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Low-dimensional ordering and fluctuations in methanol-β-hydroquinone clathrate studied by x-ray and neutron diffraction

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Methanol-β-hydroquinone clathrate has been established as a model system for dielectric ordering and fluctuations and is conceptually close to magnetic spin systems. In x-ray and neutron diffraction experiments, we investigated the ordered structure, the one-dimensional (1D) and the three-dimensional critical scattering in the paraelectric phase, and the temperature dependence of the lattice constants. Our results can be explained by microscopic models of the methanol pseudospin in the hydroquinone cage network, in consistency with previous dielectric investigations. A coupling of the 1D fluctuations to local strains leads to an anomalous temperature dependence of the 1D lattice parameter in the paraelectric regime.

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I. INTRODUCTION

Reducing the dimensionality has a drastic influence on order-disorder phenomena, as it generally enhances fluctuations. Phase transitions are shifted to lower temperatures or may be suppressed entirely. In the one-dimensional Ising model with nearest-neighbor interactions, thermal fluctuations suppress ordering at any finite temperature, independent of the strength of the interactions. Theoretical models for low-dimensional ordering and fluctuations are mostly tested on magnetically interacting materials, where the magnetic moment is well decoupled from the surrounding chemical lattice and the interaction is short ranged. Materials with low-dimensional, but long-ranged interactions like the dipole-dipole interaction are rare. Due to its small energy scale, the magnetic dipole-dipole interaction is often negligible as compared to exchange-type interactions, magnetoelastic interactions, and anisotropies induced by spin-orbit coupling and crystal field. The electric dipole-dipole (EDD) interaction in contrast is several orders of magnitude larger than its magnetic counterpart. But the electric dipole moment is connected to polar molecules or to displacements of groups of atoms against each other. Usually, the interaction with the surrounding lattice is far from being negligible. Materials, which allow testing theoretical predictions for fluctuations and ordering of "pseudospins" interacting exclusively via the EDD interaction, are extremely rare. In this context, clathrates with polar guest molecules provide an exception. They may undergo order-disorder transitions driven by the interactions between the dipole moments of the guest molecules, with practically no coupling of the orientational degrees of freedom to the host lattice.

The present article deals with methanol-β-hydroquinone clathrate, where well-defined methanol electric dipoles occupy the almost spherical hydroquinone cavities. The electric dipoles arrange in chains and are well decoupled from the surrounding host lattice. The methanol clathrate can thus be understood in terms of interacting point dipoles and has been established as a model system for dipolar ordering processes.[1–5]

Figure 1 shows the methanol molecule, which carries a dipole moment of 1.69 D (Ref. 6), in the hydroquinone cage. The geometry of the lattice combined with the EDD interaction is responsible for the formation of ferroelectric chains along the hexagonal *c* axis, reflected in the dielectric properties. Woll *et al.* have studied the dielectric response as a function of temperature and frequency.[1,2] The static dielectric constant along the hexagonal *c* axis, ε_{cs}, shows a strong deviation from the Curie-Weiss behavior already at 250 K. The temperature dependence of ε_{cs} at higher temperatures is well described by a quasi-one-dimensional (quasi-1D) Ising

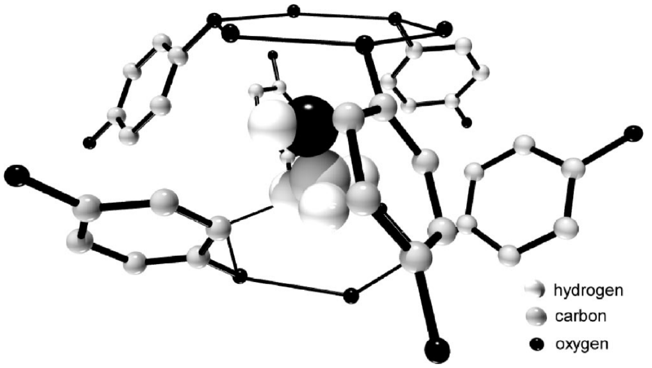

FIG. 1. The methanol molecule (CH_3OH) in the hydroquinone cage. The atoms of the guest molecules are shown with their van der Waals diameters whereas for the hydroquinone host lattice the stick-and-ball presentation is used.

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model with a ferroelectric coupling J_c to nearest neighbors in the chain and a mean-field antiferroelectric interchain interaction with coupling constant $J_\perp$ (Ref. 7). At lower $T, \varepsilon_{cs}(T)$ deviates from this mean-field Ising behavior and finally decreases with decreasing T, indicating the onset of 3D antiferroelectric interchain correlations. At $T_c=65$ K the methanol clathrate undergoes a transition into an antiferroelectrically ordered structure.

While the dielectric experiments probe the macroscopic response at the center of the Brillouin zone, diffraction experiments give access to the corresponding underlying microscopic processes and allow to study the structural susceptibility at arbitrary points in reciprocal space. In this article, we present x-ray diffraction results obtained in the ordered phase, which allow us to develop a dipolar structure model. Then we turn to the paraelectric regime, where we study 1D and 3D critical scattering by x-ray and neutron diffraction experiments, as well as the temperature dependence of the lattice parameters. We compare our results to theoretical predictions and discuss them in the context of the preceding dielectric experiments.

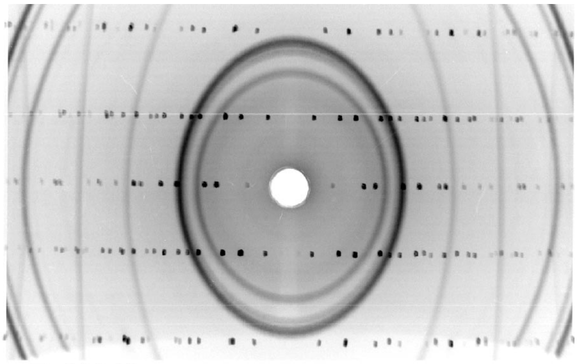
II. EXPERIMENTAL

Single crystals of methanol-β-hydroquinone clathrate have been grown from a saturated solution of quinol and methanol at 313 K. Completely deuterated samples were used for neutron experiments to minimize the incoherent background. Typical sample crystals were $2\times2\times2$ mm^3. At room temperature, the methanol clathrate has a rhombohedral $R\bar{3}$ structure.[8] Throughout this article, we use the hexagonal notation, which is better adapted to the dielectric properties of the clathrate than the rhombohedral. Exceptions are marked explicitly by $(\cdots)_{rh}$. The hexagonal lattice parameters at 300 K are $a=16.62$ Å and $c=5.56$ Å. For the x-ray investigations, we used monochromatic Cu $K\alpha$ radiation and a two-circle diffractometer, equipped with a closed-cycle refrigerator. The single-crystalline samples were oriented with c perpendicular to the scattering plane. This allows scans within the $(hk0)$ plane. Scans within planes (hkl), l constant, $l\leqslant 1$ are possible by moving the detector out of the diffractometer plane. Rotating crystal exposures have also been taken. Here the crystal was rotated about c and the incoming beam was perpendicular to the c axis. Diffuse 1D critical scattering has been measured at the two-circle neutron diffractometer D23 (CEA-CRG) at the high-flux reactor of the ILL in Grenoble, France. Here the 1D axis c was mounted in the scattering plane.

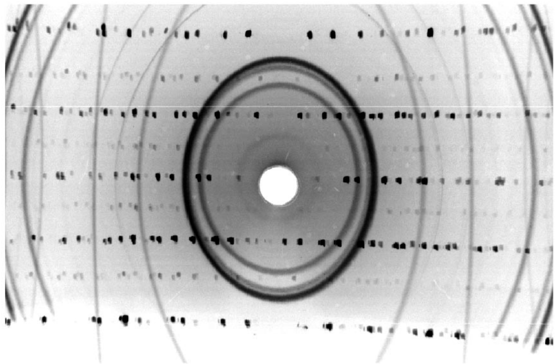
III. RESULTS

A. Ordered phase

Rotating-crystal x-ray photographs of methanol clathrate were taken above and below the phase transition at $T_c=65$ K. Figure 2 shows photographs taken in the paraelectric phase at $T=100$ K (a) and, in the ordered phase, at 39 K (b). At high temperatures, horizontal layers of reflections (hkl) with $l=0,\pm1,\pm2,\ldots$ are visible. Below T_c, additional reflections in layers with integer and half-integer values of l, $l=\pm\frac{1}{2},\pm\frac{3}{2},\ldots$ appear. The (hkl) values of the superlattice reflections can be determined from their position in the photograph. Careful analysis shows that modes with wave vectors $k_1=(00\frac{1}{2})_{rh}$ and $k_2=(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{rh}$ condense at the phase transition on the boundary of the rhombohedral Brillouin zone at the Lifshitz points F (k_1) and L (k_2). To generate all superlattice reflections as linear combinations of k_1 and k_2, L and two arms of the F star are required. Accordingly, two of the rhombohedral lattice vectors double at T_c. Additionally, the unit cell doubles in the hexagonal c direction [as indicated by the L-type vector $k_2=(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{rh}=(00\frac{1}{2})_{hex}$].



(a) T=100 K



(b) T= 39 K

FIG. 2. Rotating crystal photographs at $T=100$ K (a) in the paraelectric regime and at 39 K (b) in the ordered phase. Superlattice reflections appear below T_c in layers with integer and half-integer values of l. Elliptical lines are due to scattering from the Al windows of the cryorefrigerator.

The occurrence of k_1 indicates freezing of the methanol molecules into one of the six symmetry directions of the $R\bar{3}$ space group. The resulting structure of the dipole system in the dielectrically ordered phase is shown in Fig. 3. The dipoles are arranged in ferroelectrically ordered chains running along the hexagonal c axis, which are arranged in sheets of alternating sign. As a property of the EDD interaction and the lattice symmetry, the dipoles prefer an antiferroelectric arrangement perpendicular to the chains, which cannot be satisfied for all chains, because of the triangular lattice symmetry. As a consequence, every dipole chain is surrounded by four chains, which are oriented antiparallel and by two parallel-oriented dipole chains. The antiferroelectric interaction is satisfied by the majority. The 4:2 pattern fills the hexagonal basal plane in a regular fashion: Every dipole has

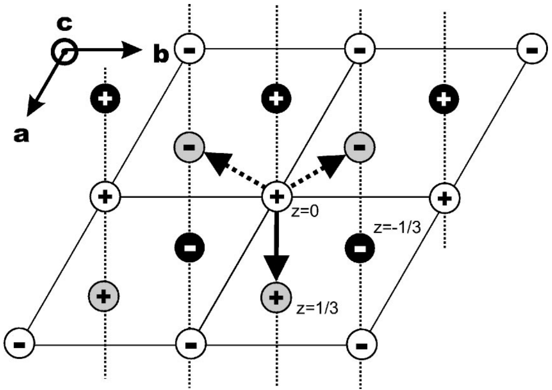


FIG. 3. Projection of the 3D ordered antiferroelectric structure onto the hexagonal basal plane: White circles: dipoles at $z=0$. Gray circles: $z=\frac{1}{3}$. Black circles: $z=-\frac{1}{3}$. $+/-$ indicates the orientation of the electric-dipole moment with respect to the hexagonal c axis. Below T_c, two of the rhombohedral lattice vectors double (indicated by the dotted arrows). The ferroelectric chains arrange in ferroelectrically ordered (100) layers with alternating sign from layer to layer, as visualized by dotted lines.

the same environment of ferroelectrically and antiferroelectrically oriented pseudospins. This 2 k_1 ground state is also obtained from Monte Carlo calculations[9] and simple lattice sum calculations, considering the EDD interaction of the guest molecules, only (see Ref. 10 for the case of acetonitrile).

The doubling of the unit cell along c, as evidenced by the occurrence of L-type k_2 reflections, indicates an antiphase arrangement in neighboring cells along c. The most plausible explanation is a dimerization with respect to an alternating distance of the methanol dipoles in the 1D chains—i.e., the appearance of pairs of strongly coupled pseudospins. Considering the EDD interaction in combination with a flat potential in the cage center, the latter dimerization is energetically favorable, as we will discuss below. The ordering of the dipole system at T_c accompanied by a structural phase transition into the triclinic space group $P1$, involving a small triclinic distortion of the host lattice below T_c (Ref. 2).

B. Paraelectric regime

The 1D fluctuations in the dipole chains in the paraelectric regime above T_c give rise to diffuse scattering which is distributed in planes perpendicular to the 1D axis (and weighted by the methanol molecular form factor). The small interchain interaction $J_\perp$ finally leads to a 3D phase transition at finite temperatures. The onset of 3D ordering close to the phase transition is indicated by diffuse scattering at the positions of the superlattice reflections of the low-T phase. The correlation length along the dipole chains, ξ_c, and perpendicular, $\xi_\perp$, follows from the quasi-1D Ising model, which has also been applied to fit the dielectric data, to[7]

$$\left(\frac{\xi_c}{c}\right)=\left(\frac{T_c}{2J_c}\right)^{(1/2)}\frac{e^{2J_c/T_c}}{2|t|^{(1/2)}}, \tag{1}$$

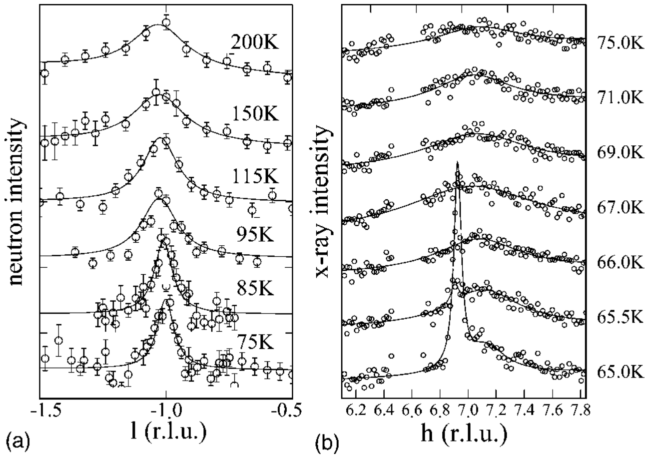


FIG. 4. Diffuse scattering observed in the paraelectric regime. (a) Diffuse 1D scattering in the $l=-1$ layer, at $q=(3,\overline{4.5},\overline{1}+\xi)$ (neutron measurement). (b) Development of diffuse 3D scattering at the position of a superlattice reflection of the ordered low-T phase, at $q=(7+\xi,\overline{3}-0.43\xi,\overline{0.5})$ (measured with x rays). At 65 K the superlattice reflection is already visible as a sharp peak. An Al powder line has been cut around $h=6.55$.

$$\left(\frac{\xi_\perp}{a}\right)=\left(\frac{T_c}{4J_c}\right)^{(1/2)}\frac{1}{|t|^{(1/2)}}, \tag{2}$$

where $t=(T-T_c)/T_c$ is the reduced temperature. Figure 4 shows diffuse 1D and 3D scattering as measured with x-ray and neutron diffraction at different temperatures in the paraelectric regime. We investigated the weak 1D scattering on a neutron diffractometer because the contribution of the methanol molecules to the total scattering is higher in neutron scattering with deuterated samples than in the x-ray experiments. The correlation lengths ξ_c and $\xi_\perp$ follow from the width of Lorentzian peak profiles and are shown in Fig. 5. The solid lines in the figure are fits after Eqs. (1) and (2). The structural data are well described by the quasi-1D Ising model and the fitting parameter J_c is determined to $J_c=202$ K, in good agreement with the dielectric results (195 K; see Ref. 1).

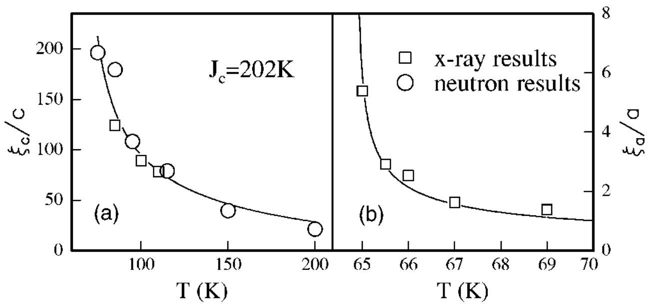


FIG. 5. Correlation length ξ_c (a) and $\xi_\perp$ (b), parallel and perpendicular to the dipole chains, as determined from Lorentzian fits to the curves in Fig. 4. Solid lines are fits after Eqs. (1) and (2). Results from neutron diffraction are marked by (∘), x-ray results by (□).

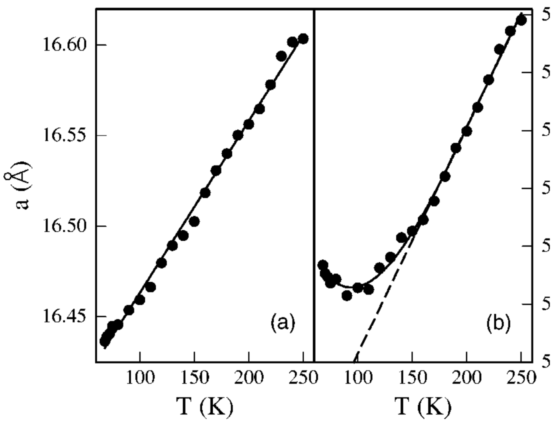


FIG. 6. Temperature dependence of the hexagonal lattice parameters a (a) und c (b). The dotted line in part (b) is a linear extrapolation of the high-temperature behavior to lower T.

As a true 1D feature, the dimerization observed in the ordered phase could already appear in the dynamically ordered chain segments in the paraelectric regime, where the 1D fluctuations reach some hundreds of unit cells. We found neither intensity at the superlattice positions of k_2, which would indicate a static dimerization of the dipole chains in the paraelectric phase, nor diffuse scattering in planes with half-integer values of l, which would indicate fluctuations of the dimerization above T_c. From calculations of the methanol structure factor[13] where we allowed a displacement of the dipoles along the 1D axis of $\delta = 0.25$ Å, the intensity of the diffuse scattering due to the dimerization can be estimated as being at least two orders of magnitude smaller than that of the 1D critical scattering. The corresponding correlation length ξ_{sp} should be smaller than ξ_c, the corresponding critical scattering, as a consequence, broader. If the dimerization of the dipole chains already occurs in the paraelectric phase, this effect presumably is too small to be seen in standard diffraction experiments.

Figure 6 shows the temperature dependence of the hexagonal lattice parameters a and c, as derived from the Bragg positions. While the a axis decreases linearly with temperature, c shows anomalous behavior below 170 K.

IV. DISCUSSION

The structure of the dipole system in the dielectrically ordered phase in methanol-β-hydroquinone clathrate, as determined from the analysis of the superlattice reflections below T_c, agrees well with the ground state calculated by Monte Carlo simulations[9] and lattice sum calculations. The temperature behavior of the correlation length ξ_c and $\xi_\perp$ is well described by the corresponding quasi-1D model by Scalapino *et al.*[7] The structural investigations therefore confirm the microscopic picture of low-dimensional ordering and fluctuations of the methanol pseudospins in the β-hydroquinone cagework, as it was suggested by the dielectric experiments.

An interesting point is the appearance of superlattice reflections of type "k_2," because they indicate a doubling of the unit cell in the 1D direction. The most probable explanation of this doubling is a dimerization of the dipoles in the 1D chains. Considering a 1D chain of electric dipoles on a deformable lattice (with distance d), interacting solely by the electric dipole-dipole interaction, a dimerization of the chain with respect to an alternating distance $d+\delta$ and $d-\delta$ of the dipoles is energetically favorable. The small lattice distortion at T_c (a first-order structural transition) probably leads to a coupling of the two otherwise independent wave vectors k_1 and k_2. The freezing of the methanol molecule and the static dimerization of the pseudospins along the chains therefore fall together at T_c. In a system with smaller coupling of the pseudospins to the surrounding host lattice, two successive transitions should occur. In 1D $S=\frac{1}{2}$ magnetic chain compounds, $CuGeO_3$ is a prominent example,[11] a structural phase transition into a statically dimerized structure is observed well above the magnetic ordering temperature. The nature of this spin-Peierls transition is purely quantum mechanical, in contrast to the present system. The pairing of neighboring antiferromagnetic $S=\frac{1}{2}$ spins to a $S=0$ singlet leads to an energy gap, thereby suppressing thermal spin fluctuations and lowering the ground-state energy.

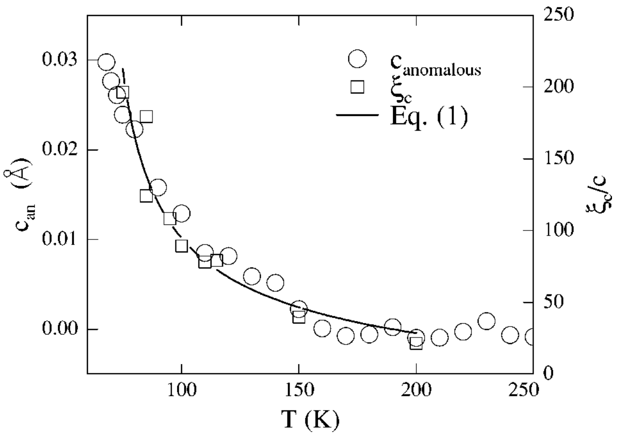


FIG. 7. Temperature dependence of the anomalous part of the lattice constant c (○) and the 1D correlation length ξ_c (□). The solid line is a fit of ξ_c after the 1D Ising model in Eq. (1).

Figure 7 shows the anomalous part of the temperature dependence of the 1D lattice parameter—i.e., the difference of the lattice parameter c [from Fig. 6(b)] to an extrapolated linear decrease with temperature, the correlation length ξ_c (Fig. 5), and the corresponding theoretical curve in the same plot. When choosing the right scaling factor, the anomalous part of c, c_{an}, and the correlation length ξ_c fall on the same curve and both are well described by the quasi-1D Ising model in Eq. (1). That suggests a coupling of the 1D fluctuations in the paraelectric regime to local strains. Such a coupling, however, is forbidden in the centrosymmetric space group $R\overline{3}$; the coefficients of the (direct) piezoelectric effect all vanish.[12] The peculiarity of the system at hand is the unusual large amplitude of the paraelectric fluctuations. Because of the reduced dimensionality of the interactions, the ferroelectric fluctuations are strongly enhanced. The anomaly of c occurs below about 170 K, where the correlation length already reaches about 40 lattice units,

$\xi_c(170\ \text{K})/c \simeq 40$ (see Fig. 5). Coupling via higher-order terms in susceptibility and strain, which become important due to the long-ranged correlations, then presumably leads to the observed electrostriction. This effect is likely to occur in other low-dimensional systems, but has not been reported before. On a microscopic scale, the increasing dynamic order—i.e., the orientation of the methanol molecules with respect to the 1D axis—presumably leads to a distortion of the (otherwise spherical) hydroquinone cages along c. The cages might be slightly stretched out in the 1D direction, leading to a small dilatation of the β-hydroquinone host lattice ($c_{an} > 0$). Considering the EDD interaction, only, and no such interaction between the guest molecules and the surrounding host lattice, a contraction along c ($c_{an} < 0$) would be energetically more favorable.

To prove that the anomaly of c is connected with the EDD interaction, we investigated methanol clathrates with methanol occupancies less than 100%. By lowering the fractional occupancy of the cavities, the interaction between the pseudospins is diluted and the transition into a dielectrically ordered state shifts to lower temperatures. Samples with a larger percentage x of filled cavities ($x > x_c \simeq 0.76$) show conventional ordering via a first-order phase transition into an antiferroelectrically ordered structure, whereas the others ($x < x_c$) freeze into dipolar glasses.[1–4] The temperature dependence of the 1D lattice parameter c for several filling degrees down to 50% is shown in Fig. 8. Comparing the structural data with the static dielectric constant for different degrees of occupation (see, e.g., Fig. 13 from Ref. 2), there is an analogous behavior: The anomalous behavior is most pronounced for the completely filled methanol clathrate. When reducing the filling, the starting point of deviation from linear decrease shifts to lower temperatures and broadens.

V. CONCLUSION

The methanol clathrate can serve as a model system for dielectric ordering and fluctuations and is conceptually close to magnetic spin systems. Because of the lattice symmetry and the peculiar property of the EDD interaction, the latter clathrate has quasi-1D dielectric properties. From analysis of the superlattice reflections in the dielectrically ordered phase, we can confirm the theoretically predicted 4:2 structure. The latter ground state can be calculated from Monte Carlo simulations and first principles, considering the EDD interactions between the guest molecules, only. We observe 1D and 3D critical scattering in the paraelectric regime in neutron and x-ray diffraction experiments. The temperature dependence of the correlation lengths ξ_c and ξ_a is well described by the corresponding quasi-1D Ising theory and agrees well with results from previous dielectric investigations, thereby confirming the microscopic picture of low-dimensional ordering and fluctuations of the methanol pseudospins in the hydroquinone cagework. The EDD interaction on a deformable lattice should be unstable against a dimerization of the dipoles in the 1D chains. At the dielectric ordering temperature T_c we find superlattice reflections that indicate a doubling of the unit cell in the 1D direction that can be interpreted as a static dimerization of the dipole chains. We find no sign of diffuse scattering in half-integer layers of l due to fluctuations of the dimerization already in the paraelectric regime. Below $T = 170$ K an anomaly in the temperature dependence of the 1D lattice parameter c occurs. The large amplitude of the 1D fluctuations in the paraelectric regime presumably leads to a coupling of the susceptibility to local strains and a piezoelectric effect in the otherwise centrosymmetric space group $R\overline{3}$. This effect is likely to be observed in low-dimensional interacting systems because fluctuations are strongly enhanced and rather long ranged.

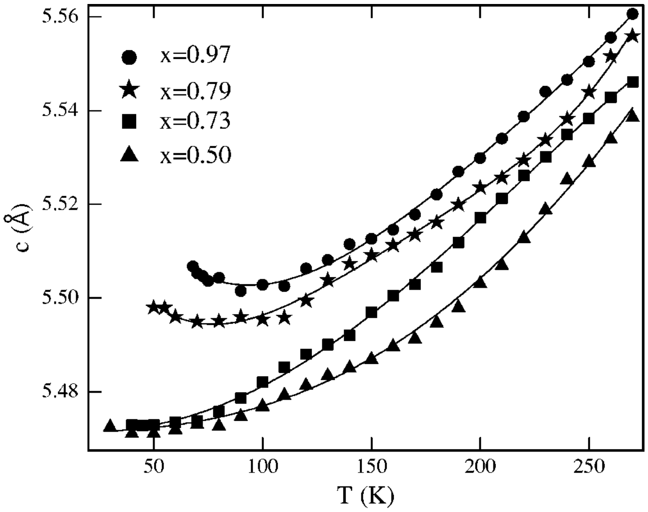


FIG. 8. Hexagonal lattice parameter c for the concentrations $x = 0.97$, $x = 0.79$, $x = 0.73$, and $x = 0.50$. At 270 K, the lattice parameters for all concentrations coincide to $c = 5.56$ Å. The curves are shifted vertically for clarity.

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