Green's-function theory of the ferroelectric phase transition in potassium dihydrogen phosphate (KDP)*

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The method of the two-time Green's function is applied to the investigation of the ferroelectric phase transition in KH_2PO_4. The zero-frequency difficulties are circumvented by means of the fermion Green's function. It is shown that the softening of the mixed mode and the onset of static long-range order take place at the same temperature.

I. INTRODUCTION

The mechanism of ferroelectric phase transition in potassium dihydrogen phosphate (KDP) and its isomorphs is often described in terms of the pseudospin model[1-3] and its modification to include interactions with the lattice.[4] Although the model has been the subject of several investigations, it appears that there has not been an attempt to treat both the static and dynamical properties of the system in a unified formalism. Generally, the static properties such as the average values of the spin operators are determined by methods such as the mean-field approximation, and dynamical quantities such as the energies of the collective modes are determined by other methods such as the linearized equation of motion method. This causes some inconsistencies between the static and dynamic properties, and there is no guarantee that the two transition temperatures, treated statically and dynamically, should be the same. The method of double-time Green's functions[5,6] offers an alternative, whereby both static and dynamical quantities may be treated in the same formalism. The poles of the Green's function correspond to the energies of the elementary excitations of the system, and the average values of the operators involved can also be calculated from the Green's function. This method will be applied to the pseudospin Hamiltonian, and it shall be seen that even very simple decoupling procedures yield the major results of the model.

II. DOUBLE-TIME GREEN'S FUNCTION METHOD

The retarded and advanced Green's functions as defined by Zubarev[5] are

$$G_{AB}^{(r)}(t,t') \equiv \langle\langle A(t) \mid B(t') \rangle\rangle^{(r)} = -i\theta(t-t')\langle [A(t), B(t')]_\eta \rangle , \tag{2.1}$$

$$G_{AB}^{(a)}(t,t') \equiv \langle\langle A(t) \mid B(t') \rangle\rangle^{(a)} = i\theta(t'-t)\langle [A(t), B(t')]_\eta \rangle , \tag{2.2}$$

where $\eta = \pm 1$, $[A,B]_\eta = AB - \eta BA$, and

$$\theta(t) = \begin{cases} 1, & t>0 \\ 0, & t<0 . \end{cases} \tag{2.3}$$

It follows from the definition that the Green's functions so defined are a function of $t-t'$ only.

The Fourier-transformed Green's function is defined by

$$G_{AB}(\omega) = \langle\langle A \mid B \rangle\rangle_\omega = \frac{1}{2\pi}\int_{-\infty}^{\infty} G_{AB}(t)\, e^{i\omega t}\, dt . \tag{2.4}$$

This Green's function satisfies the equation of motion

$$\omega \langle\langle A \mid B \rangle\rangle_\omega = \frac{1}{2\pi}\langle [A,B]_\eta \rangle + \langle\langle [A,H] \mid B \rangle\rangle_\omega . \tag{2.5}$$

The equation for $\langle\langle A \mid B \rangle\rangle_\omega$ thus involves an inhomogeneous term and a higher-order Green's function. One of the problems of this method is to decouple the higher-order Green's function and to choose appropriate Green's functions so that a closed system of equations is obtained.

In addition, Zubarev has shown that the poles of the Green's function correspond to the energies of the elementary excitations of the system. The average value of the product of two operators can be calculated from the formula

$$\langle BA \rangle = \lim_{\epsilon \to 0+} \int_{-\infty}^{\infty} \frac{i\left(\langle\langle A \mid B \rangle\rangle_{\omega+i\epsilon} - \langle\langle A \mid B \rangle\rangle_{\omega-i\epsilon}\right)}{e^{\beta\omega} - \eta} d\omega . \tag{2.6}$$

The parameter η may be arbitrarily chosen as $+1$ or -1. If A and B are Bose operators, η is generally chosen as $+1$, and if they are Fermi operators, η is chosen to be -1. Sometimes, however, the reverse choice becomes necessary. In the problem of KDP, where one deals with spin operators, it would be convenient to choose $\eta = +1$

since this would simplify the inhomogeneous terms in (2.5) considerably. However, it turns out that the Green's functions for the system have a zero-frequency pole. Under these circumstances, the formula (2.6) cannot be used with $\eta = +1$, since the integral becomes divergent. (Efforts to circumvent this problem by the addition of vanishingly small perturbation terms were unsuccessful.) One therefore has to resort to fermion Green's functions, i.e., with $\eta = -1$, to treat the pseudospin problem.

III. APPLICATION TO THE PSEUDOSPIN MODEL

The pseudospin Hamiltonian is given by

$$H = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z , \tag{3.1}$$

where S_i^x and S_i^z are components of the spin-$\frac{1}{2}$ operator. Introducing the operators $S^{\pm} = S^x \pm iS^y$, one can consider the Green's functions $\langle\langle S_g^+ | S_f^- \rangle\rangle$, $\langle\langle S_g^- | S_f^- \rangle\rangle$, and $\langle\langle S_g^z | S_f^- \rangle\rangle$. The equations for these Green's functions that correspond to (2.5) are

$$\omega \langle\langle S_g^+ | S_f^- \rangle\rangle = \frac{\langle 2S_f^- S_g^+ + \delta_{fg}(1 - 2S_f^- S_g^+) \rangle}{2\pi} - 2\Omega \langle\langle S_g^z | S_f^- \rangle\rangle + \frac{1}{2} \sum_m J_{gm} \langle\langle S_g^+ S_m^z | S_f^- \rangle\rangle + \frac{1}{2} \sum_l J_{lg} \langle\langle S_l^z S_g^+ | S_f^- \rangle\rangle ,$$

$$\omega \langle\langle S_g^- | S_f^- \rangle\rangle = \frac{2\langle S_f^- S_g^- \rangle}{2\pi} + 2\Omega \langle\langle S_g^z | S_f^- \rangle\rangle - \frac{1}{2} \sum_m J_{gm} \langle\langle S_g^- S_m^z | S_f^- \rangle\rangle - \frac{1}{2} \sum_l J_{lg} \langle\langle S_l^z S_g^- | S_f^- \rangle\rangle , \tag{3.2}$$

$$\omega \langle\langle S_g^z | S_f^- \rangle\rangle = \frac{(1 - \delta_{fg}) \langle S_f^- S_g^z \rangle}{2\pi} - \Omega \langle\langle S_g^+ | S_f^- \rangle\rangle + \Omega \langle\langle S_g^- | S_f^- \rangle\rangle .$$

The Eqs. (3.2) can be closed by decoupling the higher-order Green's functions. The two decoupling procedures that will be discussed here are the Tyablikov and the symmetric.

In Tyablikov decoupling, one assumes that

$$\begin{aligned} \langle\langle S_g^{\pm} S_m^z | S_f^- \rangle\rangle &= \langle S_m^z \rangle \langle\langle S_g^{\pm} | S_f^- \rangle\rangle , \\ \langle\langle S_l^z S_g^{\pm} | S_f^- \rangle\rangle &= \langle S_l^z \rangle \langle\langle S_g^{\pm} | S_f^- \rangle\rangle . \end{aligned} \tag{3.3}$$

Introduce the notation

$$x = \langle S^x \rangle = \langle S^{\pm} \rangle ; \quad n = \langle S^z \rangle ; \quad J_0 = \sum_j J_{ij} .$$

Then, Eq. (3.2) becomes with $f = g$ and the decoupling of (3.3):

$$\begin{pmatrix} \omega - J_0 n & 0 & 2\Omega \\ 0 & \omega + J_0 n & -2\Omega \\ \Omega & -\Omega & \omega \end{pmatrix} \begin{pmatrix} \langle\langle + | - \rangle\rangle \\ \langle\langle - | - \rangle\rangle \\ \langle\langle z | - \rangle\rangle \end{pmatrix} = \frac{1}{2\pi} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} , \tag{3.4}$$

where $\langle\langle + | - \rangle\rangle$, $\langle\langle - | - \rangle\rangle$, and $\langle\langle z | - \rangle\rangle$ are abbreviated notations for $\langle\langle S_f^+ | S_f^- \rangle\rangle$, etc.

The secular determinant for the system is given by

$$\Delta = \omega(\omega^2 - \omega_p^2) ,$$

where

$$\omega_p = [(J_0 n)^2 + (2\Omega)^2]^{1/2} . \tag{3.5}$$

From (3.4) and (3.5),

$$\langle\langle + | - \rangle\rangle = (1/2\pi\Delta)[\omega(\omega + J_0 n) - 2\Omega^2] \tag{3.6}$$

and

$$\langle\langle z | - \rangle\rangle = -(1/2\pi\Delta)\Omega(\omega + J_0 n) . \tag{3.7}$$

The application of (2.6) to (3.6) and (3.7) yields

$$\langle S^- S^+ \rangle = \tfrac{1}{2} - n = \tfrac{1}{2} + \frac{J_0 n (1 - e^{\beta\omega_p})}{2\omega_p (e^{\beta\omega_p} + 1)}$$

or

$$n = \frac{J_0 n}{2\omega_p} \tanh\left(\frac{\beta\omega_p}{2}\right) , \tag{3.8}$$

and

$$\langle S^- S^z \rangle = \tfrac{1}{2} \langle S^- \rangle = \tfrac{1}{2} \langle S^x \rangle = \frac{\Omega}{2\omega_p} \tanh\left(\frac{\beta\omega_p}{2}\right)$$

or

$$\langle S^x \rangle = \frac{\Omega}{\omega_p} \tanh\left(\frac{\beta\omega_p}{2}\right) . \tag{3.9}$$

The results (3.8) and (3.9) are identical with those obtained in the mean-field approximation. The poles of the Green's function, given by 0, $\pm\omega_p$, do not show any softening in this approximation.

In the symmetric-type decoupling, it is assumed that

$$\langle\langle S_m^z S_g^{\pm} | S_f^- \rangle\rangle = \langle S_m^z \rangle \langle\langle S_g^{\pm} | S_f^- \rangle\rangle + \langle S_g^{\pm} \rangle \langle\langle S_m^z | S_f^- \rangle\rangle . \tag{3.10}$$

Define

$$u_{fg} = \langle\langle S_g^+ | S_f^- \rangle\rangle ; \quad v_{fg} = \langle\langle S_g^- | S_f^- \rangle\rangle ; \quad w_{fg} = \langle\langle S_g^z | S_f^- \rangle\rangle \tag{3.11a}$$

and

$$\lambda_{fg} = \langle S_f^- S_g^+ \rangle + \tfrac{1}{2}\delta_{fg}(1 - 2\langle S_f^- S_g^+ \rangle);$$
$$\mu_{fg} = \langle S_f^- S_g^- \rangle ; \qquad (3.11b)$$
$$\nu_{fg} = \langle S_f^- S_g^z \rangle - \delta_{fg}\langle S_f^- S_g^z \rangle .$$

With the approximation of (3.10), and the notation of (3.11), Eqs. (3.2) become

$$\omega u_{fg} = \frac{\lambda_{fg}}{\pi} - 2\Omega w_{fg} + J_0 n u_{fg} + \sum_m x J_{mg} w_{mf} ,$$
$$\omega v_{fg} = \frac{\mu_{fg}}{\pi} + 2\Omega w_{fg} - J_0 n v_{fg} - \sum_m x J_{mg} w_{mf} ,$$
$$\omega w_{fg} = \frac{\nu_{fg}}{\pi} - \Omega u_{fg} + \Omega v_{fg} . \qquad (3.12)$$

Define the lattice Fourier transform of a variable by

$$A(\vec{k}) = \sum_g A_{fg} e^{i\vec{k}\cdot(\vec{R}_g - \vec{R}_f)} \qquad (3.13)$$

Such a transformation of the Eqs. (3.12) into momentum space gives

$$\begin{pmatrix} \omega - J_0 n & 0 & 2\Omega - xJ(\vec{k}) \\ 0 & \omega + J_0 n & -2\Omega + xJ(\vec{k}) \\ \Omega & -\Omega & \omega \end{pmatrix} \begin{pmatrix} u(\vec{k}) \\ v(\vec{k}) \\ w(\vec{k}) \end{pmatrix} = \frac{1}{\pi} \begin{pmatrix} \lambda(\vec{k}) \\ \mu(\vec{k}) \\ \nu(\vec{k}) \end{pmatrix} . \qquad (3.14)$$

The secular determinant for (3.14) is given by

$$\Delta = \omega[\omega^2 - \omega_1^2(\vec{k})] ,$$

where

$$\omega_1^2(\vec{k}) = (J_0 n)^2 + 2\Omega[2\Omega - xJ(\vec{k})] . \qquad (3.15)$$

The poles of the Green's function, and hence the energies of the collective modes occur at $\pm\omega_1(\vec{k})$.

For $T > T_c$, $n = 0$ and $\omega_1^2(0) = 2\Omega(2\Omega - xJ_0)$ which corresponds exactly with the results of Tokunaga[7] and Brout, Mueller, and Thomas.[8] Also, from (3.8) and (3.9), $x \to (2\Omega/J_0)$ as $T \to T_c$, so that $\omega_1(0) \to 0$ as $T \to T_c$. The symmetric-type decoupling thus predicts the familiar softening of the collective mode of proton motion.

Equations for the expectation values of the operators can be set up as before, by solving for the Green's functions of (3.14) and applying (2.6). This leads to

$$\tfrac{1}{2} - n = \frac{1}{N}\sum_k \lambda(\vec{k}) - \frac{1}{N}\sum_k \frac{J_0 n \lambda(\vec{k}) - [2\Omega - xJ(\vec{k})]\nu(\vec{k})}{\omega_1(\vec{k})} \times \tanh\left(\frac{\beta\omega_1(\vec{k})}{2}\right) \qquad (3.16)$$

and

$$x = \frac{1}{N}\sum \nu(\vec{k}) + \frac{1}{N}\sum_k \frac{\Omega[\lambda(\vec{k}) - \mu(\vec{k})]}{\omega_1(\vec{k})} \tanh\left(\frac{\beta\omega_1(\vec{k})}{2}\right) . \qquad (3.17)$$

An analytic solution of (3.16) and (3.17) is not possible unless very crude approximations are introduced.

IV. APPLICATION TO THE COUPLED HAMILTONIAN

The Hamiltonian proposed by Kobayashi to take into account coupling of the proton system with the lattice is given by

$$H = -2\Omega\sum_l S_l^x - \frac{1}{2}\sum_{lm} J_{lm} S_l^z S_m^z - \sum_{ql} F_{ql}(C_{-q}^\dagger + C_q) S_l^z + \sum_q \omega_q (C_q^\dagger C_q + \tfrac{1}{2}) , \qquad (4.1)$$

where $C_q^\dagger$ and C_q are the optical-mode phonon creation and annihilation operators, $F_{qe} = F_q e^{-i\vec{q}\cdot\vec{R}_l}$ and ω_q is the optical-mode frequency.

The equations for the various Green's functions are given by

$$\omega\langle\langle S_g^+ | S_f^- \rangle\rangle = \frac{\lambda_{fg}}{\pi} - 2\Omega\langle\langle S_g^z | S_f^- \rangle\rangle + \frac{1}{2}\sum_m J_{gm}\langle\langle S_g^+ S_m^z | S_f^- \rangle\rangle + \frac{1}{2}\sum_l J_{lg}\langle\langle S_l^z S_g^+ | S_f^- \rangle\rangle + \sum_q F_{qg}\langle\langle C_{-q}^\dagger S_g^+ | S_f^- \rangle\rangle \sum_q F_{qg}\langle\langle C_q S_g^+ | S_f^- \rangle\rangle ,$$

$$\omega\langle\langle S_g^- | S_f^-\rangle\rangle = \frac{\mu_{fg}}{\pi} + 2\Omega\langle\langle S_g^z | S_f^-\rangle\rangle - \frac{1}{2}\sum_m J_{gm}\langle\langle S_g^- S_m^z | S_f^-\rangle\rangle - \frac{1}{2}\sum_l J_{lg}\langle\langle S_l^z S_g^- | S_f^-\rangle\rangle - \sum_q F_{qg}\langle\langle C_{-q}^\dagger S_g^- | S_f^-\rangle\rangle$$
$$- \sum_q F_{qg}\langle\langle C_q S_g^- | S_f^-\rangle\rangle ,$$

$$\omega\langle\langle S_g^z | S_f^-\rangle\rangle = \frac{\nu_{fg}}{\pi} - \Omega\langle\langle S_g^+ | S_f^-\rangle\rangle + \Omega\langle\langle S_g^- | S_f^-\rangle\rangle ,$$

$$\omega\langle\langle C_{-q}^\dagger | S_f^-\rangle\rangle = \frac{1}{\pi}\langle C_{-q}^\dagger S_f^-\rangle + \sum_l F_{-ql}\langle\langle S_l^z | S_f^-\rangle\rangle - \omega_{-q}\langle\langle C_{-q}^\dagger | S_f^-\rangle\rangle ,$$

$$\omega\langle\langle C_q | S_f^-\rangle\rangle = \frac{1}{\pi}\langle C_q S_f^-\rangle - \sum_l F_{-ql}\langle\langle S_l^z | S_f^-\rangle\rangle + \omega_q\langle\langle C_q | S_f^-\rangle\rangle . \tag{4.2}$$

The higher-order Green's functions are decoupled symmetrically. Define

$$g(\vec{k}) = \langle\langle C_{-k}^\dagger | S_f^-\rangle\rangle , \quad h(\vec{k}) = \langle\langle C_k | S_f^-\rangle\rangle ,$$
$$\xi(\vec{k}) = \langle C_{-k}^\dagger S_f^-\rangle , \quad \text{and} \quad \eta(\vec{k}) = \langle C_k S_f^-\rangle . \tag{4.3}$$

Then the equations obtained from (4.2) on decoupling the higher-order Green's functions can be transformed into momentum space. If this is done, and only the $q = 0$ terms in the expectation values of the phonon operators (which correspond to a macroscopic displacement of the lattice) are retained, one gets

$$\begin{bmatrix} \omega - J_0 n - \langle C_0^\dagger + C_0\rangle F_0 & 0 & 2\Omega - xJ(\vec{k}) & -NxF_{kf} & -NxF_{kf} \\ 0 & \omega + J_0 n + \langle C_0^\dagger + C_0\rangle F_0 & -2\Omega + xJ(\vec{k}) & NxF_{kf} & NxF_{kf} \\ \Omega & -\Omega & \omega & 0 & 0 \\ 0 & 0 & -F_{-kf} & \omega + \omega_k & 0 \\ 0 & 0 & F_{-kf} & 0 & \omega - \omega_k \end{bmatrix} \begin{bmatrix} u(\vec{k}) \\ v(\vec{k}) \\ w(\vec{k}) \\ g(\vec{k}) \\ h(\vec{k}) \end{bmatrix} = \frac{1}{\pi} \begin{bmatrix} \lambda(\vec{k}) \\ \mu(\vec{k}) \\ \nu(\vec{k}) \\ \xi(\vec{k}) \\ \eta(\vec{k}) \end{bmatrix} . \tag{4.4}$$

The secular determinant is given by

$$\Delta = \omega[\omega^2 - \omega_1^2(\vec{k})][\omega^2 - \omega_2^2(\vec{k})] ,$$

where

$$\omega_{1_2}^2(\vec{k}) = \tfrac{1}{2}\{(\omega_k^2 + \omega_c^2) \pm [(\omega_k^2 - \omega_c^2)^2 + 16\Omega N x \omega_k |F_k|^2]^{1/2}\} , \tag{4.5}$$

in which

$$\omega_c^2 = (J_0 n + \langle C_0^\dagger + C_0\rangle F_0)^2 + 2\Omega[2\Omega - xJ(k)] . \tag{4.6}$$

Equation (4.5), which corresponds to the roots of Δ and hence to the poles of the Green's functions, gives the energies of the collective spin-phonon modes, and is similar to the result derived by Kobayashi. It is also possible to see that $\omega_2(0) \to 0$ as the transition temperature is reached, thus showing a softening of the mixed mode.

V. CONCLUSIONS

The Tyablikov approximation consists of ignoring the fluctuations in S^z and replacing this operator by its equilibrium value. The symmetric decoupling procedure includes a term corresponding to the tunneling motion of the protons. It is the presence of this correction that gives rise to softening of the mode as T approaches T_c.

Application of the method to the problem of the transverse susceptibility of KDP reproduces, with a Tyablikov-type decoupling, the results of Havlin, Litov, and Uehling.[9] The dynamics of the transverse susceptibility can also be studied with this method.

In conclusion, it appears that the use of fermion Green's functions offers a systematic approach to the study of both the static and dynamical aspects of the ferroelectric phase transition in KDP. The method can easily be applied to extend the problem to take into account the real lattice structure of KDP instead of making the usual "one spin per unit cell" assumption.

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