Multi-Welled Tunneling Model for the Magnetic-Field Effect in Ultracold Glasses

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Puzzling observations of both thermal and dielectric responses in multi-silicate glasses at low temperatures \( T \) to static magnetic fields \( B \) have been reported in the last decade and call for an extension of the standard two-level systems tunneling model. An explanation is proposed, capable of capturing at the same time the \( T \)- and \( B \)-dependence of the specific heat \( C_p \) and of the dielectric constant \( \varepsilon \) in these glasses. This theory points to the existence of anomalous multi-welled tunneling systems in the glasses – alongside the standard two-level systems – and indications are given for glasses which should achieve larger electric magnetocapacitive enhancements.

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The last decade has seen much renewed interest in the physics of cold non-metallic glasses, materials displaying some universal physical properties attributed to the low-energy excitations characterising most amorphous solids. The two-level systems (2LS) tunneling model (TM) [1] has been rather successful in explaining a variety of interesting phenomena dealing with the thermal, dielectric and acoustic properties of structural glasses at temperatures \( T < 1 \) K. Limitations and failures of the 2LS TM (treating cooperative motion in terms of single particles, mostly) on the other hand, have been also discussed [2].

These materials do not present, normally, any remarkable magnetic-field response phenomena other than possibly a weak contribution from trace paramagnetic Fe-impurities. It came thus as a great surprise when measurements showed [3] that in some multi-component silicate glasses (but not in pure \( \alpha \)-SiO\(_2\)) one is able to observe changes in the dielectric constant \( \varepsilon(T,B) \) and already in magnetic fields \( B \) as weak as a few Oe. A typical glass showing a strong response has some 100 ppm Fe\(^{3+}\) and the composition Al\(_2\)O\(_3\)-BaO-SiO\(_2\) (in short AlBaSi-O, in this paper). Measurements made on a thick sol-gel fabricated AlBaSi-O film showed changes in \( \delta \varepsilon/\varepsilon = [\varepsilon(B)−\varepsilon(0)]/\varepsilon(0) \) of order \( 10^{-4} \) and characterised by an enhancement peaking around 0.03 T for 10 mK \(< T < 200 \) mK then followed by a reduction of \( \varepsilon \) for \( B > 0.1 \) T. A further enhancement was also observed at much higher fields (\( B > 10 \) T).

Another, cleaner, multi-component silicate glass (borosilicate BK7, with 6 ppm Fe\(^{3+}\)) and a dirtier one (borosilicate Duran, with 120 ppm Fe\(^{3+}\)) have shown similar – but weaker – magnetic anomalies, \( |\delta \varepsilon/\varepsilon| \sim 10^{-5} \), seemingly excluding the paramagnetic impurities as their source [4]. Yet another multi-silicate glass, \( \alpha \)-SiO\(_{2x+y}\)-C\(_y\)H\(_z\) was investigated [5], confirming the unusual findings in AlBaSi-O. A convincing explanation for the unusual electric magnetocapacitance behavior of these cold glasses has not yet been found.

Recently, some consensus has been gained by the idea of a coupling of the standard 2LS to the magnetic field via nuclei in the glasses carrying an electric quadrupole moment as well as a magnetic dipole one [6]. The nuclear mechanism is supported by some features of the magnetic-field dependence of the polarization echo (PE) experiments in the mentioned multi-silicate glasses in the millikelvin range [7]. Moreover the amplitude of the PE in Glycerol glass was shown to become strongly \( B \)-dependent only upon deuteration and thus the introduction of quadrupole-moment carrying nuclei in the glass [8]. However, though pure \( \alpha \)-SiO\(_2\) (devoid of quadrupole-moment carrying nuclei) shows no PE-amplitude magnetic field dependence [7], Glycerol glass – deuterated or not – shows no measurable \( B \)-dependence in its dielectric constant [9]. The nuclear approach is also unable to account for the magnitude and features of the \( B \)- and \( T \)-dependence of \( \delta \varepsilon/\varepsilon \) for the multi-silicate glasses [10] and the (also unusual) \( B \)- and \( T \)-dependence of the heat capacity \( C_p \) of the latter – not entirely linked to their Fe impurity contents [11, 12] – is not even addressed. To add to the mystery, the acoustic response (also linked to the 2LS coupling to phonons) of borosilicate glasses BK7 and AF45 has been found to be independent of \( B \) [13]. Table I summarises this rather puzzling experimental situation. Therefore, either the nuclear explanation is specific to the PE magnetic effect, or an entirely new explanation should be found for all of the observations.

The purpose of this Letter is to begin to give a rationale to the situation in Table I, as well as to stimulate further experimental and theoretical research. A novel explanation, already shown to account for the unusual behavior of \( C_p(T,B) \) in the multi-silicates [12], is here shown to explain the behavior of the dielectric constant as well. This simple theory is centered on the observation, in computer simulations and experiments [14], that multi-silicate glasses present in their atomic structure both the connected network of SiO\(_4\)-tetrahedra and a collection of pockets and channels of non-networking ions showing a tendency to form microaggregates and to partially destroy the SiO\(_4\)-network. Fig. 1 shows as an example a snapshot of a simulation of the (Na\(_2\)O)-3(SiO\(_2\)) glass il-
illustrating such situation. The present theory proposes that the magnetic effects arise from anomalous tunneling systems (ATS) forming in the cooling of such structure within the non-networking (or network-modifying, NM) pockets and channels, whilst the SiO_{2}-network remains the rest of the ordinary non-magnetic 2LS.

In order to couple the ATS to the magnetic field, a simple 3D generalization of the 2LS TM is in order. As is known\,[1], in the TM the cold glass is thought to have few remaining degrees of freedom rappedresented by fictitious “particles”, each moving quantum-mechanically within a 1D double-welled potential. At low temperatures only the ground states of the individual wells \( |i\rangle \) \((i=1,2)\) are relevant and in this representation the Hamiltonian of a single 2LS reads \( \hat{H}_0 = -\frac{1}{2}\Delta \sigma_z - \frac{1}{2}\Delta_0 \sigma_x \) (\( \sigma_n \) Pauli matrices) with \( \Delta \) the ground-state energy asymmetry between the two wells and \( \Delta_0 \) the barrier’s transparency. These two parameters are linked to the real potential’s details as discussed in the TM literature and are taken, normally, to be distributed in the glass so that \( \Delta \) and \( \ln \Delta_0 \) (roughly, the potential barrier) have a uniform distribution: \( \mathcal{P}\Delta, \Delta_0 = \bar{P}/\Delta_0, \bar{P} \) being a material-dependent constant. This description holds for the network-forming (NF) TS. For the NM ATS instead, the simplest 3D generalization of the 2LS TM is that of other fictitious charged particles, each moving in a multi-welled 3D potential (see Fig. 2) and coupling to the magnetic field through their orbital motion. For the simplest case of \( n_w = 3 \) potential wells, one can use:

\[
H_0 = \begin{pmatrix} E_1 & D_0 e^{i\phi/3} & D_0 e^{-i\phi/3} \\ D_0 e^{-i\phi/3} & E_2 & D_0 e^{i\phi/3} \\ D_0 e^{i\phi/3} & D_0 e^{-i\phi/3} & E_3 \end{pmatrix}
\]

where \( D_0 \simeq h\Omega U_B/h\Omega \) is some 3D barrier’s transparency \((U_B)\) barrier height and \( \Omega \) single-well frequency), \( E_1, E_2, E_3 \) are the single wells’ ground-state energy asymmetries \((E_1 + E_2 + E_3 = 0, \text{ say})\) and

\[
\phi = 2\pi \Phi(B)/\Phi_0 \quad \Phi(B) = B \cdot S_\Delta = BS_\Delta \cos \beta
\]

is some Aharonov-Bohm phase for a “particle” carrying charge \( q \) tracing a closed path of area \( S_\Delta \) threaded by a magnetic flux \( \Phi(B) \) \((\Phi_0 \equiv h/|q| = \varphi_0 |e/|q| \) being the appropriate flux quantum \((\varphi_0 \text{ being the elementary one})\).

In this model the choice \( D_0 > 0 \) can be thought of as arising from the coheren tunneling motion of a small cluster of NM-ions; this will lead, as is seen, to high values of the product \(|q|s_\Delta D_0\). For \( D \equiv \sqrt{E_1^2 + E_2^2 + E_3^2} \ll D_0 \) and weak fields \((\phi \ll 1)\) the lowest energy gap of the model is seen to open with increasing magnetic field according to the simplified expression \[12\] \( \Delta E \simeq \sqrt{D_0^2\phi^2 + D^2} \) containing the main physics of this model (regardless of the value of \( n_w \)). One more assumption of

| glass type   | Ref. | \( \delta C_v \) | \( \delta \epsilon \) | \( \delta v_s \) | \( \delta A_{PE} \) |
|-------------|------|----------------|-----------------|----------------|----------------|
| a-SiO_{2}   | [11],[4],[7] | NO | NO | ? | NO |
| a-SiO_{2+1.5}C_yH_z | [5] | ? | YES | ? | YES |
| AlBaSi-O    | [11],[3],[7] | YES | YES | ? | YES |
| Duran       | [11],[4],[7] | weak | weak | NO | YES |
| BK7         | [11],[4],[13],[2] | weak | weak | NO | YES |
| AF45        | [13] | ? | ? | NO | ? |
| Glycerol    | [9],[8] | ? | NO | ? | weak |
| d-Glycerol  | [9],[8] | ? | NO | ? | YES |

**TABLE I:** Presence of magnetic-field induced variations in the physical properties of some cold glasses. \( C_v \): heat capacity, \( \epsilon \): dielectric constant, \( v_s \): sound velocity, \( A_{PE} \): PE amplitude [?: no investigation known]
this theory (seen to explain the nearly-flat $T$-dependence of $C_p$ for $B = 0$ in some temperature range for these glasses) is to take the parameters’ distribution uniform for $U_B$, but favoring near-degeneracy (to a degree fixed by a lower bound $D_{\text{min}} \neq 0$ for $D$) for the $\{E_i\}$:

$$P_{ATS}(\{E_i\}, \cdots ; D_0) = \frac{P^*}{(E_1^2 + E_2^2 + E_3^2 + \cdots ) D_0}. \quad (3)$$

This anomalous distribution for the ATS can be thought of as arising from a degree of devitrification in the material, as measured by the parameter $P^*$. In fact, it is reported that thick glass films prepared with the sol-gel technique (such as the AlBaSi-O films of the experiments) are multiphase materials with microcrystals embedded within an amorphous glassy matrix. Indeed, amorphous solids with the general composition Al$_2$O$_3$-MgO-CaO-SiO$_2$ are termed “glass ceramics” in the literature owing to partial devitrification occurring. It seems thus reasonable to imagine that in these glasses some NM-ions provide nucleation centres for the microcrystals and that, therefore, TS presenting near-degeneracy may provide a degree of crystallites.

This approach has provided a good description of the $C_p(T, B)$ data for AlBaSi-O and Duran; one can treat the ATS as effective 2LS having gap $\Delta E$ for “weak” fields. Within this picture, the linear-response quasi-static resonant contribution to the polarizability is

$$\alpha_{\mu\nu}^{\text{RES}} = \int_0^{\infty} \frac{dE}{2E} g_{\mu\nu} \left( \frac{E_i}{E} ; p_i \right) \tanh(\frac{E}{2k_B T}) \delta(E - \Delta E)$$

where

$$g_{\mu\nu} \left( \frac{E_i}{E} ; p_i \right) = \sum_{i=1}^{n_w} p_{\mu i} p_{\nu i} - \sum_{i,j}^{n_w} E_i E_j \frac{1}{E^2} p_{\mu i} p_{\nu j} \quad \text{(5)}$$

contains the single-well dipoles $p_i = qa_i$. This expression assumes vanishing electric fields and no TS-TS interactions, a situation which does not wholly apply to the experiments. To keep the theory simple one can still use Eq. (4) and the analogous one for the relaxation contribution to the polarizability. Eq. (4) must be averaged over the random energies’ distribution $\delta E$ (i.e., the large $\Delta E$ responsible for the high sensitivity to weak fields) and over the dipoles’ orientations and strengths ($\cdots$).

For a collection of ATS with $n_w > 2$ this averaging presents serious difficulties and one must resort to the decoupling:

$$\overline{g}_{\mu\nu} \delta(E - \Delta E) \approx \overline{g}_{\mu\nu} \cdot \left( \overline{\delta(E - \Delta E)} \right),$$

where $\overline{\delta(E - \Delta E)} = g_{ATS}(E, B)$ is the fully-averaged density of states. To calculate $\overline{g}_{\mu\nu}$, one can envisage a fully isotropic distribution of planar $n_w$-polygons to obtain:

$$\overline{g}_{\mu\nu} = \frac{1}{3} \frac{n_w}{n_w - 1} p_f (n_w - 2) E^2 + D_{\text{min}} \delta_{\mu\nu}. \quad \text{(7)}$$

The second term in the numerator of Eq. (7) gives rise to a peak in $\delta E/\epsilon$ at very low $B$, while the first term (present only if $n_w > 2$) gives rise to a negative contribution to $\delta E/\epsilon$ at larger $B$ which can win over the enhancement term for all values of $B$ if $D_{\text{max}} \gg D_{\text{min}}$ ($D_{\text{min}}, D_{\text{max}}$ corresponding to cutoffs in the distribution of ATS energy barriers $U_B$). The observations in Duran and BK7 indeed show a significant depression of $\epsilon(B)$ for weak fields, thus giving direct evidence for the existence of ATS with $n_w > 2$ in the multisilicate glasses. Carrying out the averaging $\cdots$ one gets analytical expressions for the polarizability; the uniform average over orientation angles $\beta$ must be performed numerically.

Magnetocapacitance, Al$_2$O$_3$-BaO-SiO$_2$ Glass “AlBaSi-O”

![Fig. 3: Dielectric constant’s change (real part) in a magnetic field](image)
the small values of $D_{\text{min}}/D_{\text{max}}$ and of $A$ for BK7 denote a much reduced presence of microcrystallites in the material. The values of $D_{\text{min}}$ are lower (due to the strong electric field applied) and more realistic than those used in the analysis of $C_p(T, B)$, in all cases confirming the consistency of the assumption $|E|/D_0 \ll 1$ in this theory.

Finally, the present simplified theory has focused on the weak $B$-field regime (up to 1 T). Given the large values of $D_0|q/e|S_\Delta$ thus extracted (indicating that small coherent clusters of some 5 to 10 NM-ions are involved in the magnetic-sensitive tunneling) one can expect the low-$B$ expression employed for the gap to break down around some larger field $B^* \sim \varphi_0(D_{\text{min}}/D_{\text{max}})/(2\pi|q/e|S_\Delta)$ above which the gap grows sub-linearly with $\varphi(B)$. As will be shown elsewhere, this is in turn responsible for the second enhancement of $\delta \epsilon/\epsilon$ observed in the experiments for $B > B^*$ ($B^*$ being rather material-dependent).

In summary, the ingredients of the present two-species TM together with the reasonable assumption of partial devitrification in the films (which can be checked through X-ray analysis) allows for a first good understanding of the puzzle of the magnetocapacitance in the cold multisilicate glasses. The absence of a magnetoacoustic response in such glasses with ATS can be understood in terms of the much higher resonance frequencies of the NM-pockets and channels, and experiments should be done in such conditions. As for the PE-experiments, the orbital-coupling approach with the inclusion of TS-TS interactions has been shown to provide a partial explanation for the $B$-dependence of the PE-amplitude at ultralow temperatures. The present theory, interaction improved, is expected to also provide an explanation for such data, the so-called isotope effect being, possibly, fabrication- rather than isotope-related. Further experiments are needed: clearly, if the magnetic effects are due to quadrupole moments then the response should scale with the quadrupole-carrying nuclear concentration. If tunneling paramagnetic moments are involved, as is suggested by a localised TM also capable of providing a good explanation for the $C_p$ and $\epsilon$ data, then the magnetic response should scale with the Fe-concentration. In the present approach the response scales with the NM-ions' concentration and with the degree of devitrification, thus a larger magnetic response than thus far observed should be found in the best ceramic glasses, like for instance Ceran.

The permission by its Authors to display Fig. 1 is gratefully acknowledged.

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