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Cluster Approximations for Order-Disorder–Type Hydrogen-Bonded Ferroelectrics. II. Application to KH_2PO_4

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A four-particle cluster approximation is worked out for the free energy of ferroelectric KH_2PO_4, taking into account the overlap of the protonic wave functions between the two sites in a hydrogen bond as well as short-range and long-range forces and a part of the proton-lattice interactions. The approximation reduces in the classical limit to the Slater-Takagi-Senko-Uehling treatment of the order-disorder transition in this crystal. It is shown that the changes in the Curie temperature, the spontaneous polarization, and the domain-wall mobility on deuteration can be derived from the decrease in the hydrogen overlap between the two sites and the lowering of the zero-point energy in an anharmonic potential.

I. INTRODUCTION

In the preceding paper,[1] a high-temperature cluster-expansion series has been derived for a simplified partition function of order-disorder–type hydrogen-bonded ferroelectric crystals. Here we wish to refine this model and to apply it to the case of the ferroelectric transition in KH_2PO_4.[2]

The basic experimental facts about the ferroelectric transition in KH_2PO_4 may be summarized as follows: The presence of a small but definite thermal hysteresis[3] in the dielectric constant near the critical point ($T_c = 121°K$) in KH_2PO_4, and the coexistence of the para- and ferroelectric phases in the vicinity of $T_c = 221°K$ in KD_2PO_4 as shown by the deuteron magnetic resonance data,[4] seem to prove that the ferroelectric transitions in these two crystals are of first order, though they are very close to second order. This statement is supported by the fact that in KD_2PO_4 the smallest nonzero polarization reported[5] is already about 30% of its full value. Neutron and x-ray diffractions have further shown that the ferroelectric transition in KH_2PO_4 is accompanied by an ordering[6] of protons, which are disordered in the paraelectric phase, as well as by large displacements[6] of the potassium and phosphorus ions, indicating a strong proton-lattice coupling. Direct evidence for deuteron motion from one off-center position in the hydrogen bonds to the other has been obtained from deuteron resonance relaxation-time measurements[7] in the paraelectric phase.

The rather large isotope effects in the Curie temperature,[2] in the shape of the polarization curve,[8] and in the saturation value of the spontaneous polarization ($P_{s,\mathrm{D}}$ is for about 20% larger than $P_{s,\mathrm{H}}$) on replacing hydrogen by deuterium indicated the role of the hydrogen atoms in the transition. The most striking isotope effect, however, is the big difference[9] in domain-wall dynamics between KH_2PO_4 and KD_2PO_4. The domain-wall mobility in KD_2PO_4 is about six orders of magnitude lower than in KH_2PO_4, thus reflecting the large difference between the proton and deuteron mobilities in the hydrogen bonds.

The model theories of the ferroelectric effect in KH_2PO_4 and KD_2PO_4 may be divided into two categories. The theories introduced by Slater[10] and refined by Takagi,[11] Senko,[12] and Uehling and coworkers,[13] concentrate on the short-range near-neighbor interaction of protons around a given PO_4 group. In the modifications of Senko[12] and Uehling,[13] long-range forces have also been included. So far, however, these theories neglect quantum effects, and in particular the finite overlap of the protonic wave functions between the two sites in a hydrogen bond. Nevertheless, they yield a relatively good description of most experimental facts. There are, however, two notable exceptions: a consistently too large transition entropy is predicted,[13] and a really satisfactory explanation of the observed isotope effects cannot be given.

The molecular-field theories,[14–16] on the other hand, concentrate on long-range forces and have no difficulties in taking into account quantum effects. Thus they seem to provide a basis for the understanding of the isotope effects. However, because of the neglect of short-range

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[1] R. Blinc and S. Svetina, preceding paper, Phys. Rev. **147**, 423 (1966).

[2] See for example: W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4; F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

[3] P. P. Craig, Phys. Letters **20**, 140 (1966).

[4] L. J. Bjorkstam (private communication).

[5] B. Zwicker and P. Scherrer, Helv. Phys. Acta **17**, 346 (1944).

[6] G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **230**, 359 (1955); B. C. Frazer and R. Pepinsky, Acta Cryst. **6**, 273 (1953).

[7] V. H. Schmidt and E. A. Uehling, Phys. Rev. **126**, 477 (1962).

[8] W. Bantle, Helv. Phys. Acta **15**, 373 (1942).

[9] J. L. Bjorkstam (private communication).

[10] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[11] Y. Takagi, J. Phys. Soc. Japan **3**, 271 (1948).

[12] M. E. Senko, Phys. Rev. **121**, 1599 (1961).

[13] H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. **133**, A165 (1964).

[14] W. P. Mason, *Piezoelectric Crystals* (D. Van Nostrand, Inc., New York, 1950), Chap. XI.

[15] J. Pirenne, Physica **15**, 1019 (1943); **21**, 219 (1955).

[16] R. Blinc, J. Phys. Chem. Solids **13**, 204 (1960).

correlations, they fail in some other respects and are, for instance, unable to give even an approximately correct description of the shape of the spontaneous polarization curve.

Both theories have so far assumed that the protons move in a rigid-lattice potential and have thus neglected proton-lattice coupling.[17]

Here we wish to present a high-temperature treatment which considers both short-range and long-range forces, the finite overlap of the protonic wave functions between the two sites in a given hydrogen bond, and a part of the proton-lattice coupling. The approximation, which we discuss, is based on the cluster expansion of the partition function of an order-disorder–type hydrogen-bonded ferroelectric crystal, derived in the preceding paper.[1] The interactions between the four protons surrounding a given PO_4 group are taken into account exactly and the rest is replaced by a molecular field, which is determined self-consistently. An attempt is made to account for the effect of one proton on the tunneling integral of another. The present approximation reduces in the classical limit to the Senko-Uehling modification of the Slater theory. It should be noted that in contrast to the case discussed in part I, we are dealing in KH_2PO_4 with four-body forces, and the 4-particle cluster is thus the smallest cluster appropriate for the discussion of short-range effects, as the 2-particle cluster was the smallest appropriate cluster in the case of two-body forces.

II. THE HAMILTONIAN

The Hamiltonian of our problem[18] can be written in the following form:

$$H=H_p+H_L+H_I\,, \tag{1}$$

where H_p is the full many-body proton Hamiltonian in a rigid lattice, $H_L=\sum_k \hbar\omega_k a_k^\dagger a_k$ is the Hamiltonian of the lattice vibrations in the absence of proton motion, and $H_I=\sum_k(V_k a_k+V_k^\dagger a_k^\dagger)$ stands for the proton-lattice interaction.[17] The operators V_k and $V_k^\dagger$ operate on proton variables,[17] whereas $a_k^\dagger$ and a_k are creation and annihilation operators for phonons with energy $\hbar\omega_k$.

The proton self-energy Hamiltonian H_p can be written as a sum of a tunneling term H_t, describing the motion of isolated protons between the two possible sites in a given hydrogen bond; a short-range term $H_{\rm SR}$, which accounts for the interactions of protons surrounding a given PO_4 group; and a long-range term $H_{\rm LR}$, which describes the interaction between those proton sites which do not belong to the same PO_4 ion:

$$H_p=H_t+H_{\rm SR}+H_{\rm LR}\,, \tag{2}$$

with

$$H_t=-\tfrac{1}{2}\Gamma\sum_{i=1}^{N}\sum_{j=1}^{4}(s_{ij}^{+}+s_{ij}^{-})\,, \tag{3}$$

$$H_{\rm SR}=\sum_{i=1}^{N}\sum_{k_1,k_2,k_3,k_4=\uparrow,\downarrow}\epsilon_{k_1k_2k_3k_4}n_{i1k_1}n_{i2k_2}n_{i3k_3}n_{i4k_4}\,, \tag{4}$$

and

$$H_{\rm LR}=-\tfrac{1}{4}\sum_{i,i'=1}^{N}\sum_{j,j'=1}^{4}J_{ii'jj'}(n_{ij\uparrow}-n_{ij\downarrow})(n_{i'j'\uparrow}-n_{i'j'\downarrow})\,, \tag{5}$$

where the representation of localized particles is used, and the summation extends over all N PO_4 groups in the crystal as well as over all four hydrogen sites near a given PO_4 group.

Here s_{ij}^{+} and s_{ij}^{-} are again the proton "jump" operators

$$s_{ij}^{+}=b_{ij\uparrow}^{\dagger}b_{ij\downarrow}\,,\qquad s_{ij}^{-}=b_{ij\downarrow}^{\dagger}b_{ij\uparrow}\,, \tag{6}$$

and the n_{ijk} are the proton "number" operators:

$$n_{ijk}=b_{ijk}^{\dagger}b_{ijk}\quad(k=\uparrow,\downarrow) \tag{7}$$

$b_{ijk}^{\dagger}$ and b_{ijk} being the proton creation and annihilation operators[1]: $\psi_{ijk}=b_{ijk}^{\dagger}|0\rangle$. The sign ↑ or ↓ means that the proton is created or annihilated near the upper or lower oxygen atom, respectively, of a given PO_4 group, where the expression "upper" or "lower" refers to the direction of the ferrolectric z axis. The definitions of the tunneling integral Γ_{ij} and the interaction parameter $J_{ii'jj'}$ are the same as in Ref. 1, and the $\epsilon_{k_1k_2k_3k_4}$ are the Slater-Takagi energies of the different proton configurations around a given PO_4 ion, i.e., the matrix elements

$$\langle\prod_{j=1}^{4}\psi_{ijk_j}|H_{{\rm PO}_4,i}^{*}|\prod_{j=1}^{4}\psi_{ijk_j}\rangle\,, \tag{8}$$

where $H_{{\rm PO}_4,i}^{*}$ is the complete Hamiltonian of a given PO_4 group and the integration is done over all internal coordinates of a given PO_4 ion. Higher vibrational states of the proton are not included and only the leading term in the proton overlap integral is taken into account.

The short-range interaction term for a given PO_4 ion can be written as a sum of terms describing states with zero, one, two, three, and four protons close to a given PO_4 ion:

$$H_{{\rm SR},i}=\epsilon_0N_{i0}+\epsilon_1N_{i1}+\epsilon_2'N_{i2}'+\epsilon_2(N_{i2}-N_{i2}')+\epsilon_3N_{i3}+\epsilon_4N_{i4}\,, \tag{9}$$

where

$$\begin{aligned}
N_{i0}&=N_i(\Box)\,,\\
N_{i1}&=N_i({}^{\cdot}\Box)+N_i(\Box{}^{\cdot})+N_i(.\Box)+N_i(\Box.)\,,\\
N_{i2}'&=N_i(:\Box)+N_i({}^{\cdot}\Box.)=N_i(.\Box{}^{\cdot})+N_i(\Box:)\,,\\
N_{i2}&=N_{i2}'+N_i({}^{\cdot}\Box{}^{\cdot})+N_i(.\Box.)\,,\\
N_{i3}&=N_i(:\Box{}^{\cdot})+N_i({}^{\cdot}\Box:)+N_i(.\Box:)+N_i(:\Box.)\,,
\end{aligned} \tag{10}$$

and

$$N_{i4}=N_i(:\Box:)\,,$$

with the square indices ${}^{1}_{3}\Box^{2}_{4}$ indicating which particular configuration of the four protons around a PO_4 ion is occupied. For instance, $N_i(\Box:)$ stands for the operator

$$N_i(\Box:)=n_{i1\downarrow}n_{i2\uparrow}n_{i3\uparrow}n_{i4\downarrow}\,. \tag{11}$$

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[17] R. Blinc and M. Ribarič, Phys. Rev. **130**, 1816 (1963).

[18] R. Blinc and S. Svetina, Phys. Letters **15**, 119 (1965).

Using the condition that there is one and only one proton in a given hydrogen bond,

$$n_{ij\uparrow}+n_{ij\downarrow}=1, \tag{12}$$

and summing over all PO_4 groups, we may up to a constant term rewrite H_{SR} in the following simpler form:

$$H_{SR}=\sum_{i=1}^{N}\left[w_1N_{i0}+w(N_{i1}+N_{i3})+\epsilon N_2'+w_2N_{i4}\right], \tag{13}$$

where

$$\begin{aligned} w&=\tfrac{1}{2}(\epsilon_1+\epsilon_3)-\epsilon_2,\\ \epsilon&=\epsilon_2'-\epsilon_2,\\ w_1&=\epsilon_0-\epsilon_1+\epsilon_3-\epsilon_2,\\ w_2&=\epsilon_4+\epsilon_1-\epsilon_3-\epsilon_2. \end{aligned} \tag{14}$$

As the configurations with no protons or with four protons near a given PO_4 group should have rather high excitation energies and should therefore play only a minor role in the ferroelectric behavior of KH_2PO_4-type crystals, we shall for the sake of simplicity assume that $w_2=w_1$, so that H_{SR} will depend only on 3 parameters: w_1, w, and ϵ.

As shown in Appendix A and Ref. 17, a part of the proton-lattice interaction can be taken into account by a renormalization of the proton tunneling integral and the proton-proton interaction parameters. In the following we shall assume that this has already been done and that all our parameters are renormalized.

Another part of the proton-lattice interaction (Appendix A) can be accounted for in our approximation by adding a molecular-field term,

$$H_{p-L-p}=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{4}\left[-\gamma_0\langle p\rangle(n_{ij\uparrow}-n_{ij\downarrow})+\tfrac{1}{2}\gamma_0\langle p\rangle^2\right], \tag{15}$$

to the long-range proton-proton interaction Hamiltonian. Here $\langle p\rangle$ is the mean value of the reduced hydrogen-bond dipole-moment operator

$$\langle p\rangle=\langle n_{ij\uparrow}-n_{ij\downarrow}\rangle, \tag{16}$$

and γ_0 is a proportionality constant. In view of the approximation in which we are going to work, we shall neglect other effects of the proton-lattice interactions (for instance, their dependence on the hydrogen tunneling frequency).

We shall use the technique developed in Ref. 1 and shall investigate the free energy of our crystal in a four-particle cluster approximation, as this is the lowest approximation in which we can account for the specific properties of KH_2PO_4-type crystal lattices. Thus we shall take into account the short-range interactions of the four protons surrounding a given PO_4 group exactly, and the rest only on the average. Specifically, we shall replace the long-range interaction term (5) with a molecular-field term, similar to expression (15).

The final expression for our approximate Hamiltonian is thus, up to constant terms,

$$\begin{aligned} H=\sum_{i=1}^{N}\Big\{-\tfrac{1}{2}\Gamma\sum_{j=1}^{4}(s_{ij}^{+}+s_{ij}^{-})\\ +\left[w_1(N_{i0}+N_{i4})+w(N_{i1}+N_{i3})+\epsilon N_{i2}'\right]\\ +\tfrac{1}{2}\sum_{j=1}^{4}\left[-\gamma\langle p\rangle(n_{ij\uparrow}-n_{ij\downarrow})+\tfrac{1}{2}\gamma\langle p\rangle^2\right]\Big\}, \end{aligned} \tag{17}$$

where it should be remembered that the $N_{i\sigma}(\sigma=0, 1, \cdots, 4)$ are four-particle operators and that γ is now a constant describing all long-range effects, i.e., direct proton-proton coupling as well as coupling through the lattice vibrations in a molecular-field approximation.

III. FOUR-PARTICLE-CLUSTER APPROXIMATION

Let us now divide our Hamiltonian (17) into an unperturbed part H_0 and a perturbation term H', which is equal to the difference between the total and the unperturbed Hamiltonian:

$$H=H_0+H', \tag{18}$$

with

$$\begin{aligned} H_0=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{4}\left[-(\Gamma-\eta)(s_{ij}^{+}+s_{ij}^{-})\right.\\ \left.-(\gamma\langle p\rangle+\Delta)(n_{ij\uparrow}-n_{ij\downarrow})\right]+N\gamma\langle p\rangle^2, \end{aligned} \tag{19}$$

and

$$\begin{aligned} H'=H-H_0=\sum_{i=1}^{N}\Big\{\tfrac{1}{2}\sum_{j=1}^{4}\left[-\eta(s_{ij}^{+}+s_{ij}^{-})+\Delta(n_{ij\uparrow}-n_{ij\downarrow})\right]\\ +\left[w_1(N_{i0}+N_{i4})+w(N_{i1}+N_{i3})+\epsilon N_{i2}'\right]\Big\}=\sum_{i=1}^{N}Q_i. \end{aligned} \tag{20}$$

In the unperturbed Hamiltonian, we treat each proton as moving in the average field of its neighbors. In addition to the long-range field $\gamma\langle p\rangle$, we describe the average interaction of a proton with its neighbors by two independent fields: an effective field Δ, which makes the potential well in the H bond asymmetric, and a field η which takes into account the effects of other protons on the tunneling integral of a given proton, and thus represents the change in the effective tunneling integral due to proton correlations. It should be pointed out that η is nonzero even above T_c and, in fact, goes towards zero only if $T\gg T_c$, i.e., if the different protons are in fact moving as independent particles.

Both Δ and η are obtained by a minimization of the approximately determined free energy:

$$F=F_0+F', \tag{21}$$

where

$$F_0=-kT\ln \mathrm{Tr}e^{-\beta H_0},\quad \beta=1/kT, \tag{22}$$

and

$$\begin{aligned} F'=F-F_0=-kT\ln\frac{\mathrm{Tr}e^{-\beta H}}{\mathrm{Tr}e^{-\beta H_0}}=-kT\ln \mathrm{Tr}\rho_0e^{-\beta V}\\ =-kT\ln\langle e^{-\beta V}\rangle, \end{aligned} \tag{23}$$

with ρ_0 being the unperturbed density matrix

$$\rho_0 = e^{-\beta H_0}/\mathrm{Tr}e^{-\beta H_0}, \tag{24}$$

and the operator V being defined, as in Ref. 1, by

$$e^{-\beta(H_0+H')} = e^{-\beta H_0}e^{-\beta V}. \tag{25}$$

Using the same procedure as in Ref. 1 and remembering that the link Q_i we are using is in fact a four-particle cluster, we can express V as

$$V = \sum_{i=1}^{N} Q_i' \tag{26}$$

with

$$Q_i' = Q_i + \frac{\beta}{2!}[H_0, Q_i] + \frac{\beta^2}{3!}[H_0,[H_0,Q_i]] + \cdots. \tag{27}$$

In the four-particle-cluster approximation, we then obtain[1] the correction to the unperturbed free energy as:

$$\begin{aligned} F_{(4)}' &= -kT \sum_{i=1}^{N} \ln \mathrm{Tr}\rho_0 e^{-\beta Q_i'} \\ &= -kTN[\ln \mathrm{Tr}e^{-\beta H_{(4)}} - 4 \ln \mathrm{Tr}e^{-\beta H_{(1)}}], \end{aligned} \tag{28}$$

where the four-particle-cluster Hamiltonian $H_{(4)}$ is defined as

$$\begin{aligned} H_{(4)} = \sum_{j=1}^{4} [&-(\Gamma - \tfrac{1}{2}\eta)(s_{ij}^{+} + s_{ij}^{-}) \\ &-(\gamma\langle p\rangle + \tfrac{1}{2}\Delta)(n_{ij\uparrow} - n_{ij\downarrow})] \\ &+[w_1(N_{i0}+N_{i4}) + w(N_{i1}+N_{i3}) + \epsilon N_{i2}'], \end{aligned} \tag{29}$$

and the single-particle-cluster Hamiltonian as

$$H_{(1)} = -(\Gamma - \eta)(s_{ij}^{+} + s_{ij}^{-}) - (\gamma\langle p\rangle + \Delta)(n_{ij\uparrow} - n_{ij\downarrow}). \tag{30}$$

The total free energy is in this approximation given by

$$\begin{aligned} F_{(4)} = -kTN(&\ln \mathrm{Tr}e^{-\beta H_{(4)}} \\ &- 2 \ln \mathrm{Tr}e^{-\beta H_{(1)}}) + N\gamma\langle p\rangle^2. \end{aligned} \tag{31}$$

Minimizing (31) with respect to Δ and η,

$$\partial F_{(4)}/\partial\Delta = 0, \quad \partial F_{(4)}/\partial\eta = 0, \tag{32}$$

we find that the two fields η and Δ are determined by solutions of the following equations:

$$\mathrm{Tr}(n_{ij\uparrow} - n_{ij\downarrow})\rho_{(1)} = \tfrac{1}{4}\,\mathrm{Tr} \sum_{j=1}^{4} (n_{ij\uparrow} - n_{ij\downarrow})\rho_{(4)}, \tag{33}$$

$$\mathrm{Tr}(s_{ij}^{+} + s_{ij}^{-})\rho_{(1)} = \tfrac{1}{4}\,\mathrm{Tr} \sum_{j=1}^{4} (s_{ij}^{+} + s_{ij}^{-})\rho_{(4)}, \tag{34}$$

where

$$\rho_{(1)} = e^{-\beta H_{(1)}}/\mathrm{Tr}e^{-\beta H_{(1)}} \tag{35}$$

and

$$\rho_{(4)} = e^{-\beta H_{(4)}}/\mathrm{Tr}e^{-\beta H_{(4)}}. \tag{36}$$

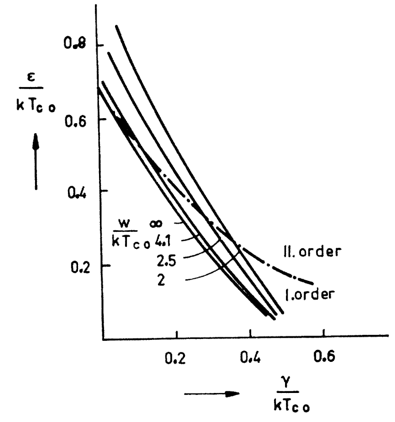

FIG. 1. Critical values of ϵ, w, and γ yielding a phase transition in the classical limit.

Again we see that the minimization of the free energy with respect to Δ and η is equivalent to the requirement that the thermal expectation values of the reduced H-bond dipole moment operator $p_{ij} = n_{ij\uparrow} - n_{ij\downarrow}$ and the proton jump operator $s_{ij} = s_{ij}^{+} + s_{ij}^{-}$ be the same whether determined from the four- or from the single-particle density matrix. The explicit form of Eqs. (33) and (34) is rather clumsy and is presented in Appendix B. However, once we know Δ and η as functions of temperature, we also know the temperature dependence of the free energy in this approximation, and can deduce all polarization properties of our system.

IV. RESULTS

Let us first investigate our approximation in the classical limit, where the potential barrier separating the two minima in a hydrogen bond is supposed to be infinite. As discussed below, such a model is probably a rather good approximation for KD_2PO_4, though not for KH_2PO_4. In this case, Γ and η are identically zero, and the energy matrix corresponding to the 4-particle-cluster Hamiltonian is already in diagonal form. By an elimination of Δ from (33) and $\langle p\rangle = \mathrm{Tr}(n_{i\uparrow} - n_{i\downarrow})\rho_{(1)}$ we can obtain a consistency equation for the spontaneous polarization:

$$\langle p\rangle = \frac{2e^{-\beta w}\sinh x + \sinh 2x}{e^{-\beta w_1} + 4e^{-\beta w}\cosh x + \cosh 2x + 2e^{-\beta\epsilon}}, \tag{37}$$

with

$$x = \tfrac{1}{2}\ln[(1+\langle p\rangle)/(1-\langle p\rangle)] + \beta\gamma\langle p\rangle. \tag{38}$$

In the limit $\langle p\rangle \to 0$, we get from the above expression an equation for the temperature T_c of the ferroelectric transition:

$$\tfrac{1}{2}e^{-\beta_c w_1} + e^{-\beta_c w} + e^{-\beta_c\epsilon} - \tfrac{1}{2} = \beta_c\gamma[1 - e^{-\beta_c w}]. \tag{39}$$

Expressions (37) and (39) give exactly the same results as the Senko-Uehling model[12,13] and may be considered as analytical expressions of the equations for the spontaneous polarization and the transition temperature of their model. This can be easily understood,

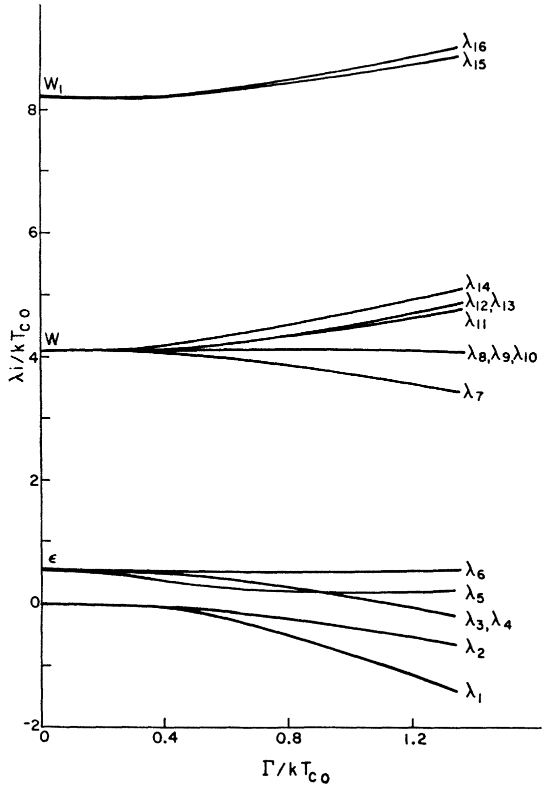

FIG. 2. Modification of the Slater-Takagi energy-level scheme due to the finite value of the overlap between the protonic wave functions at the two sites in the hydrogen bonds for $T>T_c$. Here T_{c0} stands for the transition temperature which gives in the classical limit the best agreement with the experimental KD_2PO_4 data.

since the physical situation described by the classical limit of our four-particle approximation and the Senko-Uehling model is exactly the same, though the mathematical approach is different.

In the limit that there are no long-range forces ($\gamma \rightarrow 0$) and that the configurations with four and with no "close" protons can be neglected ($w_1 \gg w,\epsilon$), Eqs. (37) and (39) yield the well-known analytical expressions of Takagi[11] for the spontaneous polarization

$$\langle p\rangle = \{1-[2e^{-\beta w}/(1-2e^{-\beta\epsilon})]^2\}^{1/2}, \qquad (40)$$

and the transition temperature

$$e^{-\beta_c w}+e^{-\beta_c \epsilon}=\tfrac{1}{2} \qquad (41)$$

of a KH_2PO_4 crystal.

Equations (37) and (39) predict, in agreement with the data of Silsbee, Uehling, and Schmidt,[13] a phase transition of first or of second order, depending on the values of the parameters ϵ, w, and γ (Fig. 1). The larger the ratio γ/ϵ, the sharper is the increase in the spontaneous polarization at T_c. Using the value of $w=625$ cm^{-1} as determined from magnetic relaxation data[7] in KD_2PO_4, Uehling and coworkers found[13] that $\epsilon=115$ cm^{-1} and $\gamma=23$ cm^{-1} gave the best fit to the experimental spontaneous polarization curve and the transition temperature $kT_c=155$ cm^{-1} of KD_2PO_4 for a second-order transition. (As w_1 should be at least twice w, the excitation energies for these configurations are so high that they have practically no influence on the ferroelectric behavior of our system and we may as well set $w_1=\infty$.)

It should be noted[2] that the occurrence of spontaneous polarization and the corresponding dielectric anomaly[11] already imply the occurrence of an elastic anomaly, irrespectively of the detailed microscopic picture.

The trouble with the classical-limit treatment is that it predicts too large a transition entropy.[13] Further, we have difficulties when we apply this model to KH_2PO_4 and use the KD_2PO_4 parameters to predict the behavior of the undeuterated crystal. Following Uehling,[13] one can show that because the protons have a higher zero-point energy than the deuterons and both move in an anharmonic potential well, ϵ of KH_2PO_4 should be smaller than ϵ of KD_2PO_4, whereas the other parameters should be approximately the same. However, if we now increase the ratio γ/ϵ so that it accounts for the nearly 2 times lower transition temperature of KH_2PO_4, we find that the onset of the spontaneous polarization should be much sharper than in KD_2PO_4, whereas in fact, the opposite was found to be true.[2]

In the following we shall show that the introduction of the tunneling term, which accounts for the finite overlap of the protonic wave functions between the two hydrogen sites in a hydrogen bond, removes at least a part of these discrepancies and improves the fit between theory and experiment.

In the case that $\Gamma\neq 0$, the energy matrix cannot be diagonalized analytically, and the two fields Δ and η have to be determined by a numerical solution of Eqs. (33) and (34). The modification of the Slater-Takagi energy level scheme by the inclusion of Γ is illustrated in Fig. 2 for the case $T>T_c$.

As can be seen from Fig. 3, the transition tempera-

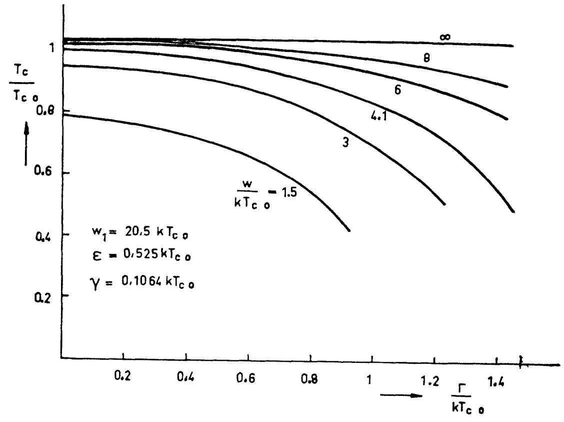

FIG. 3. Dependence of the ferroelectric transition temperatures on the tunneling integral Γ for various values of w.

tures decrease with increasing Γ, i.e., with increasing proton overlap due to an decreasing width of the potential barrier between the two sites in a hydrogen bond. As expected, this effect increases with decreasing excitation energy w for the creation of an H_3PO_4 or an HPO_4 group. If w were of the order of $10kT_c$, i.e., of the order of 1500 cm^{-1} for KD_2PO_4, then the transition temperature T_c would be practically independent of the shape of the intervening potential barrier and thus of Γ (and equal to its classical limiting value T_c) for all physically admissible values of Γ (Fig. 3). However, as borne out by the already mentioned experiments of Uehling and coworkers,[7] this is not the case in KD_2PO_4, and thus the overlap of the hydrogen wave functions between the two sites has a marked influence on the ferroelectric properties of KH_2PO_4-type crystals.

The anomalous specific heat of the transition is:

$$C_{(a)}=\delta W/\delta T, \tag{42}$$

where the internal energy W is obtained in this approximation as

$$W=N\,\mathrm{Tr}H_{i,\mathrm{PO}_4}\rho_{(4)}, \tag{43}$$

with

$$H_{i,\mathrm{PO}_4}=\tfrac{1}{2}\sum_{j=1}^{4}\left[-(s_{ij}^{+}+s_{ij}^{-})-\gamma\langle p\rangle(n_{ij\uparrow}-n_{ij\downarrow})\right]$$
$$+\left[w_1(N_{i0}+N_{i4})+w(N_{i1}+N_{i3})+\epsilon N_{i2}'+\gamma\langle p\rangle^2\right]. \tag{44}$$

As can be seen from Fig. 4, the specific-heat anomaly and the associated transition entropy,

$$\Delta S=\int_0^\infty \frac{C_{(a)}dT}{T},$$

decrease with increasing Γ. As our model in the classical limit predicts a too large transition entropy ($\Delta S\approx 0.50R$, whereas the experimental value[8,13] for KD_2PO_4 is $\Delta S\approx 0.32R$), we see that the effect has the right direction and that the fit between experiment and theory is improved if the finite overlap of the wave functions between the two hydrogen sites is taken into account.

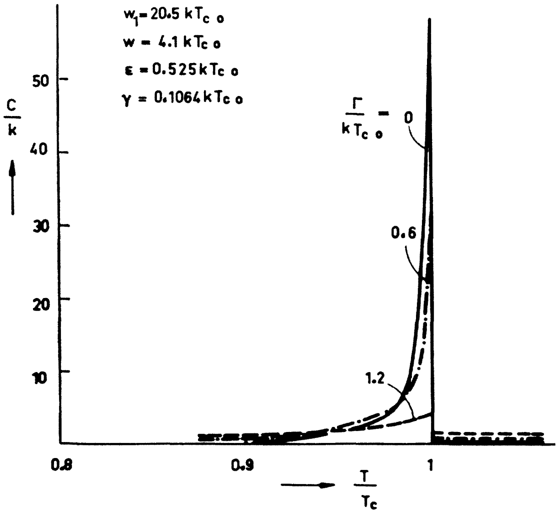

FIG. 4. Temperature dependence of the anomalous specific heat for various values of Γ.

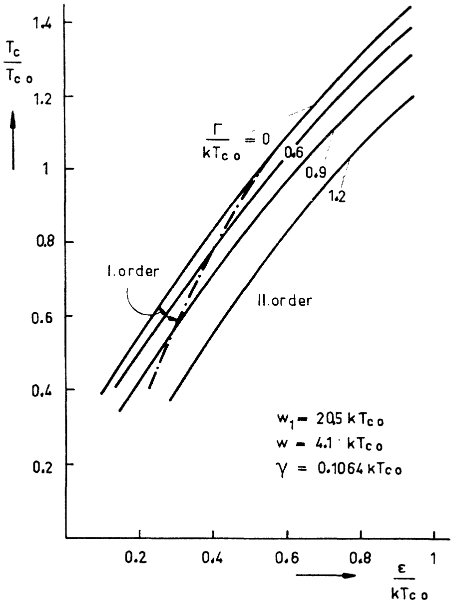

FIG. 5. Dependence of the ferroelectric transition temperatures and the boundary between first- and second-order phase transitions on ϵ and Γ.

The effect of Γ on the shape of the polarization curves is also quite remarkable. The larger Γ is, the less sharp is the rise of the spontaneous polarization near the critical point. This agrees qualitatively with the experimental fact that the onset of spontaneous polarization is generally sharper in deuterated crystals than in the undeuterated ones. That is, because of the larger mass of the deuteron, the value of Γ is distinctly smaller in the deuterated compounds than in their undeuterated analogs.

The boundary between phase transitions of first and second order also depends on Γ. If all other parameters remain unchanged, then an increase in Γ moves our critical point from the first order region towards the region of second order phase transitions (Fig. 5).

If the finite value of the proton overlap, i.e. of Γ, is taken into account, we have, in contrast to the classical case, no difficulty in accounting for the behavior of the undeuterated crystals on the basis of the KD_2PO_4 parameters.

As can be readily shown, and as was first pointed out by Uehling,[13] ϵ varies for different particles as the square of the off-center distance in the H bond. Because of their lower zero-point energy and the anharmonicity of the H-bond potential, the deuterons lie farther away from the center of the H bond than the protons, and thus $\epsilon_D>\epsilon_H$. A transition from KD_2PO_4 to KH_2PO_4 is

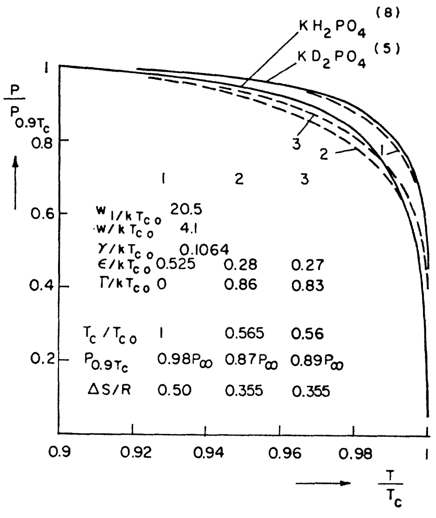

FIG. 6. Comparison of theoretical spontaneous polarization with experimental for both KH_2PO_4 and KD_2PO_4.

thus accompanied by a *decrease* in ϵ and an *increase* in Γ due to the increased overlap of the wave functions between the two sites in the hydrogen bonds.

From the observed change in the O–H with respect to the O–D bond length ($R_{O-H}-R_{O-D}\approx 0.14$ Å for KH_2PO_4-type crystals[19]) and using $(\epsilon_D/\epsilon_H)=(\zeta_D/\zeta_H)^2$, where ζ is the corresponding off-center distance of the particle site in the H bond, one finds that ϵ_H should amount to about 56% of ϵ_D. Similarly one finds that because of the smaller mass and the decreased width of the potential barrier,[19] Γ_H should be about two orders of magnitude larger than Γ_D.

As the precise value of Γ is not known, let us for the sake of simplicity assume that $\Gamma_D=0$ for KD_2PO_4. In such a case, Uehling's set of parameters $\epsilon_D=115$ cm^{-1}, $\gamma=23$ cm^{-1}, and $w=625$ cm^{-1} gives the best fit for a second-order transition and, with a slightly smaller value of ϵ_D/γ, also for a first-order one. If we now decrease ϵ_H in comparison to ϵ_D by the ratio of the squares of the off-center distances, and increase Γ_H to about 130 cm^{-1}, both the transition temperatures and the predicted shapes of the polarzation curves (Fig. 6) of KH_2PO_4 and KD_2PO_4 agree with the experimental ones. The predicted transition entropy of KH_2PO_4, $\Delta S=0.355R$, also agrees rather nicley with the experimental[20] one: $\Delta S=0.37R$.

Such a good agreement for KH_2PO_4 is probably fortuitous. As demonstrated recently,[21] the specific-heat anomaly in KH_2PO_4 exhibits a logarithmic singularity at T_c, whereas such behavior is not found in our approximation. In this connection it is interesting to note that the exact solution of the simplified ferroelectric model Hamiltonian (Ref. 1) for $\Gamma=0$ and a two-dimensional lattice *does* exhibit a logarithmic singularity in the specific heat, since it is equivalent to the corresponding Ising problem. Evidently higher approximations are needed to get a more reliable shape of the specific-heat anomaly. However, it should nevertheless be pointed out that if we allowed for a nonzero, though small, value of Γ_D we could get, even in this approximation, a still better fit between theory and experiment for KD_2PO_4 than obtained in Ref. 13. The exact value of Γ in such a fit is not critical and a relatively wide range of combinations of parameters produces similar effects. What is important, however, is the fact that if we simultaneously allow for the change in ϵ, due to the change in the zero-point energy, and for a change in Γ, due to an increased proton overlap, then we can use the KD_2PO_4 parameters to predict the properties of the undeuterated compound.

Though a more detailed treatment of the domain-wall motion is reserved for a subsequent paper, a tentative explanation can be given for the observed, rather striking difference in domain-wall dynamics[9] between KD_2PO_4 and KH_2PO_4. According to Barkla and Finlayson,[22] the motion of a domain wall in KH_2PO_4-type crystals is connected with transfer of hydrogens between the two sites in the hydrogen bonds. If we now assume that this intra-bond hydrogen transfer process is rate-determining for the domain-wall motion, then the ratio between the domain-wall mobilities of KH_2PO_4 (μ_H) and KD_2PO_4 (μ_D) can be readily evaluated using the technique of Gosar[23] or Kubo.[24] The general four-particle-cluster result is rather involved. In the limit $\Gamma\ll kT$, however, the result simplifies to

$$\mu_H/\mu_D=(\Gamma_H/\Gamma_D)^2, \tag{45}$$

provided that the two mobilities are measured at the same temperature, that the non-tunneling channels can be neglected, and that the excitation energies w for the H_3PO_4 or HPO_4 defects (which move in symmetric double minimum potentials by jumps of excess protons or vacancies from one PO_4 group to another) are the same for both crystals. The above result is only qualitatively correct. Nevertheless, it predicts the right direction and order of magnitude of the observed effects. The observed drastic decrease in domain-wall mobility on deuteration thus seems to reflect the diminished overlap of the wave functions between the two sites and the reduced chance for the heavier particle to tunnel through the potential barrier. Thus the same effect which has been invoked to help explain the isotope effects in the Curie temperature and spontaneous polarization seems to account also for the isotope effect in the domain-wall mobility, and it seems that all three phenomena can be understood from a unified point of view.

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[19] B. S. Garret, U. S. Atomic Energy Commission, Oak Ridge National Laboratory Report No. ORNL-1745, 149, 1954 (unpublished).

[20] C. C. Stephenson and J. G. Hooley, J. Am. Chem. Soc. **66**, 1397 (144); H. Danner and R. Pepinsky, Phys. Rev. **99**, 1915 (1955).

[21] J. Grindlay, Phys. Rev. **139**, A1603 (1965).

[22] H. M. Barkla and D. M. Finlayson, Phil. Mag. **44**, 109 (1953).

[23] P. Gosar, Nuovo Cimento **30**, 931 (1963).

[24] R. Kubo, J. Phys. Soc. Jap. **12**, 570 (1957).

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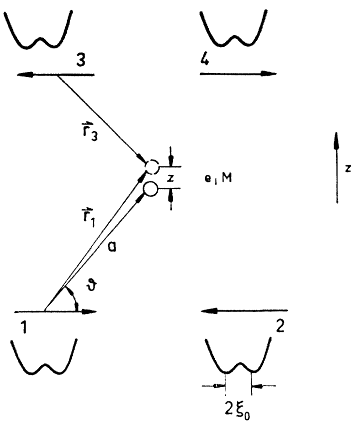

FIG. 7. Motion of an ion with mass M and effective charges e_i in the field of four surrounding hydrogen-bonded protons.

APPENDIX A. LATTICE-MEDIATED PROTON-PROTON INTERACTIONS IN KH_2PO_4

One of the results of the proton-lattice coupling[6,17] in KH_2PO_4 is an indirect, lattice-mediated proton-proton interaction. In order to get a notion of the form of this interaction, let us consider a simple, classical example of an ion (for instance K^+), moving in the harmonic potential of the lattice plus the superimposed potential of the surrounding protons.

The total potential of the ion can be written as

$$V_{\text{ion}}=\tfrac{1}{2}k(\mathbf{r}_i-\mathbf{r}_0)^2+\sum_{j=1}^{q} e_p e_i \zeta_0 \mathbf{p}_j\cdot\mathbf{r}_j/4\pi\epsilon_0 r_j^3 \qquad \text{(A1)}$$

where e_p and e_i are the effective charges of the proton and ion, respectively; $\mathbf{r}_i$ is the radius vector describing the instantaneous and $\mathbf{r}_0$ is the vector describing the equilibrium position of the ion (in the "absence" of the protons); k is the force constant of the lattice potential, which is in the "absence" of protons assumed to be harmonic ($k=M\omega^2$);

$$e_p\zeta_0\mathbf{p}_j=e_p\zeta_0(n_{j\uparrow}-n_{j\downarrow})\zeta_j/|\zeta_j|$$

is the dipole-moment operator of the jth hydrogen bond in which the given proton moves; and $\mathbf{r}_j$ is the radius vector between the instantaneous position of the ion and the center of the jth H bond. We assumed that $2\zeta_0\ll r_j$ so that each hydrogen bond can be represented by a point dipole, whose dipole moment is proportional to the off-center distance ζ_0 of the protonic site.

For each configuration of the protons we can find the corresponding equilibrium position of the ion by a minimization with respect to $\mathbf{r}_i$. This equilibrium position is different for different configurations (since $\mathbf{r}_j$ is a function of $\mathbf{r}_i$), and the corresponding minimized total ion potential contains a term

$$-\tfrac{1}{2}\sum_{j_1,j_2} J_{j_1,j_2}{}^{p-L-p}p_{j_1}p_{j_2} \qquad \text{(A2)}$$

which represents an effective indirect proton-prtoon interaction. The coupling parameter J^{p-L-p} depends on the orientation of the hydrogen bonds, the distance between the centers of the hydrogen bonds and the equilibrium position of the ion in the "absence" of protons, the "harmonic" force constant and charge of the ion, and the value of the H-bond dipole moment. For the simple case of an ion moving in the field of four surrounding protons (Fig. 7), the coupling parameter is explicitly obtained as

$$J^{p-L-p}=(1/\omega^2M)(e_ie_p\zeta_0\sin2\theta/2\pi\epsilon_0a^3)^2, \qquad \text{(A3)}$$

where the meaning of θ and a is seen from the figure.

If the ion frequency ω is larger than the frequency of proton motion between the two sites in a hydrogen bond, the lattice interacts with the instantaneous value of the proton charge density. Expression (A2), which has the same form as the direct long-range proton-proton interaction, is thus adequate for handling proton-proton interaction via tightly bonded ions. If, however, the ion frequency is smaller than the frequency of proton motion between the two sites, the lattice responds to the charge density of the proton averaged over the two sites, and the two operators p_1 and p_2 in expression (A2) have to be replaced by their mean values. The indirect proton-proton interactions via weakly bonded ions can be thus replaced by a molecular field $\gamma_0\langle p\rangle$. As the protons interact both with tightly and with weakly bonded ions, we can approximate lattice-mediated proton-proton coupling in KH_2PO_4 by an effective Hamiltonian:

$$H_{p-L-p}=\tfrac{1}{4}\sum_{i,i'=1}^{N}\sum_{j,j'=1}^{4}(-J_{i,i',j,j'}{}^{p-L-p})\cdot(n_{ij\uparrow}-n_{ij\downarrow})(n_{i'j'\uparrow}-n_{i'j'\downarrow})+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{4}\left[-\gamma_0\langle p\rangle(n_{ij\uparrow}-n_{ij\downarrow})+\tfrac{1}{2}\gamma_0\langle p\rangle^2\right], \qquad \text{(A4)}$$

where the first term stands for the interaction through "high"- and the second through "low"-frequency ions. It should be noted that the relative weights of the two terms depend on the frequency of proton motion between the two sites and hence on the mass of the hydrogen isotopes.

APPENDIX B: CONSISTENCY EQUATIONS FOR THE FOUR-PROTON CLUSTER APPROXIMATION

The explicit form of the four-proton-cluster Hamiltonian $H_{(4)}$ [Eq. (29)] in the representation of localized particles

$$\prod_{j=1}^{4} b_{ijk}{}^{\dagger}|0\rangle, \quad k=\uparrow,\downarrow \tag{B1}$$

is rather clumsy. However, after a suitable transformation $SH_{(4)}S^{-1}=U_{(4)}$, the energy matrix can be written as

$$U_{(4)}=\left[\begin{array}{cccccccccccccccc}
w & 2b & -a & & & & & & & & & & & & & \\
2b & \epsilon & 0 & & & & & & & & & & & & & \\
-a & 0 & w & & & & & & & & & & & & & \\
& & & w & 2b & -a & & & & & & & & & & \\
& & & 2b & \epsilon & 0 & & & & & & & & & & \\
& & & -a & 0 & w & & & & & & & & & & \\
& & & & & & w & 2b & -a & & & & & & & \\
& & & & & & 2b & w_1 & 0 & & & & & & & \\
& & & & & & -a & 0 & w & & & & & & & \\
& & & & & & & & & w_1 & 2b & 0 & 0 & 0 & 0 & \\
& & & & & & & & & 2b & w & 2b & 2\sqrt{2}b & -a & 0 & \\
& & & & & & & & & 0 & 2b & 0 & 0 & 0 & -2a & \\
& & & & & & & & & 0 & 2\sqrt{2}b & 0 & \epsilon & 0 & 0 & \\
& & & & & & & & & 0 & -a & 0 & 0 & w & b & \\
& & & & & & & & & 0 & 0 & -2a & 0 & b & 0 & \\
& & & & & & & & & & & & & & & \epsilon
\end{array}\right], \tag{B2}$$

where

$$b=-\Gamma+\tfrac{1}{2}\eta, \qquad a=\Delta+2\gamma\langle p\rangle.$$

The consistency equations (33) and (34) can be now explicitly written as

$$(\Gamma-\eta)-(a/\langle p\rangle-\gamma)\langle s\rangle=0, \tag{B3}$$

and

$$[(a-\gamma\langle p\rangle)^2+(\Gamma-\eta)^2]^{1/2}-\left(\frac{a}{\langle p\rangle}-\gamma\right)\tanh\{\beta[(a-\gamma\langle p\rangle)^2+(\Gamma-\eta)^2]^{1/2}\}=0, \tag{B4}$$

where

$$\begin{aligned}\langle p\rangle&=f_3/f_1,\\ \langle s\rangle&=f_2/f_1,\end{aligned} \tag{B5}$$

with

$$f_1=\sum_{i=1}^{16} e^{-\beta\lambda_i}, \tag{B7}$$

$$f_2=2\sum_{i=1}^{3} c_{i1}c_{i2}e^{-\beta\lambda_i}+\sum_{i=f}^{9} c_{i7}c_{i8}e^{-\beta\lambda_i}+\sum_{i=10}^{15}[(c_{i10}+c_{i12}+\sqrt{2}c_{i13})c_{i11}+c_{i14}c_{i15}]e^{-\beta\lambda_i}, \tag{B8}$$

$$f_3=2\sum_{i=1}^{3} c_{i1}c_{i3}e^{-\beta\lambda_i}+\sum_{i=f}^{9} c_{i7}c_{i9}e^{-\beta\lambda_i}+\sum_{i=10}^{15}(c_{i11}c_{i14}+2c_{i12}c_{i15})e^{-\beta\lambda_i}, \tag{B9}$$

and where the c_{ij} and the λ_i stand for the eigenvectors and eigenvalues of the energy matrix (B2).