{17}$	-0.018 ± 0.001
3	3 [6]	323–550	1.99×10^{17}	-0.03
	4 [6]	550–1123	1.28×10^{17}	-0.05
4*	5 [9]	323–673	$(1.36 \pm 0.01) \times 10^{17}$	-0.0351 ± 0.0004
		Single crystal (notation of Fig. 3)		
5	1, 2	573–1123	$(2.2 \pm 0.3) \times 10^{13}$	0.009 ± 0.008
6	3	573–1023	$(7 \pm 2) \times 10^{13}$	0.04 ± 0.02
7	4	523–1123	$(10 \pm 2) \times 10^{13}$	0.03 ± 0.01
8	5	573–1123	$(1.7 \pm 0.1) \times 10^{14}$	0.006 ± 0.005

*Processes carried out by us.

ber of free positions C_i^* for the dissolution of helium in Pyrex is 37% smaller than in optical quartz due to the presence of various impurities in it, which initially occupy free positons during the preparation of Pyrex. Negative values of the solution energy in glasses (table, rows 1 and 2) indicate that the characteristic size of the dissolution positions being registered is comparable with, or larger than, the helium atom size, viz., 0.25 nm (see, e.g., [9]). This conclusion is also confirmed by the data on the removal of volatile impurities that are initially present in optical quartz during saturation–degassing cycles. For example, for initial samples of optical quartz that have not yet been degassed, curve *5* in Fig. 1 shows the solubility of helium after four successive saturation–degassing operations at $T = 873$ K. The first result yielded the lowest solubility (lower than in Pyrex). Subsequent measurements yielded higher values of solubility (indicated by a vertical arrow in Fig. 1, curve *5*) to the highest reproducible value, which can be attributed to the purification of the investigated sample from volatile impurities and an increase in the number of C^* positions that correspond to the solubility of helium (2). A comparison of our results (curves *1* and *2*, Fig. 1) with the data of other authors [6] (curves *3* and *4*, Fig. 1) shows that, like in [5, 8] (curve *4*, Fig. 1), there is no kink on the temperature dependence $\ln C = f(1/T)$. This kink may be due to the presence of uncontrollable impurities (especially water) in the sample or by the peculiarities introduced when determining the solubilty of gases from the data obtained by the penetrability method. The high value of the solution energy obtained in [7] is apparently due to the same reasons, as well as due to the small temperature interval in which measurements were taken.

Three samples (nos. 1–3) were cut out of the original quartz single crystal in order to study the solubility of helium in single crystals. The experimental data on the solubility of helium in them, which were obtained in the temperature range of 573–1123 K of the existence of α- and β-phases, are presented in Fig. 3 (curves *1*–*3*). Vertical dashed lines indicate the interface between the phases. The data presented in the figure indicate that the solubility of helium is the same for sample nos. 1 and 2, but is more than double this value for sample no. 3. This may be due to the dissolution of helium in the defects of the single crystal and their nonuniform distribution in the original sample. To verify this assumption, we repeated the solubility measurements in sample no. 3 (after the first series of measurements and the thermal cycling associated with it). The solubility (Fig. 3, curve *4*) in all temperature ranges was found to increase on average by a factor of 1.4 over initial sample no. 3. A stable increase in the solubility (Fig. 3, curve *5*) by 3.5 times was obtained after the second thermal cycling of the sample (no. 3) with the corresponding measurements of solubility in the sample. The obtained results indicate that the increase in the solubility of helium in quartz single crystals is due to the emergence of additional defects in all probability dislocations formed as a result of accumulation of elastic stresses in the crystal during thermal cycling. This also explains the stabilization of the increase in the solubility after the second thermal treatment of the crystal (Fig. 3, curve *5*) because of the impossibility of further thermal cycling leading to a further increase in the number of dislocations.

The data presented above also reveal that the dependences presented for helium solubility differ negligibly at the phase-transition temperature (Fig. 3, $T_{\alpha,\beta}$ dashed line) for all the samples of quartz single crystals (see Fig. 3) to within the measuring error and can be approximated by a single Arrhenius dependence for each sample in the entire investigated temperature interval (573–1123 K). The table contains data obtained as a result of processing the temperature

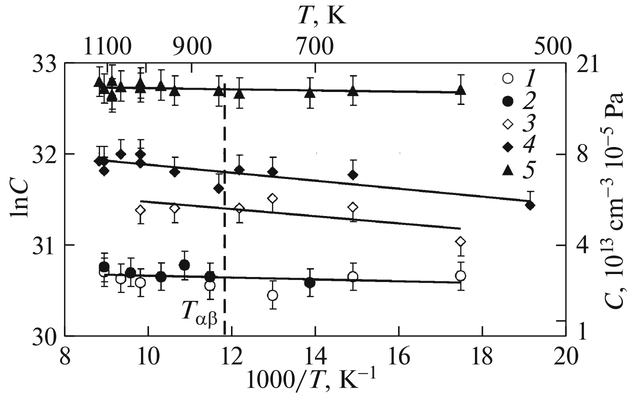

Fig. 3. Solubility of helium in quartz single crystals, $P = 1 \times 10^5$ Pa; (*1*–*3*) data for helium solubility in initial quartz single crystal sample nos. 1, 2, 3; (*4*) helium solubility in sample no. 3 after a single thermal cycling; (*5*) helium solubility in sample no. 3 after double thermal cycling.

dependence of the solubility of helium in quartz single crystals. It follows from Fig. 3 and the data presented in the table that the helium solution energies in quartz single crystals have very low, zero, or positive values compared to the solution energies in glass.

CONCLUSIONS

The experimental results on the increase in helium solubility in α- and β-quartz single crystals, which were obtained after thermal cycling of the initial single crystals, as well as the low values of helium solution energy obtained from the temperature dependences of helium solubility in α- and β-quartz, indicate that the dislocation mechanism can be responsible for the dissolution of helium in α- and β-quartz single crystals.

The data for the helium solution energy in α- and β-quartz presented in the table indicate that the size of the positions of helium dissolution in quartz single crystals is smaller than or equal to the helium atom size. This does not contradict the dislocation mechanism for dissolution or that the minimal value of the helium solubility recorded in the present work is an order of magnitude larger than that reported in [5], where experiments were carried out on single crystals with dislocation density ~10^2 cm^{-2}.

The highest value of helium solubility obtained in this work for quartz single crystals is $(6.2 \pm 0.3) \times 10^{15}$ cm^{-3} for $P = 31$ MPa and $T = 873$ K. In optical quartz crystals, the solubility of helium is about four orders of magnitude higher and is $(8.64 \pm 0.04) \times 10^{19}$ cm^{-3} for $P = 25.5$ MPa and $T = 373$ K.

Further investigation is needed to study the effect of extraneous impurities in quartz single crystals on the solubility of helium.

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