PHYSICAL REVIEW B **66**, 064105 (2002)

Dipolar ordering and relaxations in acetonitrile-β-hydroquinone clathrate

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(Received 23 January 2002; published 13 August 2002)

Single crystals of this clathrate have been studied by measurements of the frequency and temperature dependent dielectric permittivity as well as with polarization-electric field cycles and x-ray diffraction. The dipole moments of the acetonitrile guest molecules form Ising chains that are coupled by the electric dipole-dipole interaction and that are arranged in a triangular array. At 345 K a phase transition from a partially disordered antiferroelectric to a ferrielectric arrangement is observed.

DOI: 10.1103/PhysRevB.66.064105 PACS number(s): 64.60.Cn, 64.70.Pf, 77.22.Ch, 77.22.Ej

I. INTRODUCTION

In the hydroquinone clathrates, the quinol HO-C_6H_4-OH molecules form a hydrogen bonded rhombohedral $R\bar{3}$ lattice with almost spherical cavities of of about 4.2 Å diameter.[1] The cavities can host a large variety of (neutral) guest molecules, ranging from molecules as small as H_2 or Ar to larger ones such as CH_3Br and C_{60}.[2] Compared to the somewhat better known hydrate clathrates the hydroquinone clathrates have several advantages: In contrast to the former the latter compounds are stable at ambient pressure and temperature. For several of them large single crystals can be grown. The cages are all equivalent and larger than those of the hydrates. Of particular interest are polar guest molecules since these undergo structural phase transitions driven by the interactions between the dipole moments of the host molecules with practically no coupling of the orientational degrees of freedom to the host lattice.

The most detailed characterization exists for the methanol guest molecule.[3,4] It has been shown that here the relevant dipole moment is just that of the free molecule and that the intermolecular coupling is due to the electric dipole-dipole (EDD) interaction. This allows the calculation of the structural and thermodynamic behavior of such a pseudospin system from first principles. In this sense these clathrates with polar guest molecules are model systems and are conceptually close to spin systems. The methanol system is somewhat complicated by the fact that—due to the C_{3i} site symmetry of the cage center—the dipole moment has six equivalent orientations.

The guest molecule of the present study CH_3CN (with a dipole moment of 3.93D[5] has only two positions, either parallel $(+)$ or antiparallel $(-)$ to the threefold crystal axis c (Fig. 1). One can therefore refer to an Ising degree of freedom. This orientation of the molecule in the cage has been established by diffraction studies,[6–9] by force field calculations,[10] and by early dielectric results,[11,12] which showed that the permittivity is much larger with the electric field along c than perpendicular to c and that the temperature and frequency dependence is reserved to the former case. The alignment of the CH_3CN molecule along the c axis leads to a stretching of the lattice along c. Referring to the hexagonal setting with the lattice parameters c and a, the c/a ratio is 0.39 for CH_3CN compared to 0.34 for the more globular CH_3OH guest molecule. CH_3CN is in fact the most oblong molecule that can reside in the cavities and the clathrate is therefore on the verge of decomposition, a problem that will be addressed below. Based on dielectric data obtained on powder samples with a static permittivity increasing from 5 to 6 between 200 and 300 K with a weak kink at about 280 K, Sixou and Dansas[12] proposed a transition from an antiferroelectric structure to the paraelectric state at this temperature. Later on, x-ray structure determinations by Mak and others[6–9] proposed that at room temperature the space group of the acetonitrile clathrate is actually trigonal $P3$ because of two nonequivalent orientations of the three guest molecules A,B,C of the hexagonal unit cell. Two molecules are oriented parallel and one molecule antiparallel to the c axis (Fig. 2). We will refer to this ferrielectric structure as $_{+}{}^{+}{}_{-}$. The smallest spacing between guest molecules occurs along c. For qualitative discussions one can therefore think of ferroelectric chains of guest molecules propagating along c, arranged in a two-dimensional triangular pattern. (In a more realistic model the fact that the A,B,C chains are displaced with respect to each other along c by $\pm c/3$ has to be considered.) The two $+$ chains are frustrated in the sense that they are surrounded by three $+$ and by three $-$ neighboring chains whereas the $-$ chain, has $+$ neighbors only. The low-

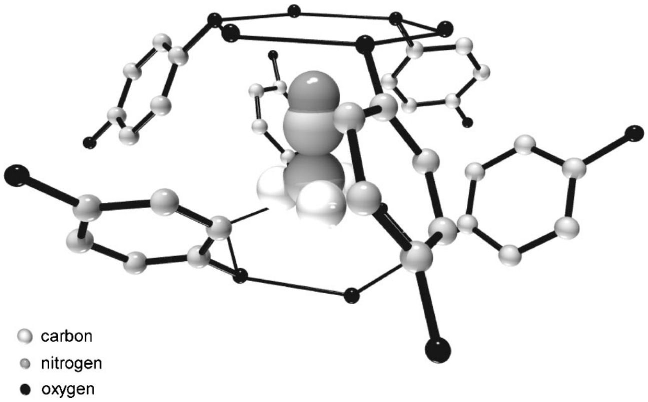

FIG. 1. The acetonitrile molecule (CH_3CN) in the quinone cagework. For the atoms of the acetonitrile molecule, the van der Waals radius is plotted, the C and O atoms of the cagework are plotted as a stick and ball model, and H atoms are omitted.

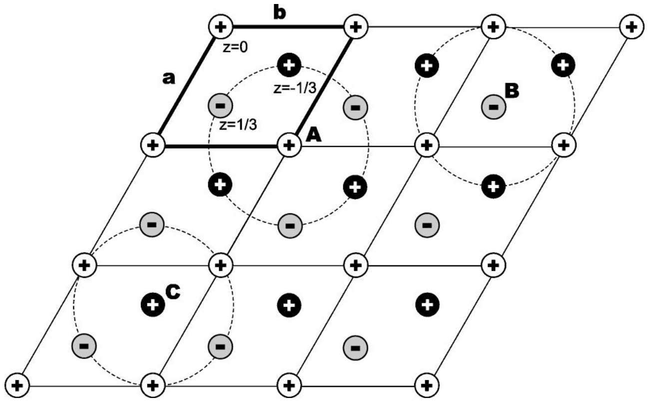

FIG. 2. Hexagonal basal plane. The unit cell contains three cages, labeled *A*, *B*, and *C*, which are shifted by $c/3$ against each other.

T structure of the methanol clathrate is different. It is an antiferroelectric arrangement $_{+}{}^{-}{}_{+}{}^{-}$ with ferroelectric (100) sheets alternating between $+$ and $-$.

In the present article we report measurements of the permittivity ε and of the electric polarization P as function the external electric field E. These results will be complemented by some structural data obtained from x-ray diffraction. Our study produces dielectric evidence for the peculiar ferrielectric ordering of this clathrate. We will also show that the system undergoes a phase transition (at about 345 K), not into the paraelectric state as has been assumed previously, but rather into a partially ordered antiferroelectric mesophase $_{+}{}^{0}{}_{-}$. The symbol 0 stands for a chain of guest molecules disordered with respect to the Ising degree of freedom. These findings are supported by estimates of the free energy of these and other arrangements of the dipole moments.

II. EXPERIMENT

Single crystals were grown from a saturated solution of quinol and acetonitrile at 313 K using the evaporation method. Chemical analysis reveals that the occupation of the cages with CH_3CN molecules is 100% with an error of 5%. Plates with the smallest dimension along c and a have been cut from the crystals. For the dielectric investigation the plates were 9×9 mm^2 and 1.4 mm thick. The sample for the x-ray diffraction study was $2\times2\times2$ mm^2. The handling of the samples is somewhat delicate. Around 373 K acetonitrile-β-quinol decomposes into α-quinol and acetonitrile vapor.[13] Already at room temperature there is considerable evaporation. A sample exposed to air was reported to lose 50% of the guest molecules within 2.5 days.[6] We therefore enclosed the samples in a leak-tight cell after adding a drop of liquid CH_3CN. For the same reason we could not sputter Au electrodes onto the faces of the sample for the dielectric measurements, but had to rely on Au foils. For the measurement of the frequency-dependent permittivity, a Solartron impedance analyzer FRA1260 in combination with a interface (Chelsea) has been employed. The temperature range from 200 K to 318 K has been explored with a helium closed cycle refrigerator. In a second run, on a fresh sample, we used a thermostat for measurements from room temperature up to 360 K (13 K short of the decomposition temperature). The same sample was also used for the polarization-field curves $P(E)$ that have been recorded with a standard Sawyer-Tower circuit and a cycling frequency of 2 Hz. Finally we examined the position and intensity of some selected $(h0l)$ reflections with an x-ray two-circle diffractometer.

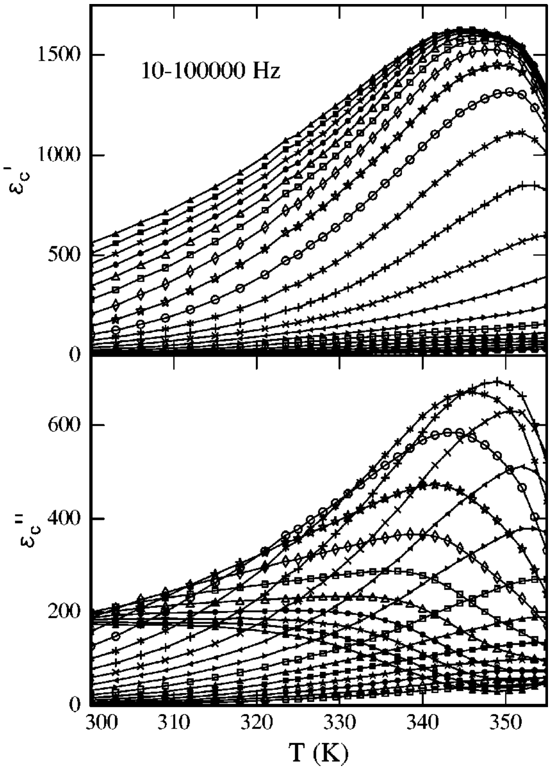

FIG. 3. The temperature dependence of the real and the imaginary part of the dielectric constant ε_c for selected frequencies, as obtained in the high-T run.

III. RESULTS

Figure 3 shows the real and imaginary part of $\varepsilon_c(\nu)$ as function of T for the high-T run. Figures 4 and 5 show the permittivity of both runs plotted versus frequency ν for a number of selected temperatures. Values of ε_c up to 1650, orders of magnitude higher than in previous studies, have been observed. ε_c shows strong dispersion over a wide T range. The permittivity perpendicular to c, ε_a, has values between 5 and 6 without any systematic variation with T or ν. Obviously the dipole moments are aligned along c and all dipolar dynamics is due to 180° flips between the $+$ and $-$ orientation. At higher temperatures there is just one dispersion step in ε_c' and one corresponding maximum of ε_c'', which at lower T split into two components. Within the overlap region, 298 K$<T<$318 K, the results of the two runs on different samples coincide at higher ν, but deviate at lower ν. See the two $T=320$ K traces of Fig. 4. These differences may be due to slightly different acetonitrile concentrations of the two samples. One could argue, e.g., that the

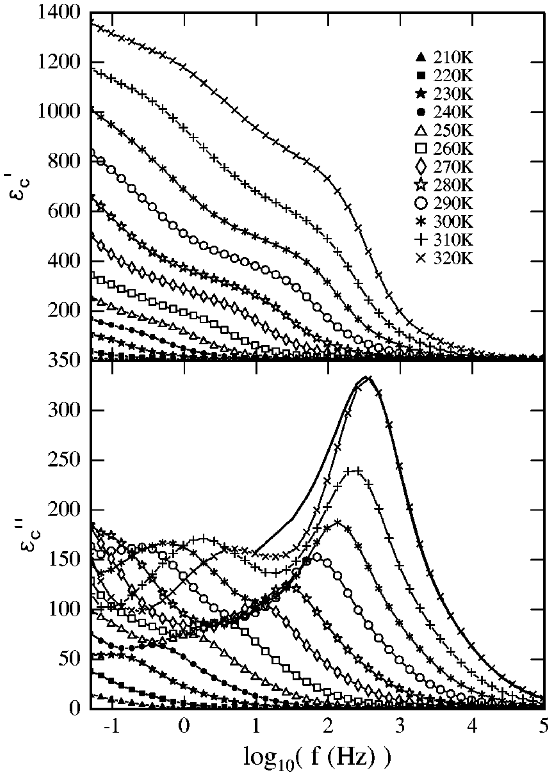

FIG. 4. The frequency dependence of ε_c, as obtained from the low-T run. For $T=320$ K, the results of the high-T run on ε_c'' are included for comparison (heavy solid line).

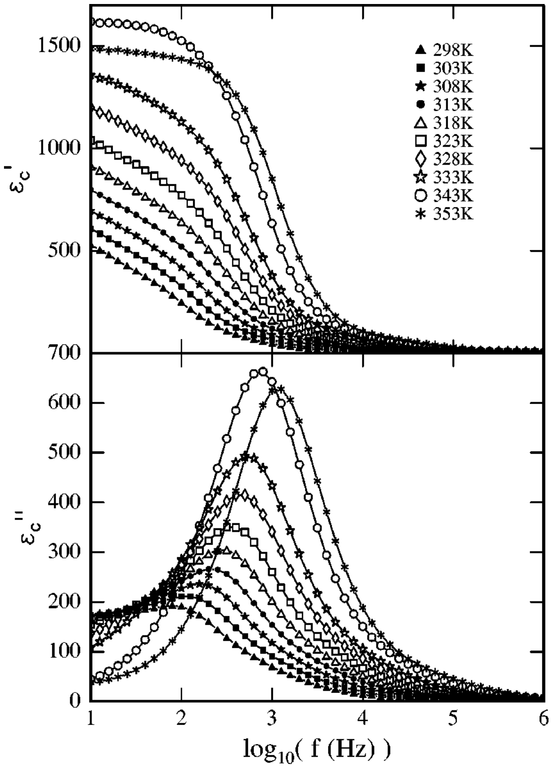

FIG. 5. The frequency dependence of ε_c, as obtained from the high-T run.

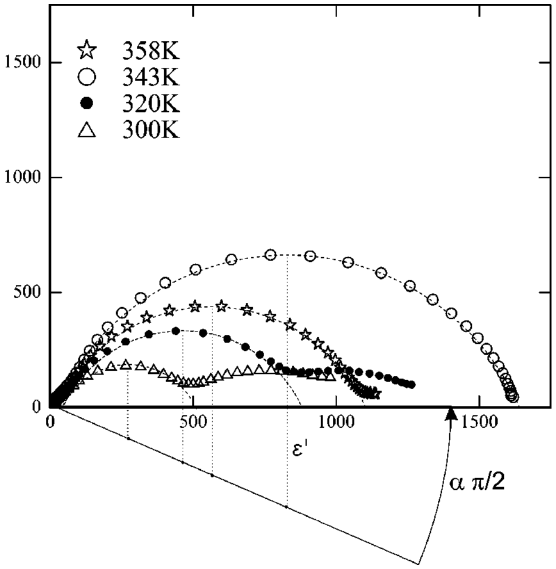

FIG. 6. Cole-Cole circles in the complex $\varepsilon_c'/\varepsilon_c''$ plane for different temperatures. The centers of the semicircles for the high-frequency relaxation lie on a common line and therefore have the same parameter α.

sample of the high-T run has a slightly higher percentage of vacant cages and that such vacancies could give rise to additional relaxational channels for the guest molecules in sites next to an empty one.

Figure 6 shows a plot of the permittivity ε_c in the complex plane. The (ε_c', ε_c'') data points lie on circular arcs with centers below the ε_c' axis and can therefore be parametrized in terms of the Cole-Cole model $\varepsilon(\omega)=\varepsilon_\infty+(\varepsilon_{stat}-\varepsilon_\infty)/[1+(i\omega\tau_0)^{(1-\alpha)}]$ for a symmetric distribution of relaxation times centered at τ_0. The relaxation at high T and its continuation, the high-ν component at lower T share the same value of α, $\alpha=0.13$, as indicated in Fig. 6. The second relaxation process at lower ν and lower T has a broader distribution, $\alpha=0.35$. Figure 7 shows the T dependence of the individual dielectric increments $\Delta\varepsilon$ of the two dispersion step. The height of the low-ν process is practically T-independent, whereas the increment of the high-ν dispersion step increases with increasing T and aims at a divergence at about 345 K. An Arrhenius plot log($1/\tau_0$) vs 1/T of all relaxation processes observed is shown in Figure 8.

On heating the relaxation rates of the two components approach each other, but eventually the maximum of the low-ν component of ε'' as function of ν is lost in the low-ν wing of the high-ν peak. This explains the blind region of the low-ν branch of Fig. 8. It is therefore difficult to decide if and at what temperature the two relaxation processes merge. Values around 345 K appear to be the best guess. The Arrhenius plot shows three quasilinear sections. The Arrhenius parameters, barrier E_B and attempt frequency ν_0, are 11 100 K and 6.3×10^{16} Hz for the high-T regime, 9850 K and 10^{14} Hz for the low-ν branch, and 7234 K and 4.3×10^{12} Hz for the high-ν branch. The Arrhenius parameters of Sixou and Dansas on a polycrystalline sample are $E_B=8100$ K, $\nu_0=1.6\times10^{15}$ Hz, those of Dryden[11] for ε_c are $E_B=9100$ K, $\nu_0=1.6\times10^{16}$ Hz. The attempt frequency of

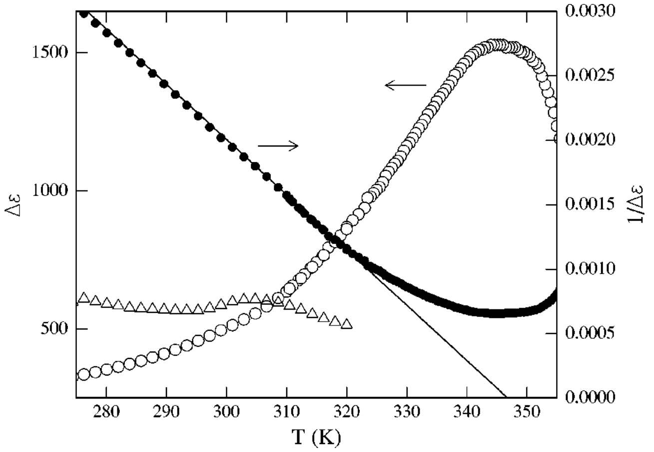

FIG. 7. The temperature dependence of the low-ν (triangles) and of the high-ν (circles) dispersion step. Also shown is the inverse of the high-ν dispersion step.

the high-ν branch is very close to the libron frequency of 2.94 THz as obtained from infrared spectroscopy.[14] The values of $\varepsilon_{c\infty}$ derived from the Cole-Cole model are about 5, which is close to ε_a. The Cole-Cole analysis also yields that ε_{c0}, the static permittivity along c, passes through a maximum at about 345 K, ε_{c0}(T) being almost identical with the 10 Hz data down to about 340 K.

$P(E)$ cycles have been recorded between 300 K and 360 K (Fig. 9). The hysteresis of the low-T data vanishes at about 345 K. Nevertheless the curves remain highly nonlinear such that a "spontaneous" polarization P_s can be determined from the intersection of the tangent at highest E with the P axis. The T dependence of P_s and of the remanent polarization P_r are displayed in Fig. 10. This figure also includes results on the intensity of the (001) Bragg reflection. Finally the lattice parameters a and c and the volume of the hexagonal unit cell are shown in Fig. 11. There is considerable thermal expansion in the basal plane below but not above 340 K.

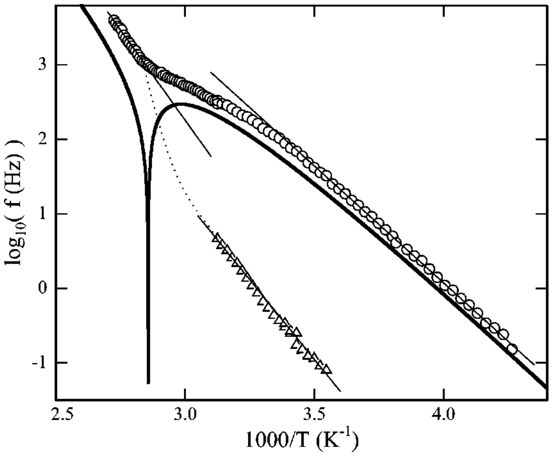

FIG. 8. Logarithm of the relaxation frequency plotted against the inverse temperature. Arrhenius laws (thin lines) have been fitted to the quasilinear sections. The heavy line is a calculation of $\tau(T)$ from the quasi-one-dimensional Ising model.

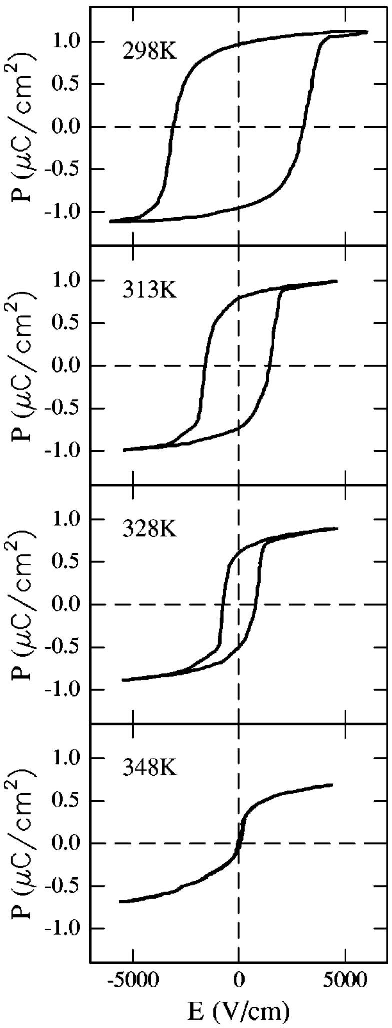

FIG. 9. Dielectric polarization vs. electric field loops at selected temperatures.

IV. DISCUSSION

The results suggest some change of the dielectric properties and of the cell parameters around $T_c \approx 345$ K. Originally we thought that this is a phase transition from the paraelectric to an ordered phase. Matsuo and Suga[15] have observed that the ordering temperatures of several β-hydroquinone clathrates roughly scale with the square of the dipole moment of the guest molecules, suggesting that the transitions are driven by the EDD coupling. The T_c predicted on this basis for the acetonitrile clathrate is in fact about 300 K. We therefore interpreted the appearance of a ferroelectric-type hysteresis of the $P(E)$ cycles at lower temperatures in combination with the slowing down and the splitting of the relaxation spectrum in terms of the ordering transition of a "relaxor ferroelectric." A prerequisite for such behavior is some degree of positional or substitutional disorder. In the present samples such a disorder could be due to small percentage of vacant cages. The idea of the low-T state being ferroelectric would be in conflict with the structure determination of Mak and other authors, but one has to realize that the $_{+}{}^{+}{}_{-}$ arrangement proposed in these studies is based on

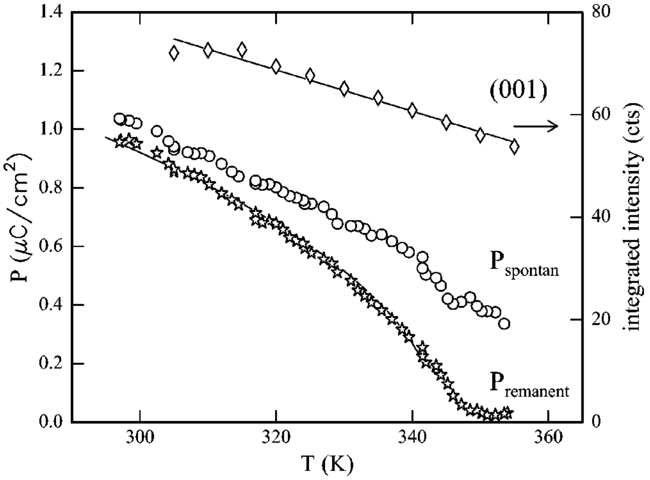

FIG. 10. The remanent, the spontaneous polarization and the integrated intensity of the (001) Bragg peak as function of temperature.

the weak intensities of Bragg reflections (hkl) of the type $-h+k+l\neq 3n$. In an empty β-hydroquinone crystal lattice as well as in a ferroelectic $_{+}{}^{+}{}_{+}$ or a paraelectric $_{0}{}^{0}{}_{0}$ state, the structure would be rhombohedral and these extra reflections would carry no intensity. The finite intensity stems from the inequivalence of the position and/or orientation of the guest molecules in the three cages A,B,C of the hexagonal cell. Our own diffraction data showed that the intensities at the nodes (hkl) with $-h+k+l\neq 3n$ are indeed veritable Bragg reflections rather than, e.g., maxima of diffuse intensity or multiple reflections, thereby confirming the $_{+}{}^{+}{}_{-}$ structure proposed by Mak and others. In this type of ferrielectric pseudospin pattern the spontaneous polarization, assuming perfectly ordered chains, is 0.83 μC/cm^2, in good agreement with what is observed experimentally around 320 K, well below T_c. The hysteresis of $P(E)$ is interpreted in terms of switching between the $_{+}{}^{+}{}_{-}$ and the $_{-}{}^{-}{}_{+}$ domain. Translational domains (such as $_{-}{}^{+}{}_{+}$ and $_{+}{}^{-}{}_{+}$) should have no effect on $P(E)$. The field induced "spin-flip" transition into the ferroelectric state $_{+}{}^{+}{}_{+}$ would require electric fields much higher than what can be achieved in the laboratory (see below).

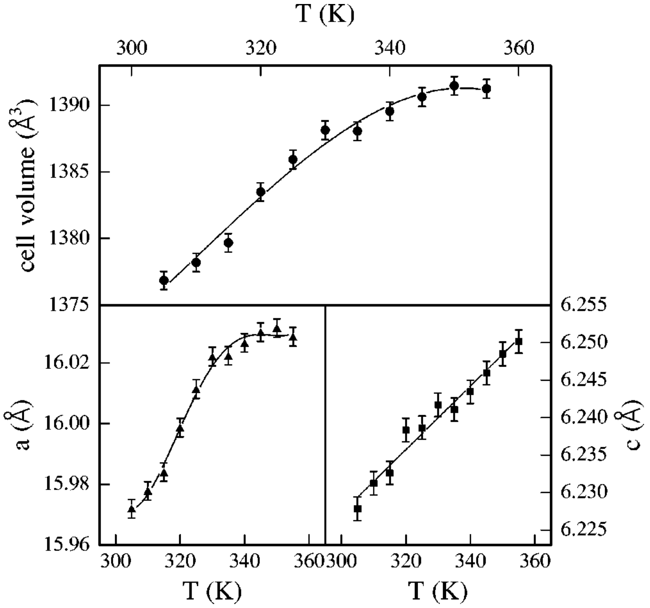

FIG. 11. Temperature dependence of the lattice constants a and c and of the cell volume of the hexagonal cell.

As far as the high-T phase, $T>T_c$, is concerned the idea of a paraelectric state is incompatible with weak, but nevertheless finite intensities of the extra reflections [see the (001) intensity in Fig. 10]. The absence of hysteresis also rules out a ferro- or ferrielectric state with a net polarization, which then could couple to the external field causing the domain pattern to change. The fact that the high-T state can be polarized by applying rather modest fields calls for a pseudospin arrangement that is partially disordered. We therefore suggest a $_{+}{}^{0}{}_{-}$ structure with two ferroelectrically ordered chains with antiparallel orientations of the pseudospins and one disordered chain. Small electric fields induce order in the disordered chain and thereby a macroscopic polarization. The field-induced configuration is then identical with the arrangement of the dipole moments in the low-T phase. For the calculation of the Bragg intensities we describe orientational disorder by split ± positions of the guest molecule. The calculated intensities of the (001) reflection of the $_{+}{}^{+}{}_{-}$ and of the $_{+}{}^{0}{}_{-}$ phase differ by just a few percent, explaining why there is no noticeable change across T_c. Note that the transition from $_{+}{}^{0}{}_{-}$ to $_{+}{}^{+}{}_{-}$ does not break a symmetry that would give rise to superlattice reflections: both structures belong to the space group $P3$, the transition is isomorphous.

In order to support this phase assignment we have calculated the coupling energies u_{ij} between the dipole moments in several pseudospin arrangements consisting of completely ordered ferroelectric chains and/or completely disordered chains, referring to the EDD interaction

$$u_{12}=\frac{1}{k_B}\frac{1}{4\pi\varepsilon_0\varepsilon_{\mathrm{sc}}}\left(\frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r_{12}^3}-3\frac{(\vec{r}_{12}\cdot\vec{\mu}_1)(\vec{r}_{12}\cdot\vec{\mu}_2)}{r_{12}^5}\right). \qquad (1)$$

For the disordered chains the individual dipole moments were simply set to zero but contribute to the orientational entropy s with $k_B \ln 2$. For the calculation of the dipole sums, all dipoles within a sphere with radius R have been considered. R has been increased until the sums change by less than 10^{-6}. (Note that because of the conditional convergence of dipole sums, other shapes of the summation volume would give other values.) The resulting plot of the free energy per pseudospin $f=u-Ts$ is shown in Fig. 12.

Here a screening constant $\varepsilon_{\mathrm{sc}}$ of the interaction has been set to 1.65 in order to make T_c coincide with the experimental value of 345 K. The sequence of equilibrium phases proposed by this model is indeed $_{+}{}^{+}{}_{-}$, $_{+}{}^{0}{}_{-}$, $_{0}{}^{0}{}_{0}$ from low to high temperatures. The free energy of the $_{+}{}^{0}{}_{0}$ state, which is next in energy, is included in the figure. The ferroelectric state $_{+}{}^{+}{}_{+}$ is at -718 K, far above the equilibrium configurations. The onset of the paraelectric phase $_{0}{}^{0}{}_{0}$ is predicted to occur at about 650 K, which is well above the decomposition temperature of 373 K. Some comments are in order. The

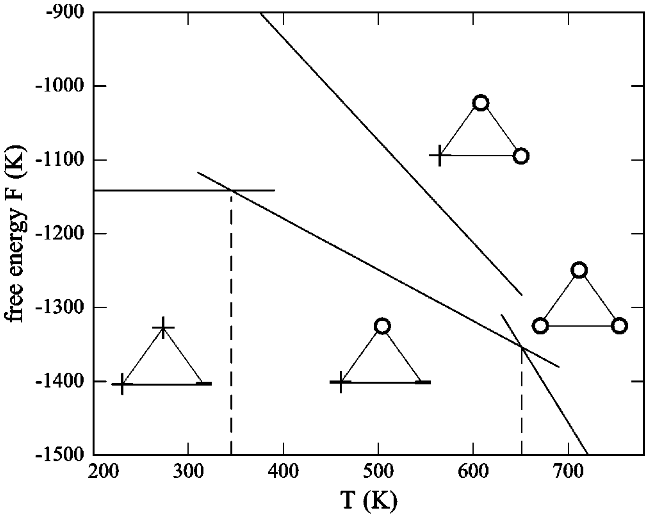

FIG. 12. Free energies of selected pseudospin configurations. The intersection points mark the temperatures of phase transitions.

model ignores fluctuations in the disordered chains and excitations of the ordered chains. The paraelectric behavior of the methanol clathrate is in fact dominated by ferroelectric correlations along the chains that extended over about hundred molecules just above the ordering temperature. This situation should also apply to the disordered chains of the present system. We therefore consider the model helpful only as far as the sequence of phases is concerned, but do not pay attention to the predicted first order character of the two transitions. Actually the T dependence of the remanent polarization P_r and the absence of discontinuities in the T dependence of the lattice parameters suggest that the phase transition at 345 K is of second order or at least almost so. On the other hand, the static permittivity ε_{cs} does not diverge at this temperature. The high but nevertheless finite values could of course be due to surface layers depleted from guest molecules, to a finite percentage of empty cavities in the bulk (see below) or to a small gap between the Au foil and the sample. The ${}_{+}{}^{-}{}_{+}{}^{-}$ arrangement of the ordered phase of the methanol clathrate turns out to be energetically degenerate with the state ${}_{+}{}^{+}{}_{-}$ of the present system. We do not know why the methanol and the acetonitrile clathrate choose different ground states. Presumably the canting of the dipoles with respect to the *c* axis is of importance, which leads to six pseudospin orientations for the methanol compound as opposed to just two for the acetonitrile compound.

Although we cannot present a quantitative explanation of the dielectric relaxations, we try to give some qualitative arguments. The excitations of an Ising system are ± flips and the dynamics is therefore purely relaxational. In the present system not only the coupling within the Ising ensemble, but also the local barriers E_{CF} of the crystal field Devonshire potential of the cage have to be considered. For the ordered $+$ and $-$ chains of both phases the energy ΔE of a flip of an individual dipole can be calculated from the EDD interaction. The resulting values are 2283 K for the flip of a dipole in the majority chains and 3129 K in the minority chains of the ${}_{+}{}^{+}{}_{-}$ low-T phase. The flip energy in the ordered chains of the ${}_{+}{}^{0}{}_{-}$ high-T phase is 2707 K. The flips in the disordered 0 chains of the high-T phase will be addressed further below. The effective barriers for flips are given approximately by $E = E_{\mathrm{CF}} + \Delta E$. One therefore expects two distinct relaxations below T_c and just one above T_c, in agreement with the experiment. A comparison with the experiment suggests that the effective barriers E are obviously dominated by the crystal field contribution E_{CF}, only about one-third is due to the EDD coupling. Based on these estimates we propose to assign the low-ν branch with the higher Arrhenius barrier to the flips of dipoles in the nonfrustrated minority chains and the high-ν branch to flips in the frustrated majority chains of the low-T phase. However, the rather small differences between the calculated ΔE values cannot quite explain the largely different values of E of the two branches (7234 and 9850 K), let alone the fact that the effective barrier of the high-T phase (11 100 K) is not intermediate to the effective barriers of the two branches of the low-T phase but actually significantly higher. Clearly the idea of flips of individual dipoles in otherwise perfectly ordered chains in the vicinity of the phase transition is too simple.

The phase transition at 345 K, from ${}_{+}{}^{0}{}_{-}$ to ${}_{+}{}^{+}{}_{-}$, can be understood as the para-ferro transition of an Ising chain of dipoles in the field of the surrounding $+$ and $-$ chains. The theory of such a quasi-one-dimensional Ising system has been worked out for a configuration slightly different from the present one, namely, an ensemble of identical chains with a next neighbor intrachain coupling $J_{\|}$ in combination with a mean field treatment of the interchain coupling. The relaxation time diverges at T_c due to a divergence of the length ξ of the correlated chain segments:[16]

$$\tau(T) = \tau_A(T)\,\frac{e^{4\beta J_{\|}}}{4\beta J_{\|}}\,\frac{1}{|T_c/T - 1|} \times \begin{cases} 1, & T > T_c \\ \dfrac{1}{2}, & T < T_c \end{cases} \tag{2}$$

where $\beta = 1/(k_B T)$. $\tau(T)$ as calculated from this equation is shown in Fig. 8. For the noncritical background relaxation time τ_A that couples the individual Ising spin to the thermal bath we assumed an Arrhenius law with the parameters taken from the high-ν branch of the low-T phase. $J_{\|}$ is calculated from u_{ij} to 563 K ($\varepsilon_{\mathrm{sc}} = 1.65$). The experiment does not produce evidence for the critical slowing down of a relaxational channel at T_c, nor does ε_{c0} diverge at T_c. A finite number of vacancies sets an upper limit to the correlation length ξ, thereby supressing the divergence of τ and ε_{c0}. Note that for 2% of vacancies, the average length of the occupied chain segments between two vacancies is already reduced to $34c$. On the other hand the T dependence of τ as proposed by the quasi-one-dimensional Ising model for temperatures somewhat away from T_c is rather close to what is observed in the experiment. In particular, the change of slope of the dominant relaxation is well reproduced.

V. CONCLUSIONS

This study has established the acetonitrile-β-quinol clathrate as a model system for electric ordering. The dipole moments of the acetonitrile guest molecules form an Ising ensemble coupled by the electric dipole-dipole interaction. The clathrate consists of ferroelectrically correlated chains in a highly frustrated triangular arrangement. At 345 K there is a phase transition from a partially ordered antiferroelectric state to the ferrielectric ground state that is accompanied by changes of dielectric relaxations. The system would be suited for computer simulations that could start practically from first principles.

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