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A relation between dielectric response and potential structure in CsH_2PO_4

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Abstract

According to its relation to the dielectric response, the potential structure of CsH_2PO_4 can successfully be modelled either as a three-well or as a single-well potential. The deviation from the Curie–Weiss law of the dielectric response has an intimate relationship to the low central potential in the unit cells, while ordering P atoms are assumed to drive its ferroelectric phase transition.

CsH_2PO_4 (CDP) and CsD_2PO_4 (DCDP) [1] undergo ferroelectric phase transitions at about 150 and 270 K, respectively. Their dielectric constants ϵ do not follow the Curie–Weiss law, unusually [1–4]. This unusual phenomenon obviously suggests the existence of particular crystal structures in CDP and DCDP. In the past, the dielectric behaviour of CDP was discussed on the basis of a quasi-one-dimensional Ising model [4]. However, this model seems inadequate for describing a three-dimensional crystal. We believe that the dielectric behaviour of CDP should originate from some other mechanisms.

Numerous experimental results on CDP, e.g., Raman spectra [7], hyper-Raman spectra [8], the relaxation-type behaviour [9], and the x-ray structure analysis [10], can be explained by an order–disorder mechanism for the PO_4 and H ions. According to a double-well potential model recently proposed for $BaTiO_3$ [5,6], the dielectric constant is expected to follow a Curie–Weiss law in the paraelectric phase. Hence, in order to explain the severe deviations observed [1–4], one has to introduce another potential structure, which might lead to the unusual dielectric behaviour of CDP. This will be tackled in the present paper.

Let us first inspect information on the order–disorder structure of KD_2PO_4 (DKDP). For KH_2PO_4 (KDP) [11] and DKDP, the dielectric constant along the *c*-axis follows the Curie–Weiss law, and the dielectric constant along the *a*-axis is very small at any temperature. This means that the ferroelectric long-range force originates from the movement of ions along the *c*-axis according to our order–disorder model [5]. It has been observed experimentally that an order–disorder structure of the P atoms exists along the *c*-axis in DKDP [12]. The analysis of high-resolution neutron diffraction data [12] showed that the P-atom distribution can be modelled as disordered over three positions along the polar axis: a central site at the mean

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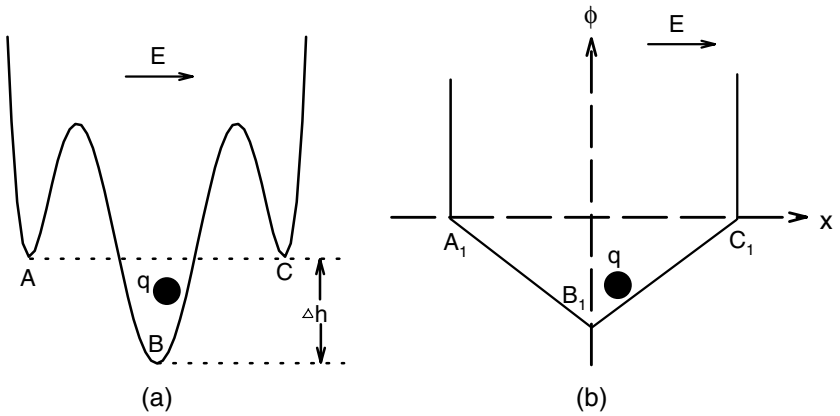

Figure 1. (a) Three-well and (b) single-well potential structures, as considered in the text.

position and two others symmetrically displaced. Thus it seems that a three-well potential model (TWPM) should be used in a phase-transition theory of DKDP and, probably, also of CDP.

In this paper, we use such a TWPM and show that it successfully explains the dielectric behaviour of CDP. Nevertheless, we also try to construct a single-well potential model (SWPM) in order to explain the same experimental results. Surprisingly, both the TWPM and the SWPM seem appropriate for describing the phase-transition behaviour of CDP satisfactorily. Physical reasons will be given for why the SWPM should in the end be preferred.

Consider a ferroelectric crystal in its paraelectric phase. The number of three-well potentials is N per unit volume. Figure 1(a) shows a three-well potential, where E is the applied field, q the effective electric charge of the off-centre ion, L the effective distance between the wells A and C. The occupation numbers of the wells A, B, and C are N_1, N_2, N_3, respectively, where $N_1 + N_2 + N_3 = N$. For $E = 0$, the depths of the wells A, B, and C are h_1, h_2, and h_1, respectively, where $\Delta h = h_1 - h_2$. The dipolar moment $q(L/2)$ is denoted by μ_0.

We first consider the response of noninteracting off-centre ions to the external field ($E \to 0$). For a noninteracting off-centre ion, we obtain the difference of the probabilities in the wells C and A:

$$\Delta n_0 = (N_3 - N_1)/N = (\mu_0/kT)2\mathrm{e}^{\frac{\Delta h}{kT}}/(1 + 2\mathrm{e}^{\frac{\Delta h}{kT}})E \tag{1}$$

and the polarization ($\Delta n_0 N\mu_0$). In order to calculate the additional field due to the induced polarization, we introduce a spherical coordinate system with the centre at the position B of the three-well potential, and the z-axis along the direction AC. Since the occupation probabilities of wells C and A change by $\pm 0.5\,\Delta n_0$, respectively, an additional field acting on one central off-centre ion is generated. It corresponds to different numbers of charges q occupying the wells C and A, respectively, and yields

$$\Delta E_1 = 0.5\,\Delta n_0 \left(\sum_{m=1}^{\infty} (1/4\pi\epsilon_0) q \cos\theta_m^+/(r_m^+)^2 - \sum_{m=1}^{\infty} (1/4\pi\epsilon_0) q \cos\theta_m^-/(r_m^-)^2 \right) \tag{2}$$

where r_m^+ (r_m^-) represents the distance of the neighbouring off-centre ions occupying the respective wells C (A), and θ_m^+ (θ_m^-) is their respective polar angle at the lattice site numbered m. Now we suppose that the interactions among the off-centre ions are turned on. In the lattice, the polarization, $\Delta n_0 N\mu_0$, modifies the local field from E to $E + \Delta E_1$. Consequently,

this modification changes the difference of the probabilities in the wells A and C again. From this feedback effect [5], we obtain

$$\Delta n_1 = (\mu_0/kT)2e^{\frac{\Delta h}{kT}}/(1+2e^{\frac{\Delta h}{kT}})(E+\Delta E_1) \tag{3}$$

where Δn_1 is the difference of the probabilities after the first feedback effect.

According the above definition, $E_{g0} = \Delta E_1/\Delta n_0$ is the ground-state internal field of ferroelectrics. In our spherical coordinate system, the well A of any three-well potential is centrosymmetric with respect to the well C of another three-well potential. Thus we have

$$E_{g0} = \sum_{m=1}^{\infty}(1/4\pi\epsilon_0)q\cos\theta_m^+/(r_m^+)^2 = -\sum_{m=1}^{\infty}(1/4\pi\epsilon_0)q\cos\theta_m^-/(r_m^-)^2 \tag{4}$$

and $\Delta n_1 = \Delta n_0 + \Delta n_0\, y$ with $y = (\mu_0 E_{g0}/kT)2e^{\frac{\Delta h}{kT}}/(1+2e^{\frac{\Delta h}{kT}})$. According to equation (4), equation (2) becomes $\Delta E_1 = 0.5n_0(E_{g0} - (-E_{g0})) = n_0 E_{g0}$. When all of the off-centre ions occupy position C, the internal field is E_{g0}. When all of the off-centre ions occupy position A, the internal field is $-E_{g0}$. Hence, charges in position A make a negative contribution to the field ΔE_1 according to thermodynamic statistics, while after a transition to position C these charges make a positive Coulombic contribution.

Now the difference of the probabilities in the wells C and A is Δn_1 in every three-well potential. Considering, again, the feedback effect, we obtain the difference after the second feedback effect:

$$\Delta n_2 = (\mu_0/kT)2e^{\frac{\Delta h}{kT}}/(1+2e^{\frac{\Delta h}{kT}})(E+\Delta n_1\, E_{g0}) = \Delta n_0\,(1+y+y^2). \tag{5}$$

Hence, after the ith feedback effect, we have

$$\Delta n_i = (\mu_0/kT)2e^{\frac{\Delta h}{kT}}/(1+2e^{\frac{\Delta h}{kT}})(E+\Delta n_{i-1}\, E_{g0}) = \Delta n_0\,(1+y+s+y^i)$$

and for $i \to \infty$ and $y < 1$, we obtain $\Delta n_\infty = \Delta n_0/(1-y)$.

The dielectric constant thus becomes

$$\epsilon = 1 + \frac{\Delta P}{\epsilon_0 E} = 1 + \frac{N\,\Delta n_\infty\,\mu_0}{\epsilon_0 E} = 1 + D\frac{2e^{\frac{\Delta h}{kT}}}{1+2e^{\frac{\Delta h}{kT}}}\Bigg/\left(T - \frac{\mu_0 E_{g0}}{k}\frac{2e^{\frac{\Delta h}{kT}}}{1+2e^{\frac{\Delta h}{kT}}}\right) \tag{6}$$

where ΔP is the polarization induced by the field, ϵ_0 the vacuum dielectric constant, and $D = N\mu_0^2/(\epsilon_0 k)$.

In equation (6), it is assumed that only off-centre ions in three-well potentials exist in the lattice. This is an oversimplification. In reality the off-centre ions are coupled to the other ions via the soft-mode eigenvector. Thus we know, in principle, the dipolar moments of the off-centre ion and other ions, respectively. We suppose that they are μ_{01} and μ_{02}. The fact that the movement of the off-centre ion occurs simultaneously with that of other ions means that all of these ions can be regarded as one equivalent dipole. Thus we deduce $\mu_0 = \mu_{01} + \mu_{02}$ in our model. Hence the ground-state internal field in the centre (point B) of the three-well potential, E_{g0}, now reads (in contrast to equation (4))

$$E_{g0} = \sum_{u=1}^{\infty}(1/4\pi\epsilon_0)q\cos\theta_u/r_u^2 \tag{7}$$

where u represents every ion except the ions in the cell centre, and r_u and θ_u are the spherical coordinates of the uth ion in the ground state.

In the paraelectric phase, μ_0 and E_{g0} are approximately constant. In the ferroelectric phase, the ordering force causes a ferroelectric distortion. Thus both the electric dipole μ and the ground-state internal field E_g are expected to be functions of P. In order to deduce adjustable parameters, we suppose $\mu = \mu_0$, and an even polynomial in P for the internal field:

$$E_g = E_{g0}\left(1 + \sum F_j P^j\right), \qquad j = 2, 4, 6\ldots. \tag{8}$$

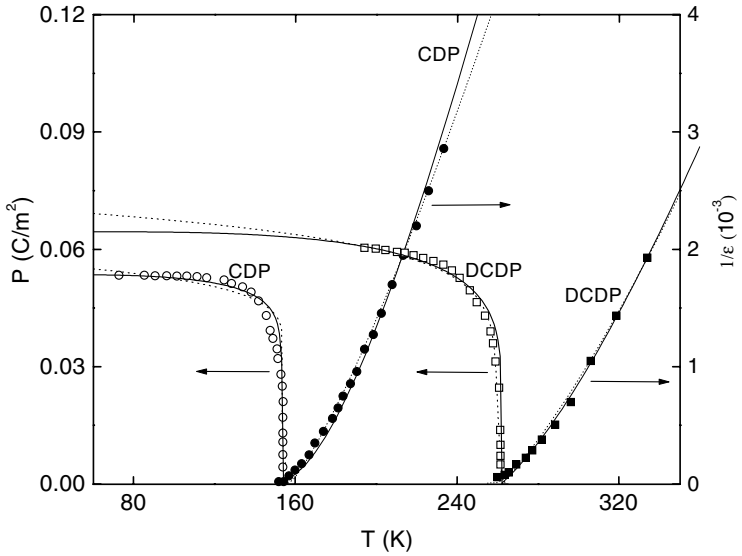

Figure 2. Temperature dependences of the reciprocal dielectric constant ϵ^{-1} for $T > T_c$ and the spontaneous polarization P for $T < T_c$. The circles and squares are the experimental data [1, 15] for CDP and DCDP respectively; the solid and dotted curves are the theoretical results from the TWPM and the SWPM, respectively (see the text).

Table 1. Parameter values for the TWPM for CDP and DCDP.

Material	ξ	μ_0 (e Å)	E_{g0} (10^9 V m^{-1})	Δh (10^{-2} eV)	F_2 (10^2 m^4 C^{-2})	F_4 (10^4 m^8 C^{-4})	F_6 (10^6 m^{12} C^{-6})
CDP	7	0.39	1.05	−1.90	0	3.00	6.00
DCDP	7	0.47	1.36	−2.95	0.27	1.20	0

The spontaneous polarization is

$$P_s = P(E=0) = N\mu_0\left(\mathrm{e}^{\frac{\Delta h + E_g P/(N\mu_0)}{kT}} - \mathrm{e}^{\frac{\Delta h - E_g P/(N\mu_0)}{kT}}\right)\Big/\left(\mathrm{e}^{\frac{\Delta h + E_g P/(N\mu_0)}{kT}} + 1 + \mathrm{e}^{\frac{\Delta h - E_g P/(N\mu_0)}{kT}}\right). \tag{9}$$

In order to account for the well-known correlation effects between the ionic displacements [13], we introduce another parameter $\xi > 1$ into equation (6), which then reads

$$\epsilon = 1 + \frac{\xi\,\Delta P}{\epsilon_0 E} = 1 + \xi D \frac{2\mathrm{e}^{\frac{\Delta h}{kT}}}{1 + 2\mathrm{e}^{\frac{\Delta h}{kT}}} \Big/ \left(T - \frac{\mu_0 E_{g0}}{k}\frac{2\mathrm{e}^{\frac{\Delta h}{kT}}}{1 + 2\mathrm{e}^{\frac{\Delta h}{kT}}}\right). \tag{10}$$

By adjusting μ_0, Δh, E_{g0}, $F_{2,4,6}$, and ξ, we obtain best-fitted theoretical results to be compared with the experimental temperature dependence of ϵ^{-1} and P for CDP and DCDP [1, 15] in figure 2. Obviously, good agreement is achieved. Table 1 shows the fitting parameter values for CDP and DCDP in the TWPM.

In figure 2, the stable state of the CDP crystal jumps discontinuously from $P \neq 0$ to $P = 0$ at T_c. Our calculation shows that the polarization is 0.02 C m^{-2} at the Curie point. Thus CDP exhibits a faint first-order phase transition. In [14], the ferroelectric phase transition of CDP was suggested to be of first order, though being close to a second-order one. In figure 2, the DCDP crystal exhibits a second-order phase transition.

Now we explain the parameter ξ. The saturated polarization P_s is 5.3 μC cm^{-2} in CDP [1]. This is equivalent to $\mu_0 = 0.39\,e$ Å. However, by using equation (6) one obtains $\mu_0 = 1.03\,e$ Å

for CDP when fitting to the experimental dielectric behaviour [15]. Thus there is an obvious difference between the former and the latter ones. Such a problem also exists in other models. In the quasi-one-dimensional model [3], the Curie constant was supposed as an independent fitting parameter to avoid this problem. In the present work, we use the picture of dipole correlation to overcome the difficulty in mean-field theory.

For $SrTiO_3$ [16], it was suggested that the atomic positions in adjacent cells are correlated, and the dipole correlations have an adjustment for the dielectric behaviour of $SrTiO_3$. In our model, the factor ξ in equation (9) is an expression characterizing the dipole correlation. In the paraelectric phase of CDP, the average-field theory, equation (6), shows that a polarization is induced by the electric field E. Thus $\Delta N = \Delta P/\mu_0$ additional dipoles will be oriented along AC in the lattice. Now we consider an arbitrary one among them. By dipolar interaction the dipole can cause the reorientation of most of the neighbouring dipoles, and give rise to a cluster or a chain. We suppose that every cluster (chain) includes ξ dipoles. Thus $\xi\,\Delta N$ dipoles will orient along AC under the field E. Consequently, we can obtain equation (9). Table 1 yields $\xi = 7$ for CDP and DCDP. Thus the size of a possible cluster should be two cells, approximately, if its shape is spherical.

In table 1, the values of Δh for CDP and DCDP are negative. Hence, we can predict that the probability in the central well is larger than $1/3$ for off-centre ions in the paraelectric phase. Furthermore, we remark that the order of the depth of our potential well is 10^{-2} eV, agreeing with values generally found for multi-site potentials [17].

Also in DKDP [12], the P-atom distribution can be modelled as disordered over three positions along the polar axis. Consequently its dielectric constant should deviate from the Curie–Weiss law according to equations (6) or (9). However, such a deviation has not been found in past experiments. Thus it is desirable to understand the internal mechanism.

Reference [2] shows that the dielectric data of CDP can be fitted to the expression

$$\epsilon = C'/(T - T_0)^{\gamma} \tag{11}$$

where $\gamma = 1.31 \pm 0.1$. If we change the value of Δh of CDP and use the other parameters in table 1, we obtain a relationship between γ and Δh as shown in figure 3. Obviously γ decreases with increasing Δh for $\Delta h \leqslant 0$. According to equation (9), we obtain $\gamma = 1$ for $0 < \Delta h < \infty$. This means that we cannot find a deviation from the Curie–Weiss law in an experiment when $\Delta h \geqslant 0$. For the three-well potential of DKDP, reference [12] showed that the population of the two displaced sites is $\geqslant 40\%$ in each, leaving only $\leqslant 20\%$ at the central site. Thus the deviation from the Curie–Weiss law should be very slight for DKDP.

Alternatively to the TWPM we have also used a SWPM in order to explain the ferroelectric phase transition of CDP.

Consider a ferroelectric crystal in the paraelectric phase. The number of unit cells is N per unit volume. Figure 1(b) shows the single-well potential in a cell, where q is the effective electric charge of the off-centre ion, and L_1 is the distance between the point A_1 and point C_1. The dipolar moment $q(L_1/2)$ is denoted by μ_1. We build an x–ϕ coordinate system in figure 1(b). At the points A_1 and C_1, the potential is zero. At the point B_1, we suppose that the negative potential is h. The local field acting on the off-centre ion is $E_{loc} = E + [E_{g1}/(N\mu_1)]P$, where E_{g1} is the ground-state internal field. Thus the potential ϕ in the single well is

$$\phi_- = (2h/L_1)x + h - qxE_{loc} \qquad (-0.5L_1 < x \leqslant 0) \tag{12}$$

$$\phi_+ = -(2h/L_1)x + h - qxE_{loc} \qquad (0 \leqslant x < 0.5L_1). \tag{13}$$

From this potential structure, we get theoretical functions of ϵ^{-1} and P versus T for CDP and DCDP (dashed curves in figure 2) according to a simple thermodynamic calculation. In

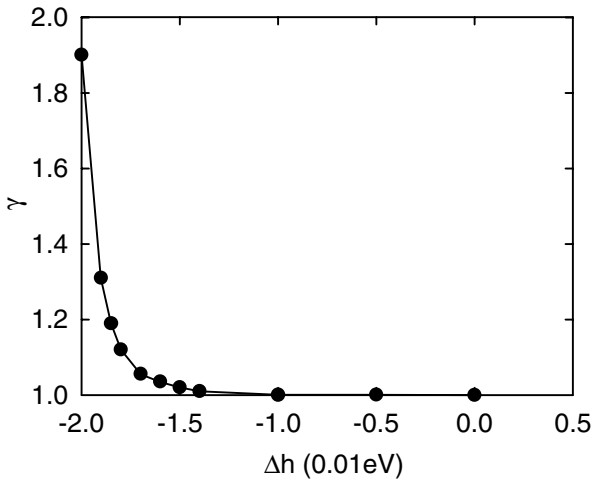

Figure 3. γ versus Δh for CDP.

Table 2. Parameter values for the SWPM for CDP and DCDP.

Material	ξ	μ_1 (e Å)	E_{g1} (10^9 V m^{-1})	h (10^{-2} eV)	F_2 (10^2 m^4 C^{-2})	F_4 (10^4 m^8 C^{-4})	F_6 (10^6 m^{12} C^{-6})
CDP	16	0.42	2.03	−3.39	0	7.70	4.00
DCDP	12	0.52	2.75	−5.69	0.20	2.30	0

figure 2, the theoretical curves are in good agreement with the experimental points [1, 15]. Table 2 shows some parameter values of CDP and DCDP within the framework of the SWPM.

In the above, both the TWPM and SWPM explain the ferroelectric phase transitions of CDP and DCDP well. It is not accidental that two different potential structures can explain the same experimental phenomena. In the paraelectric phase, the TWPM with $\Delta h < 0$ and the SWPM with $h < 0$ have a common character: off-centre ions tend to stay at the centres of unit cells because of the low central potential. The particular dielectric response in CDP originates primarily from the central potential minima. When the temperature decreases to T_c from a high temperature, off-centre ions tend to move to the centres of cells gradually. This means a rapid decrease of the effective dipolar moment in the cells. Consequently, such a decrease leads to the deviation from the Curie–Weiss law in the dielectric response.

However, the very existence of three-well potential structure in real crystals seems rather improbable in view of the conventional distance dependences of Coulombic attraction and repulsion. On the other hand, there are examples where a single-well potential may give rise to a well-defined phase transition, e.g., in $BaTiO_3$ under high pressure [17, 18]. Hence, we are inclined to believe that a single-well potential structure also leads to the unusual dielectric behaviour of CDP. Presumably, it is very difficult to find a three-well potential structure in real ferroelectrics. This artificial potential structure is obviously useful only in a theoretical simulation. For DKDP, the proposed [12] TWPM with a positive Δh is equivalent to a double-well potential model with two shallow wells. In our opinion the latter is easier to accept for actual ferroelectrics.

Let us finally comment on the mechanism of ferroelectric phase transition in the KDP family. The widely accepted theory involves the ordering of H atoms driving a displacive transition in the heavy-atom structure. In this traditional model, a small ion drives the

displacement of a big ion. This supposition seems somewhat artificial. In fact, the dielectric constant along the *c*-axis follows the Curie–Weiss law for KDP, while the dielectric constant along the *a*-axis is very small even at T_c [11]. The [001] signal field in dielectric measurements cannot induce the movement of H atoms along [100]. Thus the ferroelectric long-range force should originate from the movement of ions along the *c*-axis according to the our models. It has been observed experimentally that an order–disorder structure of the P atoms exists along the *c*-axis in DKDP [12]. Since our present models evidence the important role of P atoms in ferroelectric phase transitions, we argue that P-atom ordering might also be of relevance for the ferroelectric phase transition in the KDP family.

In summary, the potential of the P atoms in CDP and DCDP can be modelled by a three-well or by a single-well structure. P-atom ordering drives the ferroelectric phase transitions; the observed deviations of the dielectric response from the Curie–Weiss law originate from the deep central potential wells.

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References

[1] Deguchi K, Okaue E and Nakamura E 1982 *J. Phys. Soc. Japan* **51** 3569
[2] Blinc R, Žekš B, Levstik A, Filipič C, Slak J, Burgar M and Zupančič I 1979 *Phys. Rev. Lett.* **43** 231
[3] Kojyo N and Onodera Y 1988 *J. Phys. Soc. Japan* **57** 4391
[4] Žumer S 1980 *Phys. Rev.* B **21** 1298
[5] Zhang L and Zhong W L 1999 *Phys. Lett.* A **260** 279
[6] Zhang L, Zhong W L and Kleemann W 2000 *Phys. Lett.* A **276** 162
[7] Wada M, Sawada A and Ishibashi Y 1979 *J. Phys. Soc. Japan* **47** 1571
[8] Shin S, Ishida A, Yamakami T, Fujimura T and Ishigame M 1987 *Phys. Rev.* B **35** 4455
[9] Deguchi K, Nakamura E, Okaue E and Aramaki N 1982 *J. Phys. Soc. Japan* **51** 3575
[10] Itoh K, Hagiwara T and Nakamura E 1983 *J. Phys. Soc. Japan* **52** 2626
[11] Busch G 1938 *Helv. Phys. Acta* **11** 269
[12] McMahon M I, Nelmes R J, Piltz R O and Kuhs W F 1990 *Europhys. Lett.* **13** 143
[13] Comes R, Lambert M and Guinier A 1970 *J. Phys. Soc. Japan* **28** 195
[14] Levstik A, Blinc R, Kadaba P, Čižikow S, Levstik I and Filipič C 1975 *Solid State Commun.* **16** 1339
[15] Imai K, Ishida H and Seiyama T 1985 *Japan. J. Appl. Phys. Suppl.* **24** 580
[16] Hemberger J, Lunkenheimer P, Viana R, Böhmer R and Loidl A 1995 *Phys. Rev.* B **52** 13 159
[17] Cohen R E and Krakauer H 1990 *Phys. Rev.* B **42** 6416
[18] Ishidate T, Abe S, Takahashi H and Môri N 1997 *Phys. Rev. Lett.* **78** 2397