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Dielectric response of CO and Ar condensed into mesoporous glass

D. Wallacher,[1] V. P. Soprunyuk,[1] A. V. Kityk,[2] and K. Knorr[1]
[1]*Fakultät für Physik und Elektrotechnik, Universität des Saarlandes, D 66041 Saarbrücken, Germany*
[2]*Institute for Computer Science, Electrical Engineering Department, Technical University of Czestochowa, 42-200 Czestochowa, Poland*

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CO has been condensed into Vycor glass (with a pore diameter of 7 nm) and the dielectric behavior has been studied as a function of frequency and temperature from the liquid regime down to 10 K, thereby covering the liquid-solid and the solid α- solid β transition. The head-tail relaxations have been investigated in detail. The results indicate that material in the pore center is almost bulklike, but that the molecules next to the walls show a different behavior. Ar is used as a nonpolar reference system.

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I. INTRODUCTION

The dielectric behavior of water and of many organic solvents in porous or granular hosts has been studied extensively in the sixties.[1] Analogous studies have been also performed on physisorbed mono and multilayers on powders with planar facets, e.g., Xe on boron nitride.[2,3] More recently the interest in such systems shifted to porous glasses soaked with glass-forming molecular liquids such as glycerol.[4–8] These investigations were motivated by the search for size effects on the glass transitions that are expected to appear if the glass transition is a cooperative phenomenon. It turned out that the glassy relaxations were in fact faster than in the bulk state, consistent with a lowered glass temperature T_g. The interpretation in terms of the collective length scale has been however questioned since the pore filling may not be identical with its bulk counterpart because of surface fields that could modify in particular the part of the filling next to the pore walls. Furthermore in some of these studies the matrix effect on the permittivity of the pore filling has been ignored.

The present study deals with CO and Ar, two very simple molecules, in Vycor glass, a standard mesoporous matrix. The structural and thermodynamic state of these pore fillings is known from our previous work:[9–11] The first fraction of material adsorbs on the pore walls because of a strong attractive adsorbate-substrate potential. For Ar and CO, this film is two to three monolayers thick, has an amorphous structure, and does not support the phase transitions of the bulk state. For higher fillings eventually the capillary condensate forms in the pore center. This happens both in the liquid and in the solid regime. The capillary condensed component has bulklike structural properties. Solidified Ar in pores is fcc, CO even reproduces the phase sequence of the bulk state liquid-β hcp - α Pa3. The transition temperatures, the melting transition in particular, are however lower than in the bulk and show hysteresis with respect to heating and cooling.

The permittivity of Ar stems exclusively from the atomic polarizibility that is practically insensitive to intermolecular interactions. CO has a weak additional Curie-like contribution arising from the small permanent dipole moment of this molecule, the relaxations of which should of course depend on the molecular environment.

The low-T properties of CO have been a puzzle for many decades. In the low-T Pa3 phase, the center-of-mass lattice is fcc and the molecular axes are aligned along the $\langle 111 \rangle$ directions in a four-sublattice arrangement, the dipole moments (the ‘‘heads’’ and ‘‘tails’’) remain disordered. Early calorimetric experiments[12] suggested that this dipolar disorder should persist down to $T=0$ K with a residual entropy of $k_B \ln 2$. On the other hand, given the dipole moment and the center-of-mass lattice, a transition into an antiferroelectric state at about 5 K has been predicted assuming the electric dipole-dipole interaction to be the relevant intermolecular coupling.[13] Indeed such a transition has been actually observed in CO monolayers adsorbed on graphite.[14] In the bulk state a definite answer in terms of frozen-in dipolar disorder has been finally given by the dielectric study of Nary *et al.*[15] These authors have observed a Debye-like relaxation process with a relaxation time τ that obeys an Arrhenius law. For frequencies in the audio range the relaxations occur at temperatures around 30 K. The single relaxation time and the fact that the Arrhenius barrier is much larger than the estimated ordering temperature indicate that the intermolecular interactions have little effect on the freezing process, that the dipole moments freeze-in individually in the crystal-field potential of the Pa3 structure. Nevertheless, this process has some similarity with the onset of the glass state and consequently one may refer to the low-T state of CO as ‘‘dipolar glass.’’

In this paper we investigate the frequency dependent dielectric response of CO in Vycor for temperatures ranging from 10 K in the solid regime up to 70 K in the liquid regime. Attention will be paid to the phase transitions and to the dielectric relaxations of CO. We will discriminate between the first monolayer on the pore walls and the quasibulk component in the pore center. Ar will serve as a nonpolar reference.

II. EXPERIMENT

The porous matrix is a slab of Vycor glass (code 7930) with a thickness d of (234 ± 7) μm. According to the manufacturer (Corning Glass) the porosity P is 0.30 and the average pore diameter 7 nm. The electrodes for the dielectric study are sputtered Au films with an area A of 60 mm^2. Thus the geometrical capacitance $C_{\mathrm{geom}}=\varepsilon_0 A/d$ is (2.2 ± 0.1) pF. The dielectric data have been recorded at 30 different fre-

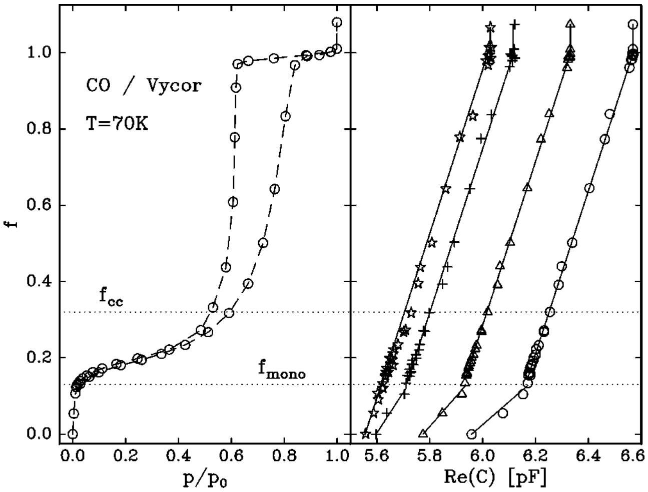

FIG. 1. A vapor pressure and a dielectric isotherm ($T=70$ K) of liquid CO in Vycor. p/p_0 is the reduced vapor pressure, f the fractional filling, and C the capacitance of the sample. C is shown for measuring frequencies of 400 kHz, 16 kHz, 100 Hz, 100 mHz, from left to right. The monolayer filling f_{mono} and the onset of capillary condensation f_{cc} are indicated.

quencies ν covering a range from 1 Hz to 1 MHz with an impedance analyzer (Solartron SI-1255) in combination with an impedance matching interface (Solartron SI-1296). The sample is mounted in a cell that is attached to the cold plate of a closed cycle refrigerator. The cell is connected via a heated capillary to an all-metal gas handling manifold equipped with capacitive membrane pressure gauges. Before filling the cell the manifold has been evacuated to a residual pressure of more than 10^{-6} mbar.

The first part of the experiment is the simultaneous measurement of a volumetric vapor pressure and a dielectric isotherm for filling and emptying the pores out of the vapor phase at a temperature T within the liquid regime of the pore filling. The results for CO (at 70 K) and Ar (at 80 K) are shown in Figs. 1 and 2. Here the vapor pressure p and the capacitance of the sample are plotted as a function of the quantity of gas N introduced into the cell. The vapor remaining in the dead volume of the cell has been corrected for. Reduced units $f=N/N_0$ and p/p_0 are used. N_0 is the dose necessary for complete filling and p_0 is the saturated vapor pressure of the bulk system. The porosity $P=0.29\pm0.01$ of the Vycor matrix derived from the volumetric isotherm agrees with the specification of the supplier. The difference of the chemical potential of the pore filling and the bulk state is related to p/p_0 via $\Delta\mu=k_{\mathrm{B}}T\ln(p/p_0)$. The vapor pressure isotherm is similar to what has been observed for several other small molecules in various mesoporous matrices, it is of type IV according to the IAPUC classification. As can be seen from the dielectric isotherms, the capacity C of the empty matrix ($f=0$) is about 6 pF and the increase due to complete filling ($f=1$) is a few percent.

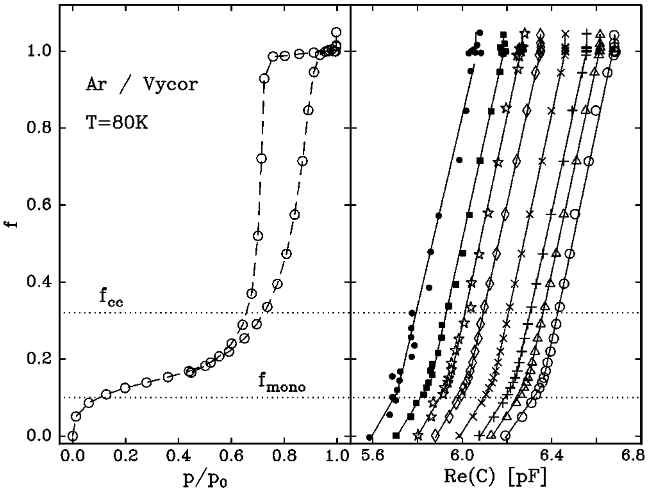

FIG. 2. Same as Fig. 1 but for liquid Ar at 80 K. This temperature is somewhat below the triple point of bulk Ar (83.8 K), but still above the solidification temperature in 7 nm pores. The measuring frequencies are 1 MHz, 100 kHz, 10 kHz, 1 kHz, 100 Hz, 10 Hz, 1 Hz, 100 mHz from left to right.

In the second part of the experiment the temperature dependence of the permittivity of the empty matrix ($f=0$) and of two CO fillings, $f=1.3$ and $f=0.1$, has been studied in cooling-heating cycles between 70 K and 10 K. The lower filling corresponds to roughly one adsorbed layer on the pore walls. The overfilled case $f=1.3$ actually represents the completely filled state ($f=1$) since the extra condensate outside the pores does not contribute to the capacity (see Fig. 1), but merely serves as a reservoir to keep the pores filled in case the pore filling contracts at lower T.

The capacitance of the empty matrix shows some variation with T and ν. Most of the variation with ν is presumably due to parasitic impedances of the circuitry. One expects that there are also T- and ν-dependent contributions from the terminating OH groups on the pore walls of the silica network, but we could not identify any well defined dispersion step or loss peak. Another complication arises from the fact that traces of the capacitance as function of T show offsets of a few tenths of pF when measured for different frequencies (see Figs. 1 and 2). The offsets disappear when referring to increments between results obtained for different fillings.

Since the data of Fig. 1 (and 2) shows that the dielectric behavior of the first monolayer is different from the rest of the pore filling, we introduce two increments that represent these two components, I and II, of the filling, $\Delta C_{\mathrm{I}}=C(f=0.1)-C(f=0)$ and $\Delta C_{\mathrm{II}}=C(f=1.3)-C(f=0.1)$. The total change due to complete filling is then $\Delta C_{\mathrm{I}}+\Delta C_{\mathrm{II}}$. The T dependence of the real and imaginary part of ΔC_{I} and ΔC_{II} is shown in Figs. 3 and 4 for some selected frequencies ν.

The behavior of ΔC_{II} across the solid-solid and the melting transition is also shown in Fig. 5. This figure also includes analogous data on the melting transition of Ar.

III. ANALYSIS AND DISCUSSION

A. Isotherms

The vapor pressure isotherms are of the usual type observed for small molecules condensed into Vycor glass. The formation of a strongly bound adsorbed film at low f, $0<f<f_{\mathrm{cc}}$ has to be distinguished from the quasibulk capillary

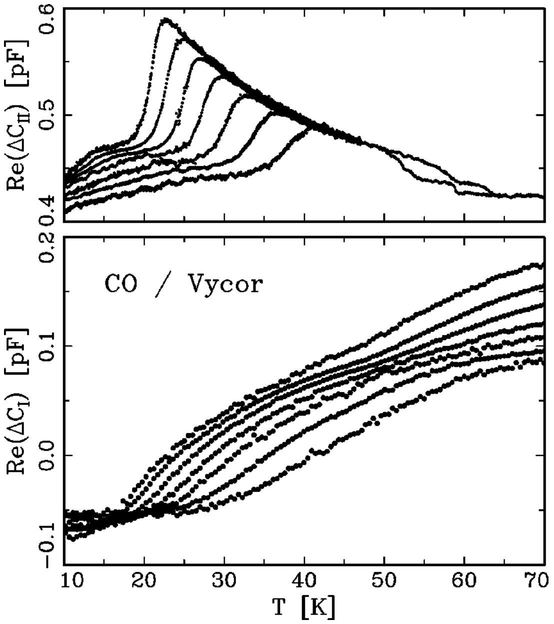

FIG. 3. The T dependence of the real part of the increments $\Delta C_{\mathrm{II}} = C(f=1.3) - C(f=f_{\mathrm{mono}})$ and $\Delta C_{\mathrm{I}} = C(f=f_{\mathrm{mono}}) - C(f=0)$ that represent the quasibulk and the monolayer component of the CO pore filling. The measuring frequencies range from 1 Hz to 1 MHz in steps of one decade.

condensate at higher f, $f_{\mathrm{cc}} < f < 1$. The adsorption and desorption of the adsorbate is reversible, capillary condensation is hysteretic. The $\Delta\mu$ value of the capillary condensate, both for CO and Ar, is of the order of $-20\ \mathrm{K}/k_{\mathrm{B}}$, that of the adsorbed monolayer at least one order of magnitude more negative. The monolayer capacity f_{mono} can be determined from the knee of the isotherm at very low values of p/p_0. The approximate values of f_{mono} and f_{cc} are indicated in Figs. 1 and 2.

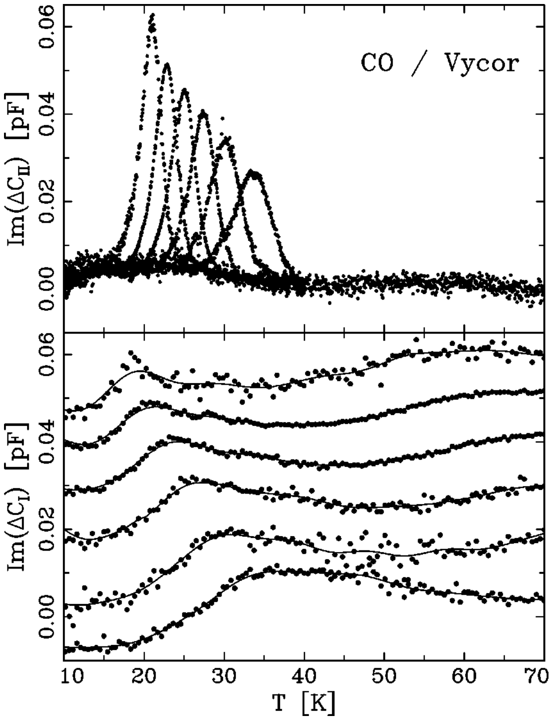

FIG. 4. Same as Fig. 3 but for the imaginary parts. For clarity the traces of Im(ΔC_{I}) are shifted vertically in steps of 0.01 pF. The vertical scale refers to the lowest trace ($\nu = 1\ \ \mathrm{MHz}$).

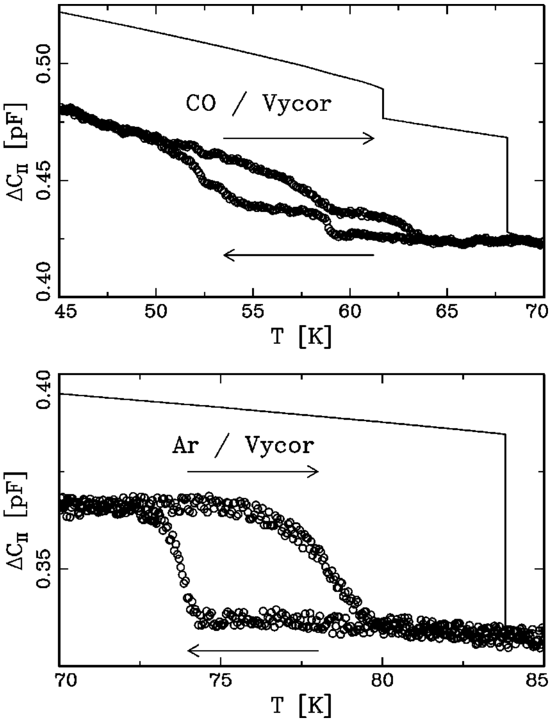

FIG. 5. The variation of the capacitance increments with temperature, both for cooling and heating, in the regime of phase transitions. For Ar and CO $\Delta C_{\mathrm{II}} = C(f=1.3) - C(f=f_{\mathrm{mono}})$. The variations expected from the T dependence of the density of the bulk material are shown by thin solid lines.

The dielectric isotherms C vs f of both fillings consist of two sections, I and II, with a change of slope s, $s = dC/df$, at about f_{mono}. s_{I} is larger than s_{II}, both for CO and Ar, but for CO s_{I} approaches s_{II} at higher ν. Segmented dielectric isotherms have been observed in most granular and porous systems that have been investigated as a function of filling. In some systems s_{I} was found to be larger, in others smaller than s_{II}. In some cases a change from one to the other situation with T or ν has been observed. Occasionally, the adsorption of the first fraction of a monolayer even reduces the capacitance of the composite.[1,3] Generally accepted explanations for these effects have not been given.

We concentrate on the second section first. It comprises not only the pore material formed by capillary condensation but also the adsorbate on the pore walls in excess to the first monolayer. We refer to this component as "quasibulk." The slope s_{II} of this section is independent of ν, both for CO and Ar.

The linearity of the C-f relation suggests that the dielectric properties of the pore filling are independent of the amount already present. We therefore feel justified to refer to the Maxwell-Wagner-Sillars (MWS) expression[16] for the effective permittivity of a composite which we have generalized for a three-component system consisting of the matrix, empty (=vapor filled) and condensate filled pores with the permittivities ε_m, ε_v, ε_p, and the volume fractions $(1-P)$, $(1-f)P$, and fP, respectively.

$$\varepsilon = C/C_{\text{geom}} = \frac{(1-P)\varepsilon_m + Pf\varepsilon_p e_p + P(1-f)\varepsilon_v e_v}{(1-P)+Pfe_p+P(1-f)e_v}.$$

The relative average fields in the pores are $e_i = \varepsilon_m/[A(\varepsilon_i-\varepsilon_m)+\varepsilon_m]$ with i="v" or "p." A is the depolarization factor of the pores. We assume that the pores are long cylinders, 2/3 perpendicular, 1/3 parallel to the external field, (but for the parameters chosen below, spheres give almost identical results). The model refers to the dilute limit and ignores any interaction between the polarized inclusions but treats the boundary conditions of the electric field and the dielectric displacement at the pore walls correctly. Inserting $P=0.29$, $\varepsilon_v=1$ and the literature value for the fused silica matrix ($\varepsilon_m=3.8$), a capacitance of 5.87 pF for the empty matrix ($f=0$) is calculated. This is in good agreement with the experiment. The model predicts a quasilinear increase of the capacitance C as function of f. This is again in agreement with the experiment. Obviously the present composite with a relatively low porosity and a low permittivity of the pore material is well described by the dilute limit. In fact, we also considered more sophisticated effective medium models[16] that go beyond the dilute limit and obtained practically identical results for $C(f)$. The experimental slope of the second segment is 0.36 pF for Ar (at 80 K) and 0.46 pF for CO (at 70 K). Fits of the model to this data yield permittivities ε_p of 1.40 for Ar and 1.50 for CO. The value for CO is acceptable (see below), but for Ar the permittivity of the pore material is significantly lower than for the bulk liquid state (=1.538). The permittivity is related to the particle density N/V and the atomic polarizability α via the Clausius-Mosotti relation. The permittivity of pore condensed Ar suggests that the product $\alpha N/V$ is reduced by about 25% with respect to the bulk liquid. α is not expected to vary much with the local environment. The density may of course be somewhat different from the bulk state, but presumably not by 25%. In fact, the volumetric isotherms of CO and Ar produced a consistent value for the porosity assuming bulk densities for both materials. In summary, one is confronted with the situation that the MWS model in combination with bulk permittivities is acceptable for CO but not quite so for Ar (See chapter III C for a discussion of the density of the solidified pore fillings).

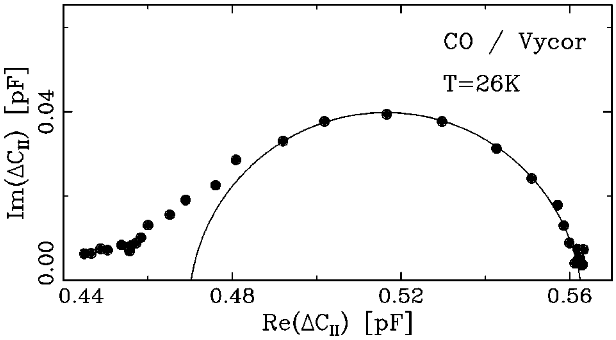

FIG. 6. A complex-plane plot, Im(ΔC_{II}) vs Re(ΔC_{II}) for CO at 26 K. The circular arc is a fit of the Cole-Cole formula to the data.

B. Head-tail relaxations of CO

Figures 3 and 4 show the dielectric response of the quasibulk component II of the CO filling. The most conspicuous feature is a dispersion step of $\Delta C'_{II}$ and a maximum of $\Delta C''_{II}$ which shift with frequency from about 20 to 40 K. A complex-plane plot for $T=26$ K is presented in Fig. 6 which includes a fit of the Cole-Cole formula to these relaxations. The Cole-Cole spread parameter α_c is 0.08. Thus the distribution of relaxation times is rather narrow and close to the Debye case. The relaxation time τ as determined from the frequency of maximum loss varies with temperature according to an Arrhenius law $\tau=\tau_0 \exp(E/T)$ with an activation energy E of (635 ± 30) K and an preexponential factor $1/\tau_0$ of 19 THz, $\log_{10}(1/\tau_0)=13.2\pm0.3$. The head-tail relaxations of bulk CO are reported to be of the Debye type ($\alpha_c=0$) with Arrhenius parameters 737 K and 78 THz.[15] Thus there is little difference between the head-tail relaxations of quasibulk component of pore condensed CO and bulk CO.

What percentage of the pore molecules supports this bulk-like behavior? In order to answer this question we refer to the MWS model with ε_p given by Debye-like permittivity of[15] bulk CO (at 29.65 K) $\varepsilon_p=\varepsilon_\infty+(\varepsilon_\infty-\varepsilon_0)/(1+i2\pi\nu\tau)$, $\varepsilon_0=1.809$, $\varepsilon_\infty=1.545$. τ is given by the Arrhenius law already quoted above. The result in the $\Delta C'-\Delta C''$ plane is a semicircle. The $\nu=0$ and $\nu=\infty$ footpoints of this semicircle are actually at $\Delta C'$ values of 0.668 pF and 0.462 pF. The corresponding values of the Cole-Cole fit are 0.562 pF and 0.472 pF. This means that $\nu=\infty$ response of the pore condensate is almost identical with that of the bulk system, but that the dispersion step is only half of that of the bulk. This would mean that all the CO molecules contribute via their polarizability to the $\nu=\infty$ response, but only 50% of them have the head-tail relaxations in the ν, T range of the bulk Pa3 crystal.

The problem of this estimate is that the Cole-Cole fit does not consider all relaxations of the quasibulk component of the pore condensate. The results shown in Figs. 3 and 4 indicate weak secondary relaxations some K below the primary ones. In the complex-plane plot (Fig. 6) these relaxations show up as a high-frequency wing. The T dependence of the relaxation rate of this secondary process roughly follows an Arrhenius law with a barrier $E=(327\pm60)$ K and a preexponential factor of the order of 1 THz $[\log_{10}(1/\tau_0)=11.5\pm1]$. The low value of E suggests that the secondary relaxations are due to molecules that can reorient more freely than the quasibulk molecules that support the primary relaxations. We think of molecules in the amorphous second and third monolayer or alternatively of molecules of the crystallized capillary condensate next to defects of the Pa3 lattice. We have argued previously[10,9] that such defects are necessary to match the crystalline pore solid to the pore geometry and could identify one type of defect, namely, stacking faults, in the diffraction patterns.

Considering these secondary relaxations, the $\nu=\infty$ limit of ΔC_{II} is definitely lower than the value of 0.472 pF quoted above. The extrapolation of the 1 MHz trace of Fig. 3 to T

$=0$ K suggests a value of about 0.4 pF. On this basis we arrive at a more realistic estimate: The $\nu=\infty$ response of the quasibulk component points to a reduced density of 86% of this pore filling and 82% of these molecules contribute to the dispersion step. The other CO molecules of component II obviously freeze in a ν, T range outside the experimental window.

The T dependence of $\Delta C'$ and of the maximum of $\Delta C''$ has been analyzed in terms of a Curie-Weiss law. For the mean-field parameter θ a value of (-4 ± 2) K is obtained, indicating an antiferroelectric coupling of the CO dipole moments. This is consistent with the hypothetical antiferroelectrically ordered low-T phase, but in disagreement with the results on bulk CO which[15] suggest weak ferrotype correlations.

C. Phase transitions

At higher temperatures the dielectric data on pores completely filled with CO and Ar show hysteresis with respect to heating and cooling (Fig. 5). There is not much of dispersion in this regime, hence the results represent the static dielectric response. For Ar one and for CO two steplike features can be localized, both on cooling and heating, the temperatures of which agree well with the phase-transition temperatures of the x-ray diffraction studies of Ar and CO and of a heat-capacity study of Ar in a controlled pore glass with a pore diameter similar to Vycor.[10,9,11] For CO, the transition temperatures are $T_f=59$ K for solidification, $T_m=63$ K for melting, $T_{\beta\alpha}=53$ K for the structural phase transition on cooling and $T_{\alpha\beta}=58$ K on heating. For Ar the pore filling solidifies at 74 K and melts at 78 K. The temperatures are 1–2 K lower than for the controlled pore glass. Since the depression of phase-transition temperatures relative to the bulk state is known to scale with the inverse pore diameter, the lower values of the present study suggest a slightly smaller pore diameter of the Vycor glass, 7 nm compared to 7.5 nm for the controlled pore glass.

How do the phase transitions affect the dielectric behavior? The transitions mentioned are all of first order with a significant jump of the density. An inspection of the MWS model shows that the effective permittivity of the composite is practically insensitive to the distribution of a given number of molecules in the pores. If the pore material contracts with the consequence that empty volume appears, the decrease of f is compensated by the larger permittivity of the denser filling. Thus, changes of the permittivity reflect changes of the number of molecules in the pores. We recall that the pores were originally overfilled by 30% in the liquid regime. On cooling the pores should stay completely filled since any contraction of the pore material causes additional molecules to condense into the pores. This mechanism requires the pore condensate to be in equilibrium with the vapor. At least at higher temperatures, the dielectric response of the pore material should therefore mimic the density ρ. Given the linear relation between ΔC_{II} and the amount of pore material (Figs. 1 and 2), the relative T-induced changes of ΔC_{II} and of the density ρ should be identical. The variation of ΔC_{II} with T expected on this basis is indicated in Fig. 5, assuming that $\rho(T)$ can be identified with the density $\rho_{\mathrm{bulk}}(T)$ of the bulk systems. For CO the increase of ρ_{bulk} between 70 K and 50 K is 18.6%, most of that is due to the discontinuities at the liquid-solid transition (about 10%) and at the β-α solid-solid transition (about 3.5%). The relative increase of ΔC_{II} is actually 11%, only. The results on Ar are similar. This means that the quasibulk component of the solidified pore filling is about 9% less dense than the bulk counterpart. The crystallographic densities ρ_{cryst}—as derived from the diffraction peaks of the crystallized part of the pore filling[10,9]—differ by not more than 1% from ρ_{bulk}. Of course there are disordered regions that contribute to the dielectric response but not to the diffraction peaks, namely the second and the third monolayer on the pore walls, which amount to a fraction of $(f_{\mathrm{cc}}-f_{\mathrm{mono}})/(1-f_{\mathrm{cc}})=0.2$ of component II. Furthermore the crystalline material contains a lot of defects, such as grain boundaries, that reduce its density without affecting ρ_{cryst}. Nevertheless it appears that a discrepancy of about 5% remains that can only be accounted for by empty pore space. Obviously the pores contain a significant percentage of voids that form upon solidification and that cannot be filled by subsequent sublimation. Clearly the particle transfer from the vapor outside the sample to a vapor bubble in the center of the sample relies on a series of distillation processes in the pore network and is therefore a very slow process that obviously did not equilibrate in the time spent for the measurements of Fig. 5 (2 days).

D. Monolayer regime

As mentioned above, the dielectric isotherms of both CO and Ar pore fillings have an anomalously large slope s_{I} in the monolayer regime. For CO (at 70 K) s_{I} decreases with increasing ν and approaches s_{II} at some 100 kHz. For Ar (at 80 K), s_{I} is almost four times larger than s_{II} and shows no variation with frequency.

We concentrate on Ar since here the anomalous behavior is even stronger, but on the other hand not complicated by the relaxational dynamics of permanent dipole moments. The large value of s_{I} cannot be accounted for by the MWS model with realistic values for ε_p. Of course, the model assumes that for $f=f_{\mathrm{mono}}\cong0.1$, a fraction f of the pores is completely filled, the others being completely empty. The actual situation is different: All pores are coated with an adsorbed film that comprises a fraction f_{mono} of the pore volume. Hence a refined model that considers a cylindrical shell with an empty core embedded in the matrix is more appropriate. It turns out however that for the present combination of dielectric media the correction with respect to the MWS average field e_p is of the order of 10%, only, and that the corresponding changes of s_{I} and the screening effect on the material in the pore center are of the same order. A second point to consider is that for a monolayer the concept of macroscopic fields may break down. The dielectric response of a planar monolayer consisting of polarizable molecules arranged in two-dimensional arrays of various symmetries resting on a semi-infinite dielectric medium has been considered in Ref. 17. It turns out that the difference between the microscopic and the macroscopic description is again of the order of 10%, far below what is observed in the experiment. Thus the anomalous large response cannot be directly due to the adsorbed molecules of the first monolayer, but must have a different reason.

Even though we could not identify any fingerprint of the polar OH groups of the pore walls in the permittivity of the empty matrix, contributions of such groups must undoubtedly exist. Considering the large area of the pore walls (which can be deduced from the monolayer capacity of the vapor pressure isotherms), the number of Si atoms on the walls and the dipole moment of the OH groups, a rough estimate suggests that the OH contribution to the capacity of the matrix may be as large as 10%, which corresponds to 0.6 pF in absolute units. The anomalous effect of the monolayer regime is about 0.1 pF, only. Hence a relatively small change of the dielectric response of the hydroxyl groups upon adsorption, ΔC_{ind}, could account for the anomalous behavior. ΔC_{ind} can be positive or negative. Think of a relaxational Curie-type response of the OH groups. A neighboring adsorbed molecule could easily change the reorientation barrier of the OH group, thereby leading to a change of the relaxation time τ_{OH}. If the shift is such that the condition $2\pi\nu\tau_{\mathrm{OH}}=1$ is approached, ΔC_{ind} will increase, otherwise decrease. The results of Figs. 1 and 2 suggest that for Ar/Vycor at 80 K and CO/Vycor at 70 K, ΔC_{ind} is positive. Infrared spectroscopy has provided direct proof for adsorbate induced changes of the stretching band of the OH groups on the pore walls of Vycor glass.[18] These studies have also shown that the OH groups exist in various configurations), hence one expects a wide distribution of dielectric relaxations rates.

From what has been said, it is clear that the increment ΔC_{I} of CO shown in Figs. 3 and 4 not only represents the direct contribution of the adsorbed monolayer ΔC_{mono} but also the adsorbate induced changes of the OH groups, or more generally of the matrix, hence $\Delta C_{\mathrm{I}}=\Delta C_{\mathrm{ind}}+\Delta C_{\mathrm{mono}}$. As a function of T and ν, ΔC_{I} shows two broad features that we interpret as dispersion steps of the real part and loss peaks of the imaginary part. The feature at lower T is somewhat stronger and the temperature position of maximum loss is sufficiently well defined for the extraction of the T dependence of τ. $\tau(T)$ follows roughly an Arrhenius law with $E=(480\pm30)$ K and $1/\tau_0=(0.18\pm0.13)$ THz. The relaxation times are comparable to those of the head-tail flips of the quasibulk component. Hence these processes refer to flips of the CO molecules of the monolayer. The second relaxation process produces a broad loss maximum centered at about 60 K in the 1 Hz measurement. For higher ν the feature moves to higher T and leaves the T range of our study. We propose that this feature is related to ΔC_{ind} and therefore represents adsorbate induced changes of the OH reorientations. The phase transitions of the quasibulk component of the pore filling do not affect ΔC_{I}.

Finally at the lowest temperatures, ΔC_{I} is negative, meaning that the capacity of the matrix filled with one monolayer is smaller than that of the empty matrix. Hence, $\Delta C_{\mathrm{ind}}<0$ and $\Delta C_{\mathrm{mono}}<|\Delta C_{\mathrm{ind}}|$. Analogous effects have been observed for several adsorbate/substrate systems, e.g., for Xe on BN. This means that adsorption of a few CO molecules shifts the relaxations of the OH groups into this T regime, either from above or from below.

IV. CONCLUSION

The present investigation shows that for a complete understanding of the dielectric behavior of pore condensates measurements for different degrees of pore filling are indispensable. The component formed by capillary condensation in the central part of the pores behaves basically bulklike and has to be distinguished from the monolayer component next to the pore walls. For the bulklike component of CO, the head-tail disorder freezes-in at temperatures and frequencies almost identical to what is observed in the bulk. But even here the distribution of the relaxation times is modified, as evidenced by the appearance of a secondary channel of relaxations. At least for a matrix of relatively low porosity and for fillings of low permittivity, the effective medium model of Maxwell, Wagner, Sillars can be used to extract the dielectric response of the filler in a quantitative way. It turns out that the dielectric response is somewhat reduced with respect to the bulk, which points to a reduced average density. In particular the contraction of the pore material upon solidification is not fully compensated by sublimation out of the vapor. Consequently, the density of the solid is lowered, by about 5% with respect to the bulk. Since this is more than obtained from a comparison of the lattice parameters of the pore and the bulk solid, some voids must exist in the pore solid.

The monolayer does not participate in the phase transition of the bulklike component. This is plausible considering the heterogeneous nature of the pore walls. The dielectric response attributed to the monolayer does not only include the direct contribution of the monolayer molecules but also the changes of the response of the terminating polar groups of the silica matrix brought forth by adsorption. For the present fillers the anomalous contribution of the monolayer is almost as large as the contribution of the bulklike material in the pore center. A pore filling is more than just bulk material subject to geometric confinement.

ACKNOWLEDGMENT

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