

FREQUENCY-DEPENDENT DIELECTRIC CONSTANT OF KH_2PO_4

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Recent theoretical studies of the properties of KH_2PO_4 have included the correlation or Ising energy of the protons as well as the energy associated with proton tunneling within the double well. In this Letter an expression is obtained for the frequency- and temperature-dependent dielectric constant just above the transition temperature. With use of this expression, the frequency-dependent dielectric response of the system can be examined subject to variations in the relative strengths of the correlation and tunneling contributions to the energy and in related damping times.

The Hamiltonian considered by de Gennes,¹ Tokunaga and Matsubara,² and others³ can be written

$$H = -\sum_{ij} J_{ij} S_{ix} S_{jx} - f \sum_i S_{i+} - f^* \sum_i S_{i-}. \quad (1)$$

The first or Ising term takes into account the correlation energy associated with a given configuration of protons. The S_x spin- $\frac{1}{2}$ operators designate the distribution of protons in the double well. Spin up indicates that the proton is in the well adjacent to an upper phosphate group and spin down indicates that the proton is in the well adjacent to a lower phosphate group. The next two terms involve the spin-flip operators and enable the proton to tunnel from one well to the other. The Hamiltonian, when written in the molecular field approximation, involves only the total spin operators of the system:

$$\bar{H} = -J \langle S_x \rangle S_x - f S_+ - f^* S_-, \quad (2)$$

with

$$S_x = \sum_i S_{ix}; \quad S_+ = \sum_i S_{i+}.$$

The equations of motion for the system can be written

$$\begin{aligned} \dot{S}_x &= \omega_f S_y - (S_x - \langle S_x \rangle) / T_1, \\ \dot{S}_y &= \Omega S_x S_z - \omega_f S_x + [\mu H(t) / \hbar] S_z - S_y / T_2, \\ \dot{S}_z &= 0, \end{aligned} \quad (3)$$

with

$$S_z = \langle S_z \rangle; \quad \hbar \omega_f = f; \quad \hbar \Omega = J.$$

These equations have been linearized and supplemented with Bloch-type damping terms. It is assumed that the expectation value of the x component of spin relaxes to the thermal-equilibrium spin value determined by the instantaneous field. This instantaneous field is not only composed of the applied field, but also of the molecular field resulting from the Ising term in the Hamiltonian. ω_f as defined is the tunneling frequency. $H(t)$, the small signal field, is applied in the x direction since we are interested in the longitudinal dielectric constant, i.e., the dielectric constant resulting from polarization along the C axis of the crystal. Two damping times, T_1 and T_2 , have been introduced. T_1 is a relaxation time describing the decay of the C -axis polarization. T_2 is the damping time of the proton tunneling motion.

One can solve the set of equations (3) to obtain expressions for the real and imaginary parts of the dielectric constant:

$$x' = \frac{\mu \sinh \beta f (\alpha \Gamma_1 \Gamma_2 + \alpha \omega_f^2 - \omega^2)(\Gamma_1 \Gamma_2 + \omega_f^2) + \omega^2 \Gamma_1 (\alpha \Gamma_1 + \Gamma_2)}{f \cosh \beta f (\omega^2 + \alpha^2 \Gamma_1^2)(\omega^2 + \Gamma_2^2) + \alpha^2 \omega_f^4 + 2\alpha \omega_f^2 (\alpha \Gamma_1 \Gamma_2 - \omega^2)}, \quad (4)$$

$$x'' = \frac{\mu \sinh \beta f \omega (\alpha \Gamma_1 + \Gamma_2)(\Gamma_1 \Gamma_2 + \omega_f^2) - \omega \Gamma_1 (\alpha \Gamma_1 \Gamma_2 + \alpha \omega_f^2 - \omega^2)}{f \cosh \beta f (\omega^2 + \alpha^2 \Gamma_1^2)(\omega^2 + \Gamma_2^2) + \alpha^2 \omega_f^4 + 2\alpha \omega_f^2 (\alpha \Gamma_1 \Gamma_2 - \omega^2)}, \quad (5)$$

with

$$\alpha = 1 - \frac{J \sinh \beta f}{f \cosh \beta f}.$$

Γ_1 and Γ_2 are just the reciprocals of the relaxation times T_1 and T_2 . ω is the driving frequency of the small signal field. As one might expect, the detailed behavior of the real and imaginary parts of the dielectric constant depends sensitively upon the values that one chooses for the tunneling frequency ω_f , the constant J , and the damping rates Γ_1 and Γ_2 . These expressions, however, reduce to several simpler expressions for various limiting cases. For example, the static dielectric constant can be written

$$x' = \frac{\mu \sinh \beta f}{(f \cosh \beta f - J \sinh \beta f)}. \quad (6)$$

This expression has been obtained previously by Tokunaga and Matsubara.² For temperatures such that the tunneling energy is small compared with the thermal energy KT , the dielectric constant obeys a Curie-Weiss law:

$$x' = \frac{C}{T - T_c}, \quad \text{for } f/KT \ll 1; \quad (7)$$

$$T_c = J/K, \quad C = \mu/K.$$

If it is assumed that the tunneling frequency is zero for the completely deuterated material, one obtains the reciprocal dielectric constant versus temperature shown to the right of Fig. 1. Note that as the tunneling frequency is increased, the curve moves to the left

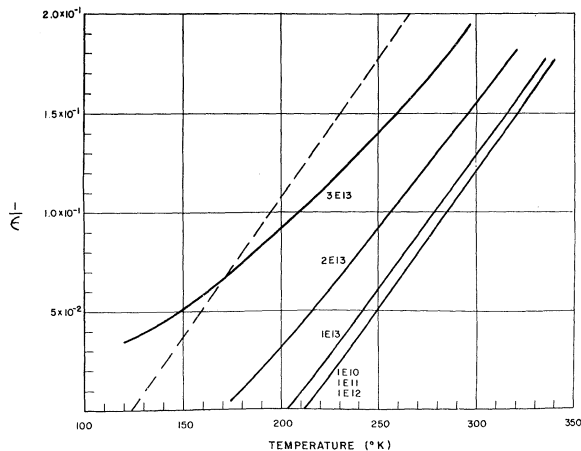


FIG. 1. Reciprocal dielectric constant as a function of temperature.

and develops curvature. The dotted line is the experimental result of Mayer and Bjorkstam⁴ for nondeuterated KH_2PO_4 . It does not appear, therefore, that tunneling can account for the isotope shift of the dielectric constant of this material.

If the damping times T_1 and T_2 are very long, or Γ_1 and Γ_2 are essentially equal to zero, the dielectric constant will exhibit resonant behavior even for the case for which the tunneling energy is small compared with the thermal energy. The dielectric constant is then given by

$$x' = \frac{\mu}{KT} \frac{\omega^2 f}{(\omega_0^2 - \omega^2)}, \quad \text{where } \omega_0^2 = \frac{f}{T} (T - T_c). \quad (8)$$

The absorption will peak at a frequency ω_0^2 , which has a temperature dependence similar to the temperature dependence of the soft mode in displacive paraelectric materials such as SrTiO_3 and KTaO_3 .

For the case of negligible tunneling frequency, the frequency-dependent dielectric constant has the following relaxation form⁵:

$$x' = \frac{\mu(T - T_c)}{KT^2} \frac{\Gamma^2}{\omega^2 + \bar{\omega}_0^2}, \quad \text{where } \bar{\omega}_0^2 = \frac{\Gamma^2}{T^2} (T - T_c)^2.$$

The absorption peaks at a frequency $\bar{\omega}_0^2$ which, as shown, has a stronger temperature dependence than the resonant case; i.e., the frequency now varies linearly with $T - T_c$. It is also interesting to note that, whereas the static dielectric constant obeys a Curie-Weiss law and therefore diverges as $T \rightarrow T_c$, the dielectric constant at any finite frequency goes to zero as $T \rightarrow T_c$.

Another case of interest is the following: Let us assume that T_1 is the shorter damping time of the two and it is this damping time at a given temperature that is sufficiently short to overdamp the resonance due to tunneling; since the effective damping time (the reciprocal of $\bar{\omega}_0$) increases as the reciprocal of $T - T_c$, one would expect that for temperatures sufficiently close to T_c , the dielectric constant will again exhibit a resonant-type behavior. In Fig. 2, the dielectric constant versus frequency is shown for several temperatures. At 300 and 126°K the dielectric constant is a monotonically decreasing function of frequency. At 0.1 and 0.01°K above the Curie temperature, the dielectric constant exhibits a resonant-type behavior. It decreases through zero, becomes neg-

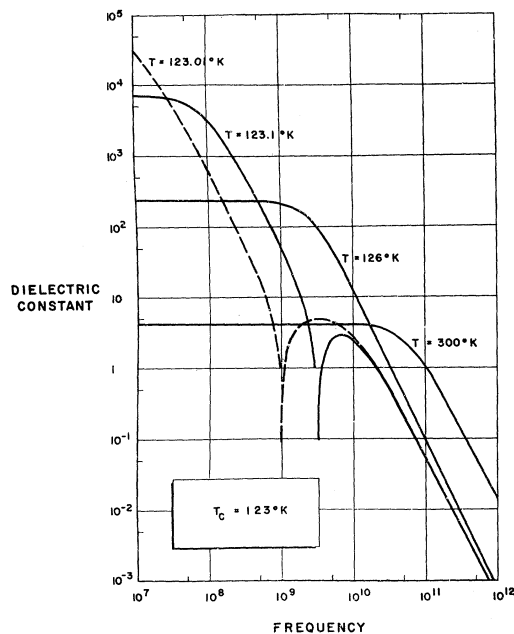


FIG. 2. Dielectric constant as a function of frequency.

ative before reaching a minimum, and then asymptotically approaches zero. In Fig. 2 the absolute value of the dielectric constant has been plotted.

There have been several experimental stud-

ies⁶ of the frequency-dependent dielectric constant of deuterated and nondeuterated KH_2PO_4 . Hill and Ichiki have measured the dielectric relaxation in deuterated KH_2PO_4 and have interpreted their results in terms of a Debye relaxation form for the dielectric constant that is averaged over a Gaussian distribution of relaxation times. One can obtain a similar expression to that of Hill and Ichiki by taking a Gaussian average over the relaxation time T_1 , with the tunneling frequency set equal to zero. In any subsequent analysis of the results of experiment, the preceding theory can be generalized, if need be, by averaging over relaxation times and energy separations in the presence of finite tunneling frequencies.

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LANDAU LEVELS AT SADDLE POINTS AND MAGNETOACOUSTIC EFFECTS

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The calculation of Landau quantization in a magnetic field, near a singular point of the surface $\epsilon = \text{const}$, is of primary importance for the study of magnetoacoustic effects in solids. Certain aspects of this problem have been considered by several authors. Lifshitz¹ gives a semiclassical treatment for a saddle point with a particular direction of the magnetic field. More recently, Baldareschi and Bassani² reconsidered the problem in connection with magneto-optical effects. They predict the disappearance of the Landau quantization at a singular point when the magnetic field falls outside a cone of angle θ (θ being determined by the effective masses).³

In this Letter we shall consider the problem in a more general aspect, i.e., the Landau quantization either near a singular point or near a saddle point, for an arbitrary orientation of the magnetic field. We shall show also that, for H outside the θ cone, Landau levels exist, in general, except for very special combinations of values of the energy ϵ and momentum ζ .

We shall use a semiclassical treatment that, at present, is the only approximation that takes into account the actual shape of the surface $\epsilon = \text{const}$. As a consequence the cyclotron frequency, which is a property of the full orbit on these surfaces, is correctly determined.