Evidence for a Phase Transition in Glasses at Very Low Temperature: A Macroscopic Quantum State of Tunneling Systems?

P. Strehlow

Physikalisch-Technische Bundesanstalt, Abbestrasse 2-12, D-10587 Berlin, Germany

C. Enss and S. Hunklinger

Institut für Angewandte Physik, Universität Heidelberg, Albert-Ueberle-Strasse 3-5, D-69120 Heidelberg, Germany

(Received 31 December 1997)

Dielectric measurements at very low temperature indicate that in the multicomponent glass BaO-Al_2O_3-SiO_2 a phase transition occurs at 5.84 mK. Below that temperature small magnetic fields of the order of 10 μT cause surprising changes of the dielectric constant although the glass is insensitive to fields up to 20 T above 50 mK. The experimental findings may be interpreted as the signature of the formation of a new phase in which many tunneling systems perform a coherent motion resulting in a macroscopic wave function. [S0031-9007(98)06333-9]

PACS numbers: 61.43.Fs, 64.90.+b, 77.22.Ch

The anomalous low-temperature properties of glasses are caused by low energy excitations present in all amorphous solids [1]. In the tunneling model (TM) [2,3] these excitations are described on a phenomenological basis by tunneling systems (TSs). In the simplest case, such a tunneling system can be represented by a particle in a double-well potential. At low temperature only the ground states in the two wells are relevant, and the system will effectively be restricted to the two-dimensional Hilbert space spanned by the two ground states. In the pseudospin representation with the Pauli matrices $\boldsymbol{\sigma}^x$ and $\boldsymbol{\sigma}^z$, the Hamiltonian of an isolated TS is given by $H_0 = (1/2)(\Delta\boldsymbol{\sigma}^z - \Delta_0\boldsymbol{\sigma}^x)$, where Δ and Δ_0 are the asymmetry energy and the tunneling matrix element, respectively. Because of the random structure of glasses the characteristic parameters Δ and Δ_0 of the TSs exhibit a broad distribution. Clearly, the Hamiltonian of an isolated TS is formally equivalent to that of a spin-1/2 particle in a magnetic field. This analogy can advantageously be used to describe the dynamics of TSs in glasses. Their interaction with acoustic and electric fields is usually treated as a weak perturbation of H_0. In this way the standard TM successfully explains many of the anomalous thermal, acoustic, and dielectric properties of glasses at temperatures below 1 K.

Upon closer consideration, however, pronounced deviations from the expected behavior are found in many cases. They probably have their origin in the interaction between the TSs which is not taken into account in the standard TM. The strength of this interaction was first deduced from acoustic hole burning experiments [4] and studied in more detail by measurements of the decay of coherent echoes [5]. Moreover, memory effects have been observed in dielectric measurements [6] which indicate the influence of the long-range interaction of TSs on both the density of states and the dielectric response [7]. Very recently, it has been argued that a transition from coherent to incoherent tunneling takes place if the mean interaction energy exceeds the tunnel splitting [8]. Taking into account the peculiarities of glasses, this concept allows an explanation of several inconsistencies arising in the standard TM.

The interaction between TSs has to date been described in terms of an elastic (or electrostatic) coupling mediated by virtual phonon (or photon) exchange. Based on the spin-boson Hamiltonian [9], the elastic interaction between the TSs in glasses can be investigated in a nonperturbative manner [10]. These calculations demonstrate that the strong TS-phonon coupling essentially leads to a renormalization of the tunneling parameter and thus modifies related quantities like density of states or relaxation times. This result explains to some extent the success of the standard TM: differently strong coupling between the TSs does not cause qualitative but only quantitative changes. However, it is known from the widely used spin-1/2 Ising model that a variation of the interaction may alter the macroscopic properties of an ensemble of two-state systems even qualitatively. This means that the exchange Hamiltonian $H_{\text{int}} = -(1/2)\sum_{i,j} J_{ij}\boldsymbol{\sigma}_i^z\boldsymbol{\sigma}_j^z$, with the potential J_{ij} between TSs at sites i and j, might be responsible for the occurrence of cooperative processes and even of continuous phase transitions.

We report here on measurements of the dielectric constant (or permittivity) of the glass BaO-Al_2O_3-SiO_2 with eutectic composition at temperatures between 700 μK and 1 K. As a sample we used a thick-film capacitance sensor ($10 \times 10 \times 0.05$ mm^3) with 30 μm thick gold electrodes on a sapphire substrate. The sensor was prepared from glass powder and gold paste by the silk-screen process and subsequent sintering at 1225 K [11]. Devices of this kind have already been used as glass capacitance thermometers [12].

The experiments were carried out in a nuclear demagnetization cryostat using an automatically balancing capacitance bridge operating at 1 kHz. In order to avoid

uncontrolled variations of the magnetic field due to the stray field of the magnet, the sample was placed in a Nb cylinder with 25 mm in diameter. Although efforts were made to screen the earth magnetic field, a residual field of $B_0 \approx 20\ \mu$T was present at the sample. Passing the transition temperature of Nb this field is frozen in. To allow for a variation of the magnetic field the sample was mounted inside a small coil fixed within the cylinder. Electric and magnetic field were pointing along the axis of the Nb cylinder. Based on an extended temperature scale [13] the temperature was measured with a ^{3}He melting curve thermometer (MCT) and a pulsed platinum NMR thermometer.

In Fig. 1 we have plotted the temperature variation $\delta\varepsilon'(T)/\varepsilon'(T_0) = [\varepsilon'(T) - \varepsilon'(T_0)]/\varepsilon'(T_0)$ of the dielectric constant ε', where $T_0 = 3D1.26$ mK is the temperature of the lowest lying data point. At high temperature the permittivity decreases with decreasing temperature, passes a minimum around 110 mK and increases again. It levels off at a few millidegrees Kelvin and approaches a constant value at the lowest temperature. An analogous behavior has been reported for other glasses [14,15].

Starting from higher temperature, the dielectric constant decreases due to relaxation processes which vanish with decreasing temperature. The increase of ε' below the minimum reflects the resonant interaction of the TSs with the electric field. The prediction of the standard TM is shown in Fig. 1 by a dashed line. At high temperature the agreement between fit and data is satisfactory whereas at low temperature significant deviations occur. As mentioned above, the variation of $\varepsilon'(T)$ in the entire temperature range can be understood within the frame of the TM if the occurrence of incoherent tunneling is taken into account [8]. As in other glasses [14–16] the exact change of the dielectric constant at low temperature depends on the strength of the applied electric field which was 15 kV/m in the measurement shown.

Extremely surprising results were obtained in studies of the influence of magnetic fields onto the dielectric constant. In Fig. 2 the relative change $\delta\varepsilon'/\varepsilon'$ of the dielectric constant at 1.85 mK in the presence of a time dependent magnetic field is plotted as a function of time. At the top of the figure the variation $\delta B(t) = B(t) - B_0$ of the field is shown. The base line in this plot is determined by the frozen-in field $B_0 = 20\ \mu$T. In the lower part of the figure the data for $\delta\varepsilon'/\varepsilon'$ are presented. Each data point was obtained by averaging the reading of the bridge for 1 min. Note that the scatter of $\delta\varepsilon'/\varepsilon'$ is only of the order of 10^{-8}. The astonishing result is that at this temperature the dielectric constant follows the variation of the magnetic field. This pronounced magnetic field dependence of ε' is especially surprising since the dielectric properties of multicomponent glasses have intensively been investigated [12] because of their applicability to capacitance thermometry under high magnetic fields. In particular, it has been established that at temperatures down to 16 mK magnetic fields up to 20 T have an imperceptible effect on the dielectric constant [17].

In Fig. 3 the same type of measurement is shown for five different temperatures. As can be seen at the top of this figure, the field changes now had the opposite sign. Astonishingly, with decreasing temperature the variation $\delta\varepsilon'$ associated with δB completely changes character. At 11 mK the dielectric constant is independent of the applied field within the scatter of our data. At 5.07 mK small changes can be seen which become clearly visible at lower temperature. They are most pronounced around 2 mK. Below that temperature the influence of the field diminishes and finally at 0.72 mK the dielectric

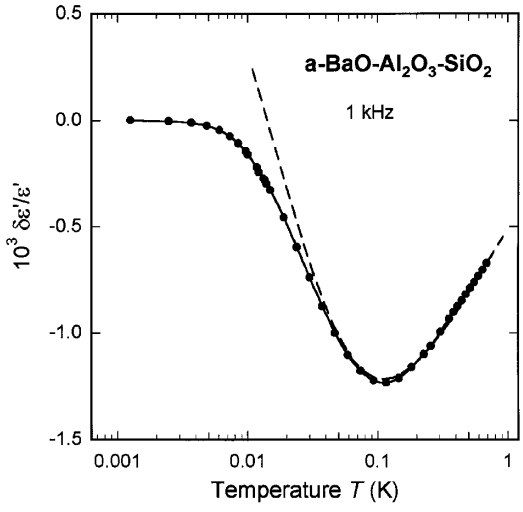

FIG. 1. Temperature variation of the dielectric constant ε' of $BaO\text{-}Al_2O_3\text{-}SiO_2$ glass measured at 1 kHz. The dashed line represents a calculation with the tunneling model.

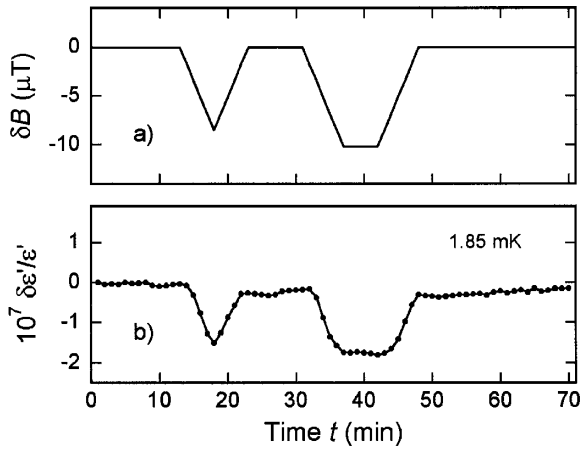

FIG. 2. Influence of the magnetic field on the dielectric constant of the $BaO\text{-}Al_2O_3\text{-}SiO_2$ glass. (a) Time variation $\delta B(t)$ of the applied magnetic field. (b) Relative change of the dielectric constant with the variation of the applied magnetic field at 1.85 mK.

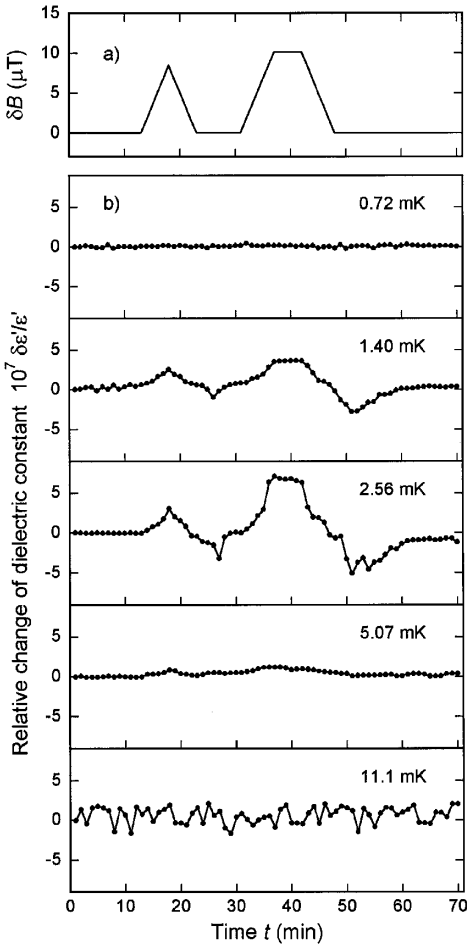

FIG. 3. Influence of the magnetic field on the dielectric constant of the $BaO\text{-}Al_2O_3\text{-}SiO_2$ glass. (a) Time variation $\delta B(t)$ of the applied magnetic field. (b) Relative change of the dielectric constant with the variation of the applied magnetic field at temperatures between 0.72 and 11.1 mK.

constant is no longer influenced by these small fields. Taking a look at the noise level reveals another surprising phenomenon. In going from 11 to 5.07 mK the scatter of the data at zero field is drastically reduced and remains small down to the lowest temperature.

There is an interesting difference between the data taken at 1.40 and 2.56 mK, and those shown in Fig. 2. The dielectric constant first follows the variation of the magnetic field. However, the decrease of ε' does not stop when the zero field B_0 is reached. It continues to decrease for several minutes and finally approaches the equilibrium value again. This behavior indicates that the relaxation of ε' from its value above the equilibrium to its equilibrium value is accompanied by the production of heat. In this case the sample warms up and ε' decreases according to Fig. 1. Since the heat is slowly flowing to the heat sink the temperature tends to its lower equilibrium value and the dielectric constant recovers with time.

In a further experiment we have carried out a very careful measurement of ε' at temperatures around 6 mK. As before, the sample was mounted in the Nb cylinder to keep the effective magnetic field constant. It was slowly cooled from 6.88 to 4.88 mK at a constant rate of 62.6 μK/min. In the upper part of Fig. 4 the recorded variation of the dielectric constant is plotted as a function of time. Within the narrow temperature range of 2 mK it can be approximated by two straight lines crossing at 5.84 mK. In order to magnify this discontinuity we have plotted in the lower part of the figure the deviation $\delta\varepsilon'_s$ of the dielectric constant from the straight line through the first and last data point. This plot demonstrates that there is an abrupt change of the slope indicating a phase transition at 5.84 mK.

Summarizing we may state that we have observed two surprising phenomena: a strong magnetic field dependence of the dielectric permittivity below 5.84 mK and a sharp discontinuity of this quantity at that temperature.

In an isotropic dielectric, devoid of free charge and free current, the general constitutive equation for the polarization $\boldsymbol{P}$ is of the form $\boldsymbol{P} = \varepsilon_0\chi_1\mathfrak{E} + \varepsilon_0\chi_2(\boldsymbol{B}\cdot\mathfrak{E})\boldsymbol{B}$,

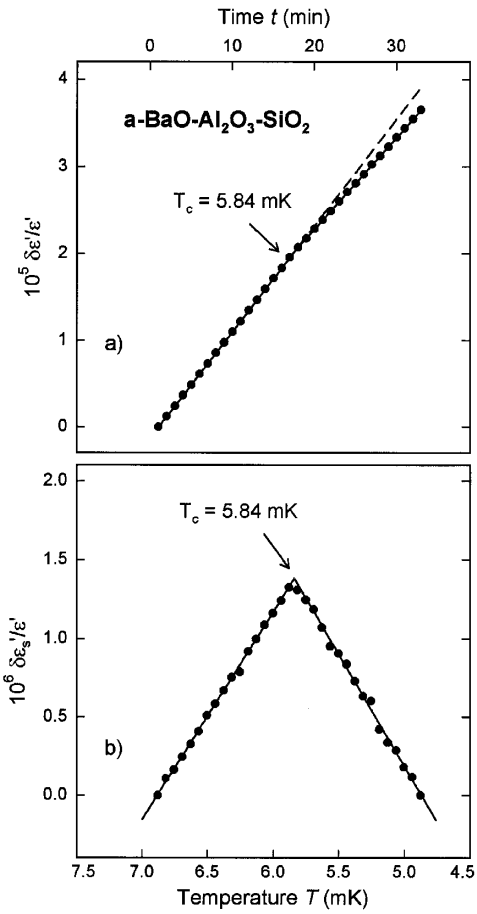

FIG. 4. (a) Dielectric constant of the $BaO\text{-}Al_2O_3\text{-}SiO_2$ glass measured at a constant cooling rate of 62.6 μK/min. The dashed line is the extrapolation of the data from higher temperature. (b) Same data after subtracting a straight line through the first and last points of the measurement. On the abscissa the time scale has been converted to temperature.

where the coefficients χ_1 and χ_2 may depend on temperature, density, and the three scalars $\mathfrak{E}^2$, B^2, and $(\mathfrak{E} \cdot \boldsymbol{B})^2$. Polarization and electromotive intensity $\mathfrak{E}$ are polar vectors, while the magnetic induction $\boldsymbol{B}$ is an axial vector. This means that under inversion, $\boldsymbol{P}$ and $\mathfrak{E}$ change their signs, while $\boldsymbol{B}$ remains invariant. Glasses are properly assumed to be linear dielectrics so that the polarization is given by $\boldsymbol{P} = \varepsilon_0 \chi_1 \mathfrak{E} = (\varepsilon - \varepsilon_0)\mathfrak{E}$ and the dielectric constant ε depends only on temperature and density (or deformation). Deviations from a linear behavior require a nonlinear constitutive equation for the magnetization $\boldsymbol{M}$ because of the integrability condition $\partial \boldsymbol{P}/\partial \boldsymbol{B} = \partial \boldsymbol{M}/\partial \mathfrak{E}$. Although the observed dependence of ε on B^2 and $(\mathfrak{E} \cdot \boldsymbol{B})^2$ can formally be explained in a nonlinear field theory, the abrupt appearance of a nonlinear magnetic behavior in glasses below 6 mK remains to be seen.

It is tempting, however, to assume that at 5.84 mK a transition takes place from the uncorrelated and incoherent tunneling motion of individual TSs to a highly correlated motion. In this way the glass would be able to reduce its free energy by minimizing the energy of interaction between the TSs. Thus the discovered low temperature phenomenon could be discussed as a continuous phase transition with a critical temperature T_c. For $T < T_c$, the thermal noise is too weak to suppress the formation of a highly coherent ensemble of TSs dressed with clouds of virtual phonons. For energies smaller than the characteristic energy scale given by $k_B T$, the dressed TSs may be considered as elementary excitations of a ground state described by the macroscopic wave function $\Psi = |\Psi| \exp(i\Phi)$. Since the equilibrium value of the modulus of Ψ is determined by the temperature, the arbitrary phase Φ parametrizes a continuously degenerated equilibrium state of glasses below T_c. In principle, the phase structure determined by the spatial dependence of the macroscopic wave function can be derived from a Ginzburg-Landau functional. Then, due to the coupling between $\boldsymbol{B}$ and Ψ, the influence of the magnetic field on the polarization below T_c can qualitatively be described.

In conclusion we have reported on surprising phenomena discovered in $BaO\text{-}Al_2O_3\text{-}SiO_2$ glass at very low temperatures which had never been observed before. We want to point out that we reproduced the measurements not only in the case of $BaO\text{-}Al_2O_3\text{-}SiO_2$ glass but have made similar findings also in other multicomponent glasses though T_c exhibited slightly different values. Therefore, we expect that the observed phase transition from uncorrelated, incoherent tunneling of individual TSs to a correlated motion of a large number of dressed TSs occurs in all glasses. Of course, we have only touched on a novel and unexpected phenomenon and much more experimental and theoretical work is needed to fully understand the underlying physical principles.

The authors thank G. Schuster, A. Hoffmann, and D. Hechtfischer for putting the MCT data at our disposal and for helping us with the realization of the nuclear demagnetization experiments. Furthermore, we are grateful to Ch. Modes and K. Deckelmann of Heraeus GmbH for preparing the thick-film sensors and acknowledge discussions with J. Classen and M. von Schickfus. This work has been supported by the Deutsche Forschungsgemeinschaft (Grant No. Hu359/11).

[1] *Amorphous Solids*, Topics in Current Physics Vol. 24, edited by W. A. Phillips (Springer, Berlin, 1984).
[2] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
[3] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).
[4] W. Arnold and S. Hunklinger, Solid State Commun. **17**, 833 (1975).
[5] J. E. Graebner and B. Golding, Phys. Rev. B **19**, 964 (1979).
[6] S. Rogge, D. Natelson, and D. D. Osheroff, Phys. Rev. Lett. **76**, 3136 (1996).
[7] A. L. Burin, J. Low Temp. Phys. **100**, 309 (1995).
[8] C. Enss and S. Hunklinger, Phys. Rev. Lett. **79**, 2831 (1997).
[9] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[10] K. Kassner and R. J. Silbey, J. Phys. Condens. Matter **1**, 4599 (1989).
[11] The thick-film sensors were manufactured by W. C. Heraeus GmbH, thick-film technology, Heraeusstrasse 12-14, D-63450 Hanau, Germany.
[12] P. Strehlow, Cryogenics **34**, 421 (1994).
[13] G. Schuster, A. Hoffmann, and D. Hechtfischer, Temperature Scale Extension below ITS 90 Based on ^{3}He Melting Pressure, Report No. CCT-96/25, 1996.
[14] H. Nishiyama, H. Akimoto, Y. Okuda, and H. Ishimoto, J. Low Temp. Phys. **89**, 727 (1992).
[15] S. Rogge, D. Natelson, B. Tigner, and D. D. Osheroff, Phys. Rev. B **55**, 11 256 (1997).
[16] P. Strehlow, C. Enss, and S. Hunklinger, Czech. J. Phys. **46**, 2231 (1996).
[17] F. Penning, M. Maior, P. Strehlow, S. Wiegers, H. van Kempen, and J. Maan, Physica (Amsterdam) **211B**, 363 (1995).