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Hole-compensated Fe³⁺ impurities in quartz glasses: a contribution to subkelvin thermodynamics

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Abstract

This paper studies the contribution of [FeO₄]⁰ impurity substitution centres to subkelvin thermodynamic properties of quartz glasses. In the scenario considered an Fe³⁺ ion substitutes for a Si⁴⁺ ion in the metallic sublattice of quartz, and one of the neighbouring oxygen ions captures a hole, which compensates the local charge defect. The Fe³⁺ cation and the O⁻ anion, on which the hole is localized, form a bound small polaron. In this configuration the Fe³⁺ cation is subject to a crystal field with an approximate C₃ symmetry axis along the Fe³⁺-O⁻ direction. This axis plays a quantization role for the Fe³⁺ electronic spin. The hole is assumed to be tunnelling between two neighbouring oxygen ions, switching the quantization axis between two directions and therefore entangling the spin states. Due to this coupling between spin and spatial degrees of freedom an [FeO₄]⁰ centre may be considered as a paramagnetic tunnelling system (PTS). An explicit form derived for a single-PTS low-energy spectrum, together with the model parameter distribution function introduced, allows for a complete thermodynamic description of the [FeO₄]⁰-based PTS ensemble. In particular, a contribution to the ac dielectric constant, derived as a function of magnetic field and temperature, allows a semiquantitative fit to recent experimental data for the iron-contaminated multicomponent glass BaO-Al₂O₃-SiO₂. Taking into account a spin interaction between Fe³⁺ and O⁻ ions also allows us to account for the anomalous magnetothermal behaviour of the low-temperature specific heat, recently reported for the glasses BaO-Al₂O₃-SiO₂ and Duran and earlier for Pyrex.

1. Introduction

The recent studies of some multicomponent quartz glasses in the subkelvin temperature range revealed a distinct and not completely explainable theoretically reaction to magnetic field. In

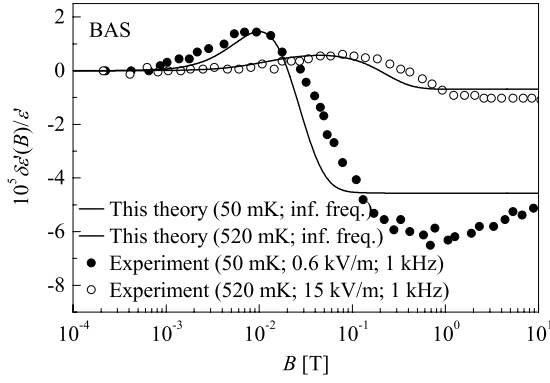


Figure 1. Relative change of the real part of the dielectric constant versus magnetic field: experimental data [1] for BAS fitted with formula (40) at conditions indicated. For the fitting parameters see table 2.

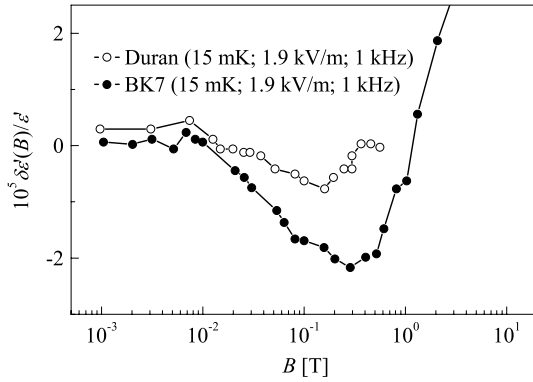


Figure 2. Relative change of the real part of the dielectric constant versus magnetic field: experimental data for Duran [2] and BK7 [7] at conditions indicated. For better perception the data points are connected with straight lines and the data for Duran are shifted up along the vertical axis.

figure 1 the dots stand for experimental data [1] on the relative variation of the real part of the dielectric constant versus magnetic field ($\delta\epsilon'(B)/\epsilon'$) for the glass BaO–Al₂O₃–SiO₂ (BAS) at two different temperatures. It is clearly seen that $\delta\epsilon'(B)/\epsilon'$ is nonmonotonic with applied magnetic field $0 < B < 1$ T and that the magnitude of the effect decreases with temperature. A somewhat different nonmonotonic dependence $\delta\epsilon'(B)/\epsilon'$ is also reported for the borosilicate glass Duran [2] (see figure 2).

On the other hand, according to experimental data [2], in the glasses BAS and Duran the temperature variation of specific heat $C_p(T)$ in the range $T \leq 1$ K turned out to depend on magnetic field in the range $0 \leq B \leq 8$ T (see figures 3(a) and (b)). From figures 3(a) and (b) one finds that in zero magnetic field the measured $C_p(T)$ has a plateau-like form which transforms nonmonotonically versus B until at $B \geq 8$ T it approaches the low-temperature dependence usual for glasses:

$$C_g(T) = \gamma_{ph}T^3 + \gamma_{TS}T. \quad (1)$$

In formula (1) the first term accounts for the Debye-type contribution of acoustic phonons, and the second is usually attributed to specific low-energy excitations in vitreous solids—the so-called tunnelling systems (TSs) [3].

A curious fact, pointed out by Jug [4], is that a similar $C_p(T, B)$ dependence has been observed already in the pioneer work by Zeller and Pohl [5] at $B = 0$ and later by Stephens [6] at finite B in the Pyrex-type borosilicate glasses (see figure 3(c)).

It is worth noting that for all glasses mentioned above a considerable concentration of Fe³⁺ impurities is reported: 102 ppm for BAS and 126 ppm for Duran [2], 100 ppm for Pyrex 7740 and 12 ppm for Pyrex 9700 [5, 6].

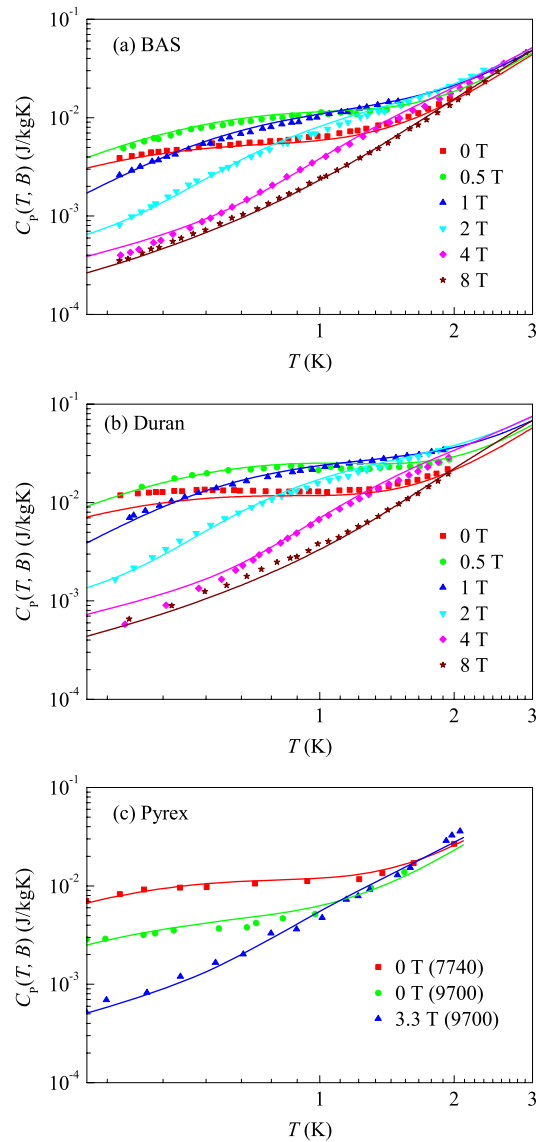


Figure 3. Specific heat as a function of temperature and magnetic field: experimental data for (a) BAS [2], (b) Duran [2] and (c) Pyrex 7740 [5] and 9700 [6], fitted with expression (48) at the conditions indicated. For the fitting parameters see table 3.

(This figure is in colour only in the electronic version)

Another borosilicate glass studied, BK7, for which a concentration of only about 6 ppm of iron is reported [2], demonstrates a low-temperature dependence of $\delta\epsilon'(B)/\epsilon'$ [7] qualitatively similar to that in Duran (see figure 2). Yet, a magnetic field in the range $0 \leq B \leq 4$ T has no detectable influence on the specific heat of BK7 [2] at subkelvin temperatures. The nonmonotonic behaviour of $\delta\epsilon'(B)/\epsilon'$ was also detected in the structural glass $a\text{-SiO}_{2+x}\text{C}_y\text{H}_z$ [8], for which there are no reports on concentration of paramagnetic impurities.

Another anomalous subkelvin property, observed in BAS, Duran and BK7, is the B -dependence of spontaneous polarization echo amplitude [9]. Experiments show that this property is specific to multicomponent glasses, because in pure amorphous SiO_2 (Suprasil I) the effect is absent.

All theoretical models that have been proposed to explain the above-mentioned magnetic anomalies are based on modifications of the standard tunnelling model [3], leading to the B -dependence of the energy spectrum of a certain subsystem of TS ensemble. These models and their applications are described in [4, 8, 10–15].

As mentioned above, the glasses BAS, Duran and Pyrex, which demonstrate similar anomalous behaviour of the low-temperature $C_P(T, B)$, contain a considerable concentration of Fe^{3+} impurities. At the same time the glass BK7, containing much less iron, does not demonstrate such an anomaly. Therefore, one can draw the conclusion that the $C_P(T, B)$ anomaly in these glasses is due to Fe^{3+} impurities.

The situation with magnetoelectric anomalies is somewhat more difficult. It is established that in BAS, Duran and BK7 the B -dependences of spontaneous polarization echo amplitude are qualitatively similar [9]. In the frame of the quadrupole tunnelling model [13] this behaviour may be explained by the presence of impurities with nonzero nuclear quadrupole moment (^{27}Al , $^{10,11}\text{B}$ etc). On the other hand, the shape of $\delta\varepsilon'(B)/\varepsilon'$ for BAS is different from those for Duran and BK7 in the presence of a distinct maximum at $B_{\text{max}} \sim 10^{-2}$ T in the former case (cf. figures 1 and 2). These features have no theoretical explanation up to now.

In our previous publication [15], the model of the four-level paramagnetic tunnelling systems (PTSs) was formulated. It considers an abstract particle, moving in a one-dimensional double-well potential. The particle possesses a magnetic moment $J > 1/2$. In each potential well this moment is quantized along the local axial-symmetric electric field gradient (EFG) in such a manner that a doublet of states $|\pm J\rangle$ is found in the ground state. Under a certain temperature threshold the population of the rest of the spin states may be neglected and therefore the particle may be treated as a pseudospin-1/2 one. The EFG axes in the two potential wells are supposed to be nonparallel. Therefore, the tunnelling transitions between the potential wells switch between the EFG orientations and thus entangle the spin states $|\pm J\rangle$. This coupling between spatial and spin degrees of freedom affects the B -dependence of the PTS energy spectrum. In the frame of the PTS model we attempted to explain the above-mentioned $\delta\varepsilon'(B)/\varepsilon'$ behaviour in quartz glasses to be due to hole-compensated impurity $[\text{AlO}_4]^0$ or $[\text{BO}_4]^0$ centres, where the orbital states $|p_x\rangle$, $|p_y\rangle$ of the O^- ion are the symmetric and antisymmetric combinations of the orbital moment eigenstates $|\pm 1\rangle$. However, for such centres in crystalline quartz the initial (at $B = 0$) ground-state splitting between $|p_x\rangle$ and $|p_y\rangle$ is about 0.5 eV due to a minor nonaxiality of the EFG, affecting the O^- ion [16]. Thus these orbital states are insensitive to magnetic fields which produce Zeeman splittings much less than the $B = 0$ one. Of course, in glasses the $B = 0$ splitting is expected to be a random variable, obeying a certain distribution function with a tail to smaller values, but nevertheless the attribution of the $\delta\varepsilon'(B)/\varepsilon'$ anomaly to such a mechanism in the range $B \leq 1$ T seems doubtful.

The present work considers the contribution of hole-compensated $[\text{FeO}_4]^0$ substitution impurity centres to subkelvin thermodynamic properties of quartz glasses.

The paper is organized as follows. In section 2 the microscopic structure of the $[\text{FeO}_4]^0$ centre in the quartz lattice is discussed, and based on the model spin Hamiltonian proposed an expression for its ground energy quadruplet is derived. In section 3 the PTS model is applied to the $[\text{FeO}_4]^0$ centre, the single-PTS energy spectrum and free energy are derived and the ensemble-averaged (over the model parameter distribution function) contribution $\delta\varepsilon'(B)/\varepsilon'$ is found, assuming the dielectric response to be purely resonant. Then the expression for $\delta\varepsilon'(B)/\varepsilon'$ obtained is fitted to experimental data for BAS (figure 1). In section 4 the contribution of the $[\text{FeO}_4]^0$ ensemble to $C_P(T, B)$ is calculated and fitted to experimental data for BAS, Duran and Pyrex (figures 3(a)–(c)). In section 5 the results obtained are analysed and discussed and section 6 is left for conclusions.

Table 1. Electronic properties of paramagnetic ions in an $[\text{FeO}_4]^0$ centre.

Ion	Configuration	Ground spin state	J	g_0
Fe^{3+}	$3d^5$	^6S	$5/2$	2
O^-	$2p^5$	^2S	$1/2$	2

2. The structure and low-energy spin states of $[\text{FeO}_4]^0$ centres in quartz glasses

In many iron-doped glasses, EPR absorption spectra were observed with peaks in particular at $g \approx 4.3$ and $g \approx 6$ [17]. The intensities of these peaks turned out to be proportional to the concentration of Fe^{3+} impurities in the samples [18]. These EPR peaks can be unambiguously attributed to Fe^{3+} impurities at Si^{4+} sites in a quartz lattice [18]. Reported model spin-Hamiltonian-based calculations [18] show that for a perfectly tetrahedrally coordinated Fe^{3+} ion only the $g = 2$ isotropic value should be observed. The $g \approx 4.3$ isotropic value comes from two extra equal charges at the corners of the tetrahedron. The $g \approx 6$ anisotropic component results from one extra charge at the tetrahedron corner. The carriers of these extra charges may be either interstitial ions or trapped holes.

In quartz glasses a considerable fraction of oxygen ions is in a nonbridging state¹. Assuming interatomic bonds in the quartz lattice to be purely ionic, an oxygen ion in a nonbridging state may be considered as an O^- ion, i.e. an O^{2-} ion which has trapped a hole. Above a certain temperature threshold this hole is able to diffuse across the oxygen sublattice. So, if it meets an O^{2-} ion neighbouring an Fe^{3+} ion in a network-forming (substitution) position at a Si^{4+} site, the occurrence of the $\text{Fe}^{3+}-\text{O}^-$ bound state becomes highly probable due to compensation of the local charge defect. On the other hand, even in a perfect quartz lattice, an Fe^{3+} impurity at a Si^{4+} site under certain conditions (e.g. ionizing radiation treatment) can capture a hole at one of the neighbouring oxygens, as occurs e.g. in the case of $[\text{AlO}_4]^0$ centres in α -quartz (see [19] and references therein). The ions Fe^{3+} and O^- form a small bound polaron [16]. Following the terminology established, these centres will be denoted $[\text{FeO}_4]^0$.

Consider the following general form of the spin Hamiltonian of the $[\text{FeO}_4]^0$ centre:

$$\hat{H}_{[\text{FeO}_4]^0} = \hat{H}_Z + \hat{H}_D + \hat{H}_Q. \quad (2)$$

Here the first term denotes the Zeeman coupling of the total electronic magnetic moment of the centre to external magnetic field, the second denotes the electronic dipole coupling between the spins of the Fe^{3+} and O^- ions, and the third stands for the electronic quadrupole interaction with the local EFG. The terms entering Hamiltonian (2) have orders of magnitude $H_Q \sim 10$ K, $H_Z(1 \text{ T}) \sim 1$ K, $H_D \sim 0.5$ K. Other possible terms, not included in (2), such as those responsible for the nuclear quadrupole, dipole electron–nuclear and nuclear Zeeman interactions, have orders of magnitude of 10^{-3} K and smaller.

Here and below the energy is denoted in units of the Boltzmann constant k_B and therefore it has the dimension of temperature.

The electronic shell configuration and spin properties of paramagnetic ions in an $[\text{FeO}_4]^0$ centre are given in table 1.

In Fe^{3+} the tetrahedral coordination in the quartz lattice does not change the free-ion ground orbital state S. Due to the above-mentioned large value of the $B = 0$ ground-state orbital splitting in O^- , the B -field corrections to its orbital levels $|p_x\rangle$, $|p_y\rangle$ may be neglected in the range $B \leq 10$ T, i.e. the O^- orbital moment is effectively quenched too.

¹ A bridging oxygen ion is one which bridges two silicon ions, i.e. is shared between two tetrahedral cells.

For $[\text{AlO}_4]^0$ centres in α -quartz, which have the spatial structure similar to $[\text{FeO}_4]^0$ ones, the interpretation of EPR spectra showed that the principal axes z_s of both ^{27}Al quadrupole and $^{27}\text{Al-O}^-$ dipole tensor matrices coincide with the unit radius-vector \mathbf{u} , connecting Al^{3+} and O^- sites, with precision up to several degrees [19]. Of course, the spatial distribution of charge and spin density in an Fe^{3+} electronic shell is different from that in a ^{27}Al nucleus, but as an approximation the principal axes z_s of \hat{H}_Q and \hat{H}_D matrices will be assumed to be collinear to \mathbf{u} . Furthermore, since, according to the estimations above, $H_Q \gg H_D$ in (2), the possible small nonuniaxiality of the \hat{H}_D matrix will be neglected. Therefore one can choose the principal axes of the \hat{H}_Q matrix to define the local basis. In this basis the spin Hamiltonian (2), assumed to contain only quadratic terms in \hat{H}_Q , takes the form

$$\hat{H}_{[\text{FeO}_4]^0} = g_0\beta (\mathbf{s} + \mathbf{S}) \cdot \mathbf{B} + V_\perp (s_x S_x + s_y S_y) + V_z s_z S_z + D_0 S_z^2 + E_0 (S_x^2 - S_y^2). \quad (3)$$

Here β is the Bohr magneton, \mathbf{s} and \mathbf{S} are the spin operators of O^- and Fe^{3+} ions respectively, $V_\perp = V_{xx} = V_{yy}$ and V_z are the principal values of the dipole interaction matrix and D_0 and E_0 are constants, proportional to the EFG tensor principal values.

If an Fe^{3+} ion were situated in the centre of a regular tetrahedron with the vertices at O^{2-} sites, as for an $[\text{FeO}_4]^-$ centre, the condition $D_0 = E_0 = 0$ would hold. If any two vertex sites were occupied by O^- ions, and the remaining two by O^{2-} ions, as for $[\text{FeO}_4]^+$, the condition $D_0 = 0, E_0 \neq 0$ would hold. If one of the vertex sites is occupied by an O^- ion and the other three by O^{2-} ions, as in the case of an $[\text{FeO}_4]^0$ centre, then the axis \mathbf{u} is a C_3 one and therefore

$$D_0 \neq 0, \quad E_0 = 0. \quad (4)$$

Here an important remark should be made, that at a Si^{4+} site the exact tetrahedral symmetry does not hold even in crystalline α -quartz [19]. Moreover, in the case of amorphous quartz even stronger random distortions of the tetrahedral symmetry are expected and thus $D_0 \neq 0, E_0 \neq 0$ hold. Nevertheless, it is reasonable to assume that for an $[\text{FeO}_4]^0$ centre even in the amorphous case the condition

$$|D_0| \gg |E_0| \quad (5)$$

is realized and as a zero-order approximation one can assume condition (4) to be satisfied. In this case, the eigenvalues of operator S_z are the proper quantum numbers and the energy spectrum of \hat{H}_Q takes the simple form

$$E_{Q_M}^{(0)} = D_0 M^2, \quad M = \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}. \quad (6)$$

According to the EPR data for $[\text{AlO}_4]^0$ centres in α -quartz [19] and estimations of the Fe^{3+} electronic quadrupole moment, one finds that for an $[\text{FeO}_4]^0$ centre the following condition holds:

$$D_0 < 0. \quad (7)$$

Therefore, the ground energy level of \hat{H}_Q is a degenerate doublet with $M = \pm\frac{5}{2}$:

$$E_{Q_G}^{(0)} = \frac{25}{4} D_0. \quad (8)$$

Since the first excited doublet is separated from the ground one by a gap of $-4D_0 \sim 40$ K, the thermodynamic population of the levels with $M = \pm\frac{3}{2}, \pm\frac{1}{2}$ may be neglected in the temperature region

$$T \ll |D_0|. \quad (9)$$

The lattice distortions, inherent to the glass structure, violate the C_3 symmetry at an Fe^{3+} site and give rise to the spectrum corrections due to $E_0 \neq 0$. According to the Kramers theorem, these corrections cannot lift the doublets' degeneracy, but only change the gaps between the

degenerate doublets. Nevertheless, if condition (5) is satisfied, the ground level (8) remains the only thermodynamically relevant one and therefore the corrections due to $E_0 \neq 0$ may be neglected.

In the zero-order approximation one can use products of eigenfunctions of the operators S_z and s_z as a basis set:

$$\Psi_{M,m}^{(0)} = |M, m\rangle, \quad M = \pm\frac{5}{2}; \quad m = \pm\frac{1}{2}. \quad (10)$$

The first-order corrections from \hat{H}_Z, \hat{H}_D to the ground energy level (8) and the corresponding eigenstates are as follows:

$$E_{1/3}^{(1)} = -\frac{5}{2}g_0\beta B_z \mp \sqrt{\frac{1}{4}g_0^2\beta^2 (B_x^2 + B_y^2) + \left(\frac{5}{4}V_z - \frac{1}{2}g_0\beta B_z\right)^2}, \quad (11)$$

$$E_{2/4}^{(1)} = \frac{5}{2}g_0\beta B_z \mp \sqrt{\frac{1}{4}g_0^2\beta^2 (B_x^2 + B_y^2) + \left(\frac{5}{4}V_z + \frac{1}{2}g_0\beta B_z\right)^2};$$

$$\Psi_{1/2}^{(1)} = \frac{\left(-\frac{5}{4}V_z \mp 2g_0\beta B_z - E_{1/2}^{(1)}\right) |\mp\frac{5}{2}, \mp\frac{1}{2}\rangle - \frac{1}{2}g_0\beta (B_x \mp iB_y) |\mp\frac{5}{2}, \pm\frac{1}{2}\rangle}{\sqrt{\left(-\frac{5}{4}V_z \mp 2g_0\beta B_z - E_{1/2}^{(1)}\right)^2 + \frac{1}{4}g_0^2\beta^2 (B_x^2 + B_y^2)}}, \quad (12)$$

$$\Psi_{3/4}^{(1)} = \frac{\left(\frac{5}{4}V_z \mp 3g_0\beta B_z - E_{3/4}^{(1)}\right) |\mp\frac{5}{2}, \pm\frac{1}{2}\rangle - \frac{1}{2}g_0\beta (B_x \pm iB_y) |\mp\frac{5}{2}, \mp\frac{1}{2}\rangle}{\sqrt{\left(\frac{5}{4}V_z \mp 3g_0\beta B_z - E_{3/4}^{(1)}\right)^2 + \frac{1}{4}g_0^2\beta^2 (B_x^2 + B_y^2)}}.$$

The second-order corrections to the ground quadruplet (11), affecting the levels' positions relative to their 'mass centre', are as follows:

$$E_{1/2}^{(2)} = \frac{5g_0^2\beta^2 V_\perp^2 (B_x^2 + B_y^2)}{16D_0 \left[\left(-\frac{5}{4}V_z \mp 2g_0\beta B_z - E_{1/2}^{(1)}\right)^2 + \frac{1}{4}g_0^2\beta^2 (B_x^2 + B_y^2) \right]}; \quad (13)$$

$$E_{3/4}^{(2)} = \frac{5V_\perp^2 \left(\frac{5}{4}V_z \mp 3g_0\beta B_z - E_{3/4}^{(1)}\right)^2}{16D_0 \left[\left(\frac{5}{4}V_z \mp 3g_0\beta B_z - E_{3/4}^{(1)}\right)^2 + \frac{1}{4}g_0^2\beta^2 (B_x^2 + B_y^2) \right]}.$$

The condition of smallness of the Zeeman energy relative to the quadrupole one,

$$g_0\beta B \ll |D_0|, \quad (14)$$

holds in the range of magnetic fields $B \ll 10$ T, in which most of the experimental data under consideration are obtained. Therefore the spin \mathbf{S} may be considered to be quantized along the axis \mathbf{u} .

The condition of smallness of the Zeeman energy relative to the dipole interaction,

$$g_0\beta B \ll |V_z|, \quad (15)$$

holds in the range $B \ll 1$ T, in which the spin \mathbf{s} is quantized along \mathbf{S} due to the dipole coupling. In this case \mathbf{u} is a proper quantization axis for the $[\text{FeO}_4]^0$ total spin $\mathbf{J} = \mathbf{S} + \mathbf{s}$. Thus, if condition (15) is satisfied, the only linear B -field contribution appearing in spectrum (11) is that proportional to B_z .

If condition (15) is not met, the spin \mathbf{s} behaves like a free one and therefore the terms $\pm\frac{1}{2}g_0\beta B$ appear in spectrum (11).

It should be mentioned that transitions between the states $|\pm\frac{5}{2}\rangle$ under the influence of alternating B -field are forbidden according to the selection rule $\Delta M = \pm 1$ and therefore cannot be observed by the EPR methods.

3. $[\text{FeO}_4]^0$ centres as paramagnetic tunnelling systems and their dielectric susceptibility

It is established that the four O^{2-} anions neighbouring the Si^{4+} cation in a perfect crystalline lattice of α -quartz are equivalent in pairs. Namely, two of them form the long bonds to Si^{4+} with length 1.6145 Å, and two the short ones with length 1.6101 Å. A similar situation also occurs for the $[\text{AlO}_4]^0$ substitution centres in α -quartz [19]. Therefore, the hole traps at the long-bonded anions are about 0.03 eV deeper than those at the short-bonded ones. This means that in the subkelvin temperature range the hole is surely localized at one of the long-bonded oxygens. It is established for $[\text{AlO}_4]^0$ in α -quartz that at $T \leq 15$ K only the ground hole states in each trap are relevant [20]. Therefore the accessible hole states are restricted to the ground states $|l\rangle$ and $|r\rangle$ in an effective one-dimensional symmetric double-well potential.

If condition (15) is satisfied, the ground spin Hamiltonian doublet E_1, E_2 is separated from the next doublet E_3, E_4 with a gap $\Delta E \approx 2.5|V_z| \sim 1$ K and therefore only E_1, E_2 energy levels are thermodynamically relevant at

$$T \ll |V_z|. \quad (16)$$

Therefore, in the subkelvin temperature range both coordinate and spin relevant degrees of freedom in the effective Hamiltonian of the $[\text{FeO}_4]^0$ centre may be introduced in the pseudospin-1/2 representation and the centre itself may be treated in the frame of the PTS formalism [15].

An overlap of the states $|l\rangle$ and $|r\rangle$ leads to the hole delocalization between them and causes a tunnelling splitting Δ_0 of the ground energy level. For the $[\text{AlO}_4]^0$ centres in crystalline α -quartz $\Delta_0 \approx 12.4$ mK [20], and for the $[\text{FeO}_4]^0$ centres such experimental data are absent. Moreover, in the case of the $[\text{FeO}_4]^0$ centres in amorphous quartz it is natural to assume that the double-well potential in the general case is an asymmetric one with the ground energy difference h and tunnelling splitting Δ . The values h and Δ are random quantities obeying a certain distribution function $P_{\text{PTS}}(h, \Delta)$. Hereafter, the parameters h and Δ are assumed to be independent and thus the distribution function has the form $P_{\text{PTS}}(h, \Delta) = f(h)g(\Delta)$. The distribution function $f(h)$ is assumed to be Gaussian, centred at zero and with half-width δh , which is a fitting parameter of the theory. Moreover, the distribution $g(\Delta)$ is expected to have a maximum at Δ close to Δ_0 , the value corresponding to $[\text{FeO}_4]^0$ centres in crystalline quartz. This function is also expected to vanish quite rapidly when the argument approaches zero or infinity. The simplest one-parameter function meeting these conditions is a Poisson distribution. Then for the PTS distribution normalized to unity one has

$$P_{\text{PTS}}(h, \Delta) = \frac{4\Delta^2}{\sqrt{2\pi}\delta h\Delta_0^3} \exp\left(-\frac{h^2}{2\delta h^2}\right) \exp\left(-\frac{2\Delta}{\Delta_0}\right). \quad (17)$$

Let Pauli matrices $\hat{\sigma}_x, \hat{\sigma}_y$ and $\hat{\sigma}_z$ be the dimensionless components of the PTS dipole moment and act in the subspace of coordinate states with the basis $\{|l\rangle, |r\rangle\}$ (basis states correspond to the hole localization in two accessible traps). Moreover, let Pauli matrices $\hat{\tau}_x, \hat{\tau}_y, \hat{\tau}_z$ be the dimensionless components of the PTS magnetic moment and act in the subspace of spin states with the basis $\{|p\rangle, |a\rangle\}$ (basis states correspond to $\Psi_{1,2}$).

Let us also define operators

$$\hat{\sigma}_{\pm} = \frac{1}{2}(\hat{\sigma}_x \pm i\hat{\sigma}_y); \quad \hat{\tau}_{\pm} = \frac{1}{2}(\hat{\tau}_x \pm i\hat{\tau}_y), \quad (18)$$

acting on the basis states as follows:

$$\begin{aligned} \hat{\sigma}_+ |l\rangle &= \frac{1}{2} |r\rangle, & \hat{\sigma}_+ |r\rangle &= 0, & \hat{\sigma}_- |l\rangle &= 0, & \hat{\sigma}_- |r\rangle &= \frac{1}{2} |l\rangle; \\ \hat{\tau}_+ |p\rangle &= \frac{1}{2} |a\rangle, & \hat{\tau}_+ |a\rangle &= 0, & \hat{\tau}_- |p\rangle &= 0, & \hat{\tau}_- |a\rangle &= \frac{1}{2} |p\rangle. \end{aligned} \quad (19)$$

Radius-vectors, connecting the Fe^{3+} and O^- ions in the states $|l\rangle$ and $|r\rangle$, will be denoted $\mathbf{r}_{|l\rangle}$ and $\mathbf{r}_{|r\rangle}$ respectively. They define the $[\text{FeO}_4]^0$ dipole moment in these states:

$$\mathbf{p}_{|r\rangle,|l\rangle} = e\mathbf{r}_{|r\rangle,|l\rangle}, \quad (20)$$

where e is an elementary charge.

In the α -quartz crystalline lattice the vectors $\mathbf{r}_{|l\rangle}$ and $\mathbf{r}_{|r\rangle}$ form an angle $\alpha_0 \approx 108^\circ$. It is to be expected that in an amorphous network the angle α is a random variable, obeying a certain distribution function $P(\alpha)$. However, in further discussion $P(\alpha) = \delta(\alpha - \alpha_0)$ will be taken for simplicity.

Under condition (15), the linear Zeeman splitting between the states $|p\rangle$ and $|a\rangle$ in each of the states $|l\rangle$, $|r\rangle$ is given by formula (11):

$$u_{|l\rangle,|r\rangle}^Z(\mathbf{B}) = 6g_0\beta\mathbf{u}_{|l\rangle,|r\rangle} \cdot \mathbf{B}, \quad (21)$$

where $\mathbf{u}_{|l\rangle}$ and $\mathbf{u}_{|r\rangle}$ are the unit vectors, corresponding to $\mathbf{r}_{|l\rangle}$ and $\mathbf{r}_{|r\rangle}$ and defining the directions of the axis z in the states $|l\rangle$ and $|r\rangle$.

The external electric field \mathbf{E} applied affects the double-well potential asymmetry in the following way:

$$h(\mathbf{E}) = h_0 + (\mathbf{p}_{|l\rangle} - \mathbf{p}_{|r\rangle}) \cdot \mathbf{E}, \quad (22)$$

where h_0 is the asymmetry value at $\mathbf{E} = 0$.

Since $\mathbf{u}_{|l\rangle}$ and $\mathbf{u}_{|r\rangle}$, being the spin quantization axes in the states $|l\rangle$ and $|r\rangle$, are not parallel, transitions between these states are accompanied by rotation of the coordinate system, within which the spin components \hat{t}_x , \hat{t}_y and \hat{t}_z are defined.

The single-well PTS spin wavefunction ψ_s is a spinor, which transforms at the coordinate system rotation on arbitrary angle α around a unit vector \mathbf{n} according to the following formula (see e.g. [21]):

$$\begin{aligned} \psi'_s &= \mathbf{U}_n \psi_s, & \psi_s &= \begin{pmatrix} c_{|p\rangle} \\ c_{|a\rangle} \end{pmatrix}, \\ \mathbf{U}_n &= \cos(\alpha/2) + \mathbf{i}\mathbf{n} \cdot \hat{\mathbf{t}} \sin(\alpha/2), & \hat{\mathbf{t}} &= \begin{pmatrix} \hat{t}_x \\ \hat{t}_y \\ \hat{t}_z \end{pmatrix}. \end{aligned} \quad (23)$$

Using the notations defined above, the off-diagonal (tunnelling) part of the PTS Hamiltonian reads

$$\hat{H}_{\text{PTS}}^{\text{o.-d.}} = -\frac{1}{2}\Delta (\hat{\sigma}_+ \mathbf{U}_n + \hat{\sigma}_- \mathbf{U}_n^{-1}) = -\frac{1}{2}\Delta [\hat{\sigma}_x \cos(\alpha/2) - \hat{\sigma}_y \mathbf{n} \cdot \hat{\mathbf{t}} \sin(\alpha/2)], \quad (24)$$

where Δ denotes the tunnelling matrix element between the states $|l\rangle$ and $|r\rangle$ in the Hamiltonian of a spinless (two-level) TS.

Since the rotation can affect only the spin components \hat{t}_x and \hat{t}_z , the vector \mathbf{n} is directed along y : $n_x = n_z = 0$, $n_y = 1$.

Then the PTS Hamiltonian takes the form

$$\hat{H}_{\text{PTS}} = -1/2 (h\hat{\sigma}_z + \delta\hat{\sigma}_x + u_+^Z \hat{t}_z + u_-^Z \hat{t}_z \hat{\sigma}_z - D\hat{\sigma}_y \hat{t}_y), \quad (25)$$

where

$$u_+^Z = \frac{1}{2} (u_{|r\rangle}^Z + u_{|l\rangle}^Z), \quad u_-^Z = \frac{1}{2} (u_{|r\rangle}^Z - u_{|l\rangle}^Z); \quad (26)$$

$$\delta = \Delta \cos(\alpha/2), \quad D = \Delta \sin(\alpha/2). \quad (27)$$

The essential feature of the PTS Hamiltonian (25) is the last term, accounting for the tunnelling-induced entanglement of spin states. Without loss of this feature one can consider the simplified case $u_-^Z = 0$, corresponding to the situation when \mathbf{B} is directed along the bisector

line of the angle α . By introducing a brief notation $u^Z \equiv u_+^Z$, this simplified Hamiltonian reads

$$\hat{H}_{\text{PTS}} = -1/2 (h\hat{\sigma}_z + \delta\hat{\sigma}_x + u^Z\hat{\tau}_z - D\hat{\sigma}_y\hat{\tau}_y). \quad (28)$$

By projecting \hat{H}_{PTS} (28) onto the basis $\{|l, a\rangle, |r, a\rangle, |l, p\rangle, |r, p\rangle\}$ and finding the principal values of the resulting matrix, one readily obtains the PTS energy spectrum:

$$U_{1/4} = \mp \frac{1}{2} \sqrt{G_+^2 + D^2}; \quad U_{2/3} = \mp \frac{1}{2} \sqrt{G_-^2 + D^2}. \quad (29)$$

In formula (29) a brief notation $G_{\pm} = u^Z \pm \sqrt{h^2 + \delta^2}$ is introduced.

From (29) one can see that a nonzero value of the parameter D , being the tunnelling matrix element between the states with different spin projections (and therefore accounting for the tunnelling-induced entanglement of spin states), prevents degeneration of the levels U_2 and U_3 at $u^Z = \sqrt{h^2 + \delta^2}$. This is an essential feature of the PTS model, giving rise to the nonmonotonic B -dependence of the PTS dynamic dielectric susceptibility (see (35), (36) and speculations below).

Using the energy spectrum (29), it is straightforward to write down an expression for the isolated single-PTS free energy:

$$f_{\text{PTS}} [u^Z(\mathbf{B}), h(\mathbf{E}), \delta, D, T] = -T \ln \left[2 \cosh \left(\sqrt{G_+^2 + D^2} / 2T \right) + 2 \cosh \left(\sqrt{G_-^2 + D^2} / 2T \right) \right]. \quad (30)$$

Using the PTS free energy (30) together with the PTS parameter distribution function (17), one is able to derive the PTS contribution to thermodynamic quantities. As an example the calculation of the PTS ensemble dielectric susceptibility is presented below. In further discussion the dielectric response of the PTS ensemble is assumed to be isotropic and therefore the susceptibility function is a scalar.

The static dielectric susceptibility of a single PTS is given by the expression

$$\chi_{\text{PTS}}^{\text{stat}} = -\partial^2 f_{\text{PTS}} / \partial E^2. \quad (31)$$

For the sake of brevity, in equation (31) and below the arguments $u^Z(\mathbf{B})$, $h(\mathbf{E})$, δ , D and T of the free energy (30) and its derivatives are omitted where possible.

To account for the PTS relaxation dynamics at a finite frequency ω of external electric driving field one needs to separate the static expression (31) into the resonant $\chi_{\text{PTS}}^{\text{res}}$ (frequency-independent) and the relaxation $\chi_{\text{PTS}}^{\text{rel}}$ (frequency-dependent) parts. This separation looks natural if one notes that the expression for PTS polarization $\mathbf{P}_{\text{PTS}} = -\partial f_{\text{PTS}} / \partial \mathbf{E}$ is a sum (over the four PTS energy levels) of products of the relative population factors (obeying the Gibbs distribution in the static case) and the corresponding diagonal elements of the PTS dipole operator (in the energy representation). Thus the expression for $\chi_{\text{PTS}}^{\text{res}}$ contains the result of differentiation of the dipole matrix elements keeping the population factors constant, and the expression for $\chi_{\text{PTS}}^{\text{rel}}$ contains the result of differentiation of the population factors keeping the dipole matrix elements constant. Moreover, the population factors are the frequency-dependent quantities, since equilibration of a PTS with its environment takes a finite time.

The general form of the expression for the PTS dielectric susceptibility at a finite frequency ω is as follows:

$$\chi_{\text{PTS}}(\omega) = \chi_{\text{PTS}}^{\text{res}} + \chi_{\text{PTS}}^{\text{rel}} \phi(\omega, \{\tau\}), \quad (32)$$

where $\{\tau\}$ denotes a set of (three in the general case) PTS-lattice relaxation times, and $\phi(\omega, \{\tau\})$ denotes a complex function, accounting for the nonequilibrium PTS response to ac external driving field.

The explicit forms of $\chi_{\text{PTS}}^{\text{res}}$ and $\chi_{\text{PTS}}^{\text{rel}}$ are as follows:

$$\chi_{\text{PTS}}^{\text{res}} = \frac{(p_{\text{eff}}^2/3) \sinh\left(\sqrt{G_+^2 + D^2}/2T\right) \left[G_+ \delta^2 (G_+^2 + D^2) + h^2 D^2 \sqrt{h^2 + \delta^2}\right]}{\left[\cosh\left(\sqrt{G_+^2 + D^2}/2T\right) + \cosh\left(\sqrt{G_-^2 + D^2}/2T\right)\right] \left[(h^2 + \delta^2) (G_+^2 + D^2)\right]^{3/2}} - \frac{(p_{\text{eff}}^2/3) \sinh\left(\sqrt{G_-^2 + D^2}/2T\right) \left[G_- \delta^2 (G_-^2 + D^2) - h^2 D^2 \sqrt{h^2 + \delta^2}\right]}{\left[\cosh\left(\sqrt{G_+^2 + D^2}/2T\right) + \cosh\left(\sqrt{G_-^2 + D^2}/2T\right)\right] \left[(h^2 + \delta^2) (G_-^2 + D^2)\right]^{3/2}}, \quad (33)$$

$$\chi_{\text{PTS}}^{\text{rel}} = \frac{(p_{\text{eff}}^2/3) h^2 \left[\cosh\left(\frac{\sqrt{G_+^2 + D^2}}{2T}\right) \frac{G_+^2}{G_+^2 + D^2} + \cosh\left(\frac{\sqrt{G_-^2 + D^2}}{2T}\right) \frac{G_-^2}{G_-^2 + D^2}\right]}{2T (h^2 + \delta^2) \left[\cosh\left(\sqrt{G_+^2 + D^2}/2T\right) + \cosh\left(\sqrt{G_-^2 + D^2}/2T\right)\right]} - \frac{(p_{\text{eff}}^2/3) h^2 \left[\sinh\left(\frac{\sqrt{G_+^2 + D^2}}{2T}\right) \frac{G_+}{\sqrt{G_+^2 + D^2}} - \sinh\left(\frac{\sqrt{G_-^2 + D^2}}{2T}\right) \frac{G_-}{\sqrt{G_-^2 + D^2}}\right]^2}{2T (h^2 + \delta^2) \left[\cosh\left(\sqrt{G_+^2 + D^2}/2T\right) + \cosh\left(\sqrt{G_-^2 + D^2}/2T\right)\right]^2}, \quad (34)$$

where $p_{\text{eff}}^2 = (\mathbf{p}_{\parallel}) - \mathbf{p}_{\parallel r})^2$.

Both $\chi_{\text{PTS}}^{\text{res}}$ and $\chi_{\text{PTS}}^{\text{rel}}$ contain contributions which depend nonmonotonically on u^Z at nonzero $\sqrt{h^2 + \delta^2}$. Let us denote them $\tilde{\chi}_{\text{PTS}}^{\text{res}}$ and $\tilde{\chi}_{\text{PTS}}^{\text{rel}}$ respectively:

$$\tilde{\chi}_{\text{PTS}}^{\text{res}} = \frac{(p_{\text{eff}}^2/3) \sinh\left(\sqrt{G_-^2 + D^2}/2T\right) h^2 D^2}{\left[\cosh\left(\sqrt{G_+^2 + D^2}/2T\right) + \cosh\left(\sqrt{G_-^2 + D^2}/2T\right)\right] (h^2 + \delta^2) (G_-^2 + D^2)^{3/2}}; \quad (35)$$

$$\tilde{\chi}_{\text{PTS}}^{\text{rel}} = \frac{(p_{\text{eff}}^2/3) h^2 \cosh\left(\sqrt{G_-^2 + D^2}/2T\right) G_-^2 / (G_-^2 + D^2)}{2T (h^2 + \delta^2) \left[\cosh\left(\sqrt{G_+^2 + D^2}/2T\right) + \cosh\left(\sqrt{G_-^2 + D^2}/2T\right)\right]}. \quad (36)$$

At $u^Z = \sqrt{h^2 + \delta^2}$, $\tilde{\chi}_{\text{PTS}}^{\text{res}}$ and $\tilde{\chi}_{\text{PTS}}^{\text{rel}}$ reach their maximum and minimum values respectively. The characteristic width of these ‘humps’ is proportional to D . Therefore, a nonzero value of the parameter D , which accounts for the tunnelling-induced entanglement of spin states (see (24) and (27)), causes the PTS dynamic dielectric susceptibility (32) to be a nonmonotonic function of u^Z .

The function $\phi(\omega, \{\tau\})$ has the following limits:

$$\lim_{\omega \rightarrow 0} \phi(\omega, \{\tau\}) = 1; \quad \lim_{\omega \rightarrow \infty} \phi(\omega, \{\tau\}) = 0. \quad (37)$$

In practice a frequency may be considered either infinitely small or large if the conditions either $\omega \tau_{\text{max}} \rightarrow 0$ or $\omega \tau_{\text{min}} \rightarrow \infty$ are met, where $\tau_{\text{max}(\text{min})}$ is a maximal (minimal) value from the set of PTS relaxation times.

At finite values of $\omega(\tau)$ (τ is a characteristic relaxation time) the imaginary part of $\phi(\omega, \{\tau\})$ is nonzero, and therefore the PTS dynamic dielectric susceptibility (32) is a complex value.

It is easy to see that a sum of nonmonotonic contributions (35) and (36) is a monotonic function of u^Z at $D \ll T$ (the condition which holds in the major part of the experimental temperature range; see (27) and table 2). Therefore, from (37) one finds that the static PTS susceptibility (31) $\chi_{\text{PTS}}^{\text{stat}} = \lim_{\omega \rightarrow 0} \chi_{\text{PTS}}(\omega)$ is a monotonic function of u^Z .

The relaxation of dielectric response of the $[\text{AlO}_4]^{0-}$ centres in α -quartz was experimentally studied at $B = 0$ [20]. Assuming the phonon-mediated ground-state relaxation time of these

Table 2. Fitting parameters in expression (40) for BAS.

n (m ⁻³)	α_0	$\sqrt{p_{\text{eff}}^2}$ (D)	ε_m	Δ_0 (K)	δh (K)
3.23×10^{24}	108° [20]	5.2 [20]	7.0 [2]	25×10^{-3}	2.3×10^4

centres at $T \gg \Delta$ to be inversely proportional to temperature and extrapolating the data [20] obtained, for the temperature $T \sim 10^{-1}$ K one finds

$$\langle \tau \rangle \approx 5 \times 10^{-2} \text{ s.} \quad (38)$$

From (38) for the experimental frequency $\nu = 1$ kHz one obtains $\omega \langle \tau \rangle \approx 300$, the value corresponding to almost completely resonant response character. Meanwhile, experimental data [1] give comparable magnitudes of relative variations of the real and imaginary parts of the susceptibility, which fact contradicts the estimated value (38). The reason for this misfit may be that the values of the double-well potential parameters, characteristic to glasses, especially the energy asymmetries h , are quite different from those characteristic to crystals, which may lead to a considerable decrease of $\langle \tau \rangle$.

The problem of derivation of an explicit form of the function $\phi(\omega, \{\tau\})$ at finite values of ω and B is outside the scope of the present investigation and will be considered elsewhere. Here the calculations are restricted to the high-frequency limit of the PTS ensemble linear dielectric susceptibility (the pure resonant response):

$$\lim_{\omega \rightarrow \infty} \chi_{\text{PTS}}(\omega) = \chi_{\text{PTS}}^{\text{res}}. \quad (39)$$

Since $\delta\varepsilon'(B) \ll \varepsilon'$, the following formula for $\delta\varepsilon'(B)/\varepsilon'$ in the high-frequency limit is true:

$$\begin{aligned} \lim_{\omega \rightarrow \infty} \delta\varepsilon'(B, T)/\varepsilon' &= \frac{n \left[\langle \chi_{\text{PTS}}^{\text{res}}(B, T) \rangle_{\text{PTS}} - \langle \chi_{\text{PTS}}^{\text{res}}(0, T) \rangle_{\text{PTS}} \right]}{\varepsilon_m \varepsilon_0} \\ &= \frac{n}{\varepsilon_m \varepsilon_0 k_B} \int_0^\infty d\Delta \int_{-\infty}^\infty dh P_{\text{PTS}}(h, \Delta) \\ &\quad \times \left\{ \chi_{\text{PTS}}^{\text{res}} \left[6g_0\beta B \cos\left(\frac{\alpha_0}{2}\right), h, \Delta \cos\left(\frac{\alpha_0}{2}\right), \Delta \sin\left(\frac{\alpha_0}{2}\right), T \right] \right. \\ &\quad \left. - \chi_{\text{PTS}}^{\text{res}} \left[0, h, \Delta \cos\left(\frac{\alpha_0}{2}\right), \Delta \sin\left(\frac{\alpha_0}{2}\right), T \right] \right\}, \end{aligned} \quad (40)$$

where n is a PTS volume concentration, ε_m and ε_0 are the material and vacuum dielectric constants respectively and $\langle \dots \rangle_{\text{PTS}}$ denotes averaging over the PTS distribution function (17).

The results of fitting equation (40) to experimental data [1] for BAS are presented in figure 1. The values of fitting parameters are gathered in table 2.

4. A contribution of $[\text{FeO}_4]^0$ centres to specific heat

In this section a contribution from the $[\text{FeO}_4]^0$ ensemble to the specific heat as a function of B and T is calculated.

Since the specific heat anomalies in some quartz glasses are observed mainly in the subkelvin temperature range, in which condition (9) is satisfied, one can restrict a partition function to the ground quadruplet of the $[\text{FeO}_4]^0$ spin Hamiltonian, within the second order of perturbation theory given by expressions (11) and (13). One should take into account that the structural disorder, characteristic to glasses, makes the parameters V_z and V_\perp of the

dipole interaction operator \hat{H}_D random variables. The values V_z and V_\perp are interdependent and obey a relation which for a pair of point dipoles reads $V_z = -2V_\perp$. Therefore, a single-argument distribution function $G(V_z)$ is enough to account for the randomness of \hat{H}_D . The distribution function $G(V_z)$ must approach zero while its argument approaches either zero or infinity and have a maximum at a definite argument value V_0 . The simplest one-parameter function demonstrating such properties is a Poisson distribution:

$$G(V_z) = \frac{4V_z^2}{V_0^3} \exp\left(-\frac{2V_z}{V_0}\right), \quad V_z \in (-\infty; 0]. \quad (41)$$

One should remember that V_z is a negative value (the ground state corresponds to the parallel dipole orientation) and therefore $V_0 < 0$.

The angular distribution of quantization axes \mathbf{u} in vitreous solids may be assumed to be isotropic:

$$H(\theta, \varphi) = (4\pi)^{-1}. \quad (42)$$

Tunnelling transitions between the coordinate states $|l\rangle$ and $|r\rangle$ ensure their equilibrium population at any temperature and therefore their contribution should be considered too. Since the experimental data on specific heat are taken in the temperature range $T \gg \Delta_0$, one may neglect the contribution of tunnelling splitting to the energy difference between these states and assume it to be equal to h , where h is a random value, obeying distribution (17).

If one assumes $\Delta = 0$, the tunnelling-induced coupling between the spatial and spin degrees of freedom vanishes and therefore the free energy of an $[\text{FeO}_4]^0$ centre reduces to a sum of spin and tunnelling contributions.

Thus, the subkelvin-range free energy of the $[\text{FeO}_4]^0$ ensemble, with the volume concentration n and obeying distribution functions (17), (41) and (42), reads

$$F_{[\text{FeO}_4]^0}(T, B) = F_{\text{spin}}(T, B) + F_{\text{tun}}(T), \quad (43)$$

where

$$F_{\text{spin}}(T, B) = -Tn \int_{-\infty}^0 dV_z G(V_z) \times \frac{1}{2} \int_0^\pi d\theta \sin(\theta) \times \ln \left[\sum_{i=1}^4 \exp\left(-\frac{E_i^{(1)} + E_i^{(2)}}{T}\right) \right], \quad (44)$$

$$F_{\text{tun}}(T) = -Tn \int_0^\infty d\Delta \int_{-\infty}^\infty dh P_{\text{PTS}}(h, \Delta) \times \ln \left[2 \cosh\left(\frac{h}{2T}\right) \right]. \quad (45)$$

The contribution from the $[\text{FeO}_4]^0$ ensemble to specific heat of a unit-mass sample with the mass density ρ is as follows:

$$C_{[\text{FeO}_4]^0}(T, B) = -\frac{T}{\rho} \frac{\partial^2 F_{[\text{FeO}_4]^0}(T, B)}{\partial T^2}. \quad (46)$$

In (46), as usual for solids, the difference between specific heat at a constant pressure and a constant volume is neglected.

From (45) one finds that the contribution from tunnelling transitions to specific heat reads

$$C_{\text{tun}}(T) = \sqrt{\frac{2n}{\pi}} \frac{T}{\rho} \frac{1}{\delta h} L\left(\frac{\delta h}{T}\right); \quad (47)$$

$$L\left(\frac{\delta h}{T}\right) = \int_{-\infty}^\infty x^2 \exp\left[-\frac{2x^2}{(\delta h/T)^2}\right] (\cosh x)^{-2} dx.$$

At $\delta h \gg T$ L is a constant and the value $C_{\text{tun}}(T) \propto T/\delta h$ may be neglected due to large characteristic values of δh for glasses (see table 2).

Table 3. Fitting parameters in formula (48) for different glasses.

Glass	n/ρ (kg ⁻¹)	γ_{ph} (J kg ⁻¹ K ⁻⁴)	γ_{TS} (J kg ⁻¹ K ⁻²)	V_0 (K)	D_0 (K)
BAS	1.05×10^{21}	1.55×10^{-3}	3.1×10^{-4}	-0.42	-10
Duran	2.5×10^{21}	2.0×10^{-3}	2.5×10^{-4}	-0.42	-10
Pyrex 7740	2.3×10^{21}	2.5×10^{-3}	7×10^{-4}	-0.42	-10
Pyrex 9700	0.8×10^{21}	2.5×10^{-3}	7×10^{-4}	-0.42	-10

The final expression for specific heat per unit-mass of an amorphous solid, containing $[\text{FeO}_4]^0$ centres, reads

$$C_P(T, B) = C_g(T) + C_{\text{spin}}(T, B), \quad (48)$$

where $C_g(T)$ is given by (1) and $C_{\text{spin}}(T, B)$ is obtained from (44).

The results of fitting formula (48) to experimental data on specific heat for BAS, Duran and two sorts of Pyrex are presented in figures 3(a)–(c). The values of fitting parameters are collected in table 3.

5. An analysis of the results obtained

In this section the results obtained are discussed and compared to the experimental data available. From figure 1 one can see that the dependence $\delta\varepsilon'(B)/\varepsilon'$ for BAS, calculated in the approximation of linear resonant response of the $[\text{FeO}_4]^0$ -based PTS ensemble, is in a semiquantitative agreement with experimental data [1] at $T = 50$ and 520 mK.² In particular, the increase of B_{max} as well as the decrease of the amplitude $\delta\varepsilon'(B)/\varepsilon'$ with increasing temperature is reproduced. At the same time some quantitative disagreement is observed, which may be attributed both to the oversimplicity of the model and to nonlinear effects. The former includes the simplification of the PTS Hamiltonian (28) and the simplest possible form of the model distribution function $P_{\text{PTS}}(h, \Delta)$ (17) used. Another significant simplification is consideration of only the two lowest energy levels E_1 and E_2 of the spin Hamiltonian and only the two lowest coordinate states of the hole. Nevertheless, in the region of small B and T , where conditions (15) and (16) are satisfied, the agreement between the theory and the experiment is good, but outside this region only a qualitative agreement is achieved.

The effect of relaxation on the dielectric response of the PTS ensemble at finite frequencies will be published elsewhere.

The value of PTS volume concentration n derived is close to the reported data of chemical analysis [2], according to which BAS contains about 100 ppm of Fe^{3+} impurities. It is worth noting that, since not all Fe^{3+} ions necessarily form the $[\text{FeO}_4]^0$ centres, an exact coincidence between the value of n derived and the data of chemical analysis is not expected.

The large value obtained for the half-width δh (see table 2) of the distribution (17) of the double-well potential asymmetries, ~ 1 eV, seems quite reasonable and reflects the degree of the lattice distortion compared to crystalline quartz, where this value is ~ 1 K [20]. Therefore, a conclusion may be drawn that at equal concentrations of $[\text{FeO}_4]^0$ centres in amorphous and crystalline quartz in the latter case the amplitude of $\delta\varepsilon'(B)/\varepsilon'$ should be a few orders of magnitude larger, because δh enters the denominator of formula (40).

One can see that although the concentrations of $[\text{FeO}_4]^0$ centres in BAS and Duran have equal orders of magnitude (see table 3), for Duran the magnitude of $\delta\varepsilon'(B)/\varepsilon'$ at $B_{\text{max}} \sim 10^{-2}$ T

² The remaining data [1] are taken in the strongly nonlinear regime (see (49) and speculations below) and cannot be fitted with the linear expression (40).

is about 10 times smaller than that for BAS (cf. figures 1 and 2). This behaviour may be explained by a larger value of δh for Duran due to larger lattice distortions (caused by network-modifying impurities, different production technologies etc).

For the function $\delta\varepsilon'(B)/\varepsilon'$ at $T = 15$ mK the present theory gives $B_{\max} \approx 4 \times 10^{-3}$ T, about half the experimental value for Duran in figure 2. The reason for this misfit is probably nonlinear effects, leading to a shift of B_{\max} towards larger values. This conjecture is supported by experimental studies of nonlinear dielectric response in BAS [1].

Generally speaking, the PTS nonlinear susceptibility function may be represented through the series expansion in powers of the parameter

$$\eta = \sqrt{p_{\text{eff}}^2 E / k_B T}, \quad (49)$$

where E is an amplitude of driving electric field. Thus the value of η determines the ‘degree of nonlinearity’ of the response. From equation (49) one finds that at the experimental conditions given in figure 2 $\eta \approx 0.8$, i.e. these data are obtained in a strongly nonlinear regime. The nonlinearity effect may also be the reason for some misfit between the maxima of theoretical and experimental data for BAS at $T = 520$ mK and $E \approx 15$ kV m⁻¹ in figure 1, when the degree of nonlinearity makes up a noticeable value $\eta \approx 0.17$. Indeed, at $T = 50$ mK and $E \approx 0.6$ kV m⁻¹ in figure 1 one finds $\eta \approx 0.07$, and the agreement between experimental and theoretical maxima of $\delta\varepsilon'(B)/\varepsilon'$ at these conditions is much better. Moreover, finally, the similar behaviour of $\delta\varepsilon'(B)/\varepsilon'$ in the borosilicate glasses Duran and BK7 in figure 2, in particular a tendency to an increase of $\delta\varepsilon'(B)/\varepsilon'$ in strong magnetic field, may be explained by a B -field reaction of a subsystem other than the ensemble of $[\text{FeO}_4]^0$ -based PTSs.

As concerns $C_P(T, B)$ of the BAS, Duran and Pyrex glasses, shown in figures 3(a)–(c), a good agreement between the experimental data [2, 5, 6] and the results of the present theory is observed. This fact, together with the realistic values for the concentration n and the $\text{Fe}^{3+}\text{--O}^-$ dipole coupling V_0 derived, is strong evidence for $[\text{FeO}_4]^0$ centres to be present in these glasses. Some quantitative disagreement may be attributed to the oversimplicity of the model distribution function (41) used. At the same time, there is a minor misfit between the experimental and theoretical dependence $C_P(T)$ for Duran at zero magnetic field (figure 3(b)). To a certain extent it may be removed by introducing into calculations the value of residual magnetic field $B_0 \approx 0.05$ T. The same situation occurs with a fit of these experimental data in the frame of the theory of Jug [4] (with a somewhat larger value of B_0).

In general, the values of fitting parameters collected in tables 2 and 3 are in a reasonable agreement with the literature data available. Some of the values in table 2 are adopted from literature sources for the $[\text{AlO}_4]^0$ centres in α -quartz.

Another value which should be B -dependent due to the PTS contribution is the sound velocity v . Calculations performed show that in the resonant (high-frequency) regime

$$\delta v'(B)/v' \propto -\delta\varepsilon'(B)/\varepsilon'. \quad (50)$$

The calculated magnitude of the relative variation of the sound velocity versus magnetic field in Duran is found to be $\delta v'(B)/v' \sim 10^{-8} \dots 10^{-7}$. Similar to the dielectric constant case, one can expect that at the same $[\text{FeO}_4]^0$ concentration, in crystalline quartz the amplitude of $\delta v'(B)/v'$ would be some orders of magnitude larger due to much smaller lattice distortions.

One can also expect for other experimentally observable effects from $[\text{FeO}_4]^0$ -based PTS in quartz, in particular the B -dependent contribution to the amplitude of the spontaneous polarization echo, which will be considered elsewhere.

6. Conclusions

The results presented in this paper argue in favour of a suggestion that the substitution hole-compensated $[\text{FeO}_4]^0$ centres are present in some quartz glasses containing Fe^{3+} impurities, and contribute to their thermodynamic properties in the subkelvin temperature range.

Taking into account the ground quadruplet of states of the $[\text{FeO}_4]^0$ model spin Hamiltonian, a good fit of experimental data on the magnetothermal dependence of the specific heat for the BAS, Duran and Pyrex glasses is produced (see figures 3(a)–(c)).

Taking into account the tunnelling motion of the trapped hole, in the frame of the model of paramagnetic tunnelling systems, a satisfactory fit of experimental data on dielectric constant as a function of temperature and magnetic field is produced for the glass BAS (see figure 1).

Based on the model predictions, one can expect that the contribution from $[\text{FeO}_4]^0$ centres to $C_P(T, B)$ should be qualitatively similar in both amorphous and crystalline quartz (apart from a finite tunnelling contribution (47) in the latter case). At the same time the contribution to $\delta\varepsilon'(B)/\varepsilon'$ and $\delta v'(B)/v'$ in crystalline quartz should be some orders of magnitude larger than it is in amorphous quartz due to the essentially smaller local lattice distortions in the former case. An experimental check of these assumptions would be an additional verification of the model.

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