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Perturbational approach to glasslike low-energy excitations of interacting tunneling dipoles and quadrupoles

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Second- and third-order perturbation theory is used to calculate the low-energy spectrum of pairs of interacting tunneling dipoles (TD's) and tunneling quadrupoles (TQ's). The TD's or TQ's are assumed to be in an n-orientational potential well, determined by the local environment; hence assume n directions of orientation. For each of the orientations, the TD's or TQ's are allowed to tunnel only to their nearest-neighbor potential wells. We derive equations which relate the energy eigenvalues of a pair of interacting TD's or TQ's to the energies of the noninteracting tunneling Hamiltonian. We show that the pair has low-energy excitations provided the interaction potential is sufficiently greater than the tunneling matrix element. In particular we show that dilute concentrations of strongly interacting TQ's randomly distributed in a nondipolar crystalline host give low-energy excitations at low temperature T. Our calculation predicts that the very low T thermal properties of very small concentrations of eight-orientational TQ's (CN^- in KBr) are different than those of TD's and other TQ's dissolved in alkali halides.

I. INTRODUCTION

Amorphous materials and glasses[1] exhibit a set of anomalies[2–4] in their thermal and relaxation properties at low temperature. A phenomenological model based on two-level tunneling states[5,6] (TLS's) with an assumed constant density of states explained some of the observed low-temperature anomalies. There is, however, as yet no microscopic model for the tunneling states or for the constant density, i.e., no one knows what is tunneling or why the density of states is a constant.

Glasslike properties were also observed when tunneling electric dipoles (TD's) or elastic dipoles, denoted here as tunneling quadrupoles (TQ's), are randomly distributed in an alkali-halide host matrix. Examples for such tunneling impurities are OH^- dissolved in KCl (Refs. 7 and 8) forms a six-orientational (6-O) TD; Li^+ (Ref. 9) in KCl forms an eight-orientational (8-O) TD; CN^- in KBr forms an 8-O TQ.[10,11] There is a large group[12–19] of impurities which when dissolved in alkali halides form interacting TD's and/or TQ's.

To develop a microscopic model for interacting tunneling units, one of the authors has recently considered the statistical mechanics of very dilute interacting 8-O tunneling electric dipoles[20–22] and 4-O tunneling quadrupoles.[23,24] The idea involved in this approach is as follows: consider a system of TD's or TQ's randomly distributed in a crystalline host matrix. For dilute concentrations the free energy is approximated by the first two virial coefficients, i.e., terms up to c^2. For both of the above cases the calculations gave glasslike[23,24] properties, i.e., low-energy excitations with an approximate constant density of states from fundamental considerations for very low temperature T. The solution for the 8-O TD (Refs. 20–22) could be carried out relatively easily because its partition function could be expressed in terms of a product of Ising partition functions,[25] which greatly simplified the mathematics of the problem. For this specific dipole system the theory predicted glassy[20,21] properties in the density of states, specific heat, thermal conductivity, thermal expansion, and in the complex dielectric constant. Several of the glassy properties were observed for small concentrations of Li^+ ions in KCl.[9] For the 4-O TQ's one also finds low-energy excitations with an approximately constant density of states at low T. However, in order to obtain the excitation energies of a pair of n-orientational tunneling units one has to solve for the eigenvalues of an $n^2 \times n^2$ matrix analytically, which becomes quite difficult. Thus, to get the energy spectrum of the 8-O CN^- in KBr one has to find the eigenvalues of a 64×64 matrix.

The purpose of this paper is to solve for the low-energy excitations of a pair of n-orientational interacting TD's or TQ's using second- and third-order perturbation theory. Previous calculations[20–24] have shown that it is the *strongly* interacting tunneling units that determine the low-energy excitations of the system. We use this information to obtain the lowest excitation energies of the pair perturbationally. The zeroth-order Hamiltonian is assumed to be the interacting, or longitudinal, part. We then use the transverse, or tunneling part, of the Hamiltonian as the perturbation.

We use perturbation theory, since the exact solution for a pair becomes more difficult as the number of orientations (dimension of the tunneling matrix) increases. Furthermore exact solutions are easy to carry out only for specific symmetries, which in general do not exist in glasses. The perturbation approach does not suffer from these restrictions and applies to more general cases.

II. THE HAMILTONIAN

Consider N tunneling impurities placed at random positions $\mathbf{r}_i$ in a crystalline solid. Each impurity is assumed to have either an electric or elastic (but not both) dipole moment. The elastic moment will be denoted a quadrupole moment. The possible orientations of the dipoles and quadrupoles are determined by the local potential minima in the crystalline environment around the impurity.[7,8] We assume that the directions of orientation are not changed by the dipole-dipole or quadrupole-quadrupole interaction. For a cubic crystal one has usually 6, 8, or 12 orientations.[8]

The Hamiltonian is assumed to have the form $H = H^L + H^T$, where H^L is the interaction (longitudinal) Hamiltonian between all pairs of impurities. We approximate H^L by

$$H^L = \sum_{i<j}^{N} H_{ij}^L \ , \quad H_{ij}^L = -J_{ij}(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)^k \tag{1}$$

with $k = 1$ for TD's and $k = 2$ for TQ's;[23,24] H^T is the tunneling (transverse) Hamiltonian. Each site i is assumed to have a tunneling Hamiltonian H_i^T associated with it. Let $\boldsymbol{\mu}_i^{(\alpha)}$ be unit vectors at site i, position $\mathbf{r}_i$, which can point in either one of n directions $(\alpha = 1, \ldots, n)$. Let $\boldsymbol{\mu}_i$ be a vector operator at site i and $|\phi_i^{(\alpha)}\rangle$ be an eigenstate of $\boldsymbol{\mu}_i$, such that

$$\boldsymbol{\mu}_i|\phi_i^{(\alpha)}\rangle = \boldsymbol{\mu}_i^{(\alpha)}|\phi_i^{(\alpha)}\rangle \ , \quad \langle\phi_i^{(\alpha)}|\phi_i^{(\beta)}\rangle = \delta_{\alpha\beta} \ , \tag{2}$$

where $\alpha, \beta = 1, \ldots, n$ and $\delta_{\alpha\beta}$ is the Kronecker symbol. For simplicity we assume that the depth of each potential well is the same and that the directions of orientation $\boldsymbol{\mu}_i^{(\alpha)}$ are the same independent of site i; hence we can replace $\boldsymbol{\mu}_i^{(\alpha)}$ in Eq. (2) by $\boldsymbol{\mu}^{(\alpha)}$. Thus for a general n-fold potential the ground state may be multiple degenerate. Part or all of the degeneracy is removed when the dipoles or quadrupoles are allowed to tunnel to neighboring potential wells. We assume that *only* tunneling to the nearest-neighbor wells is important. Let the tunneling operator H_i^T be defined by

$$\langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\beta)}\rangle = \begin{cases} -\Delta \ , & \text{if } \alpha, \beta \text{ nearest-neighbor wells} \\ 0 \ , & \text{otherwise} \ , \end{cases} \tag{3}$$

with a tunneling matrix element $\Delta > 0$.[26] For N tunneling units the total Hamiltonian is given by

$$H = \sum_{i<j}^{N} H_{ij}^L + \sum_{i=1}^{N} H_i^T \ . \tag{4}$$

The tunneling operators for different sites i and j are independent. For example, let $\boldsymbol{\mu}_i$ be a classical Ising operator with eigenvalues ± 1. We can choose a matrix representation for $\boldsymbol{\mu}_i = I_2 \otimes \cdots \otimes I_2 \otimes \sigma_z \otimes \cdots \otimes I_2$, where $\otimes$ indicates a direct product, σ_z is the z component of the Pauli spin matrix, I_2 is the two-dimensional identity matrix, and σ_z appears at the ith position. According to Eq. (2), $|\phi_i^{(\alpha)}\rangle$ for this case will be two possible states representing spin up and down: $\boldsymbol{\mu}_i|\phi_i^{\uparrow}\rangle = |\phi_i^{\uparrow}\rangle$, $\boldsymbol{\mu}_i|\phi_i^{\downarrow}\rangle = -|\phi_i^{\downarrow}\rangle$. The tunneling Hamiltonian at site i is given by $H_i^T = -\Delta(I_2 \otimes \cdots \otimes I_2 \otimes \sigma_x \otimes \cdots \otimes I_2)$ with σ_x is the x component of the Pauli spin matrix and appears in the ith position.

III. PERTURBATIONAL APPROACH

We are interested in the low-energy excitations of the pair Hamiltonian

$$H_{ij}^P = H_{ij}^L + H_i^T + H_j^T \ . \tag{5}$$

We consider the case of a large *positive* interaction potential J_{ij}.[27] Our approach is to let the interaction H_{ij}^L be the zeroth-order Hamiltonian and then use the tunneling Hamiltonian as a perturbation. H_{ij}^L is already diagonal in the representation introduced in Eq. (2) and the perturbation is easily done up to second order. In the following we shall suppress the double subscript ij since we are dealing with a single pair only.

Let us label the energy eigenvalues and pair wave functions of the unperturbed Hamiltonian H^L as follows:

$$E_{\alpha\beta}^{(0)} = -J(\boldsymbol{\mu}^{(\alpha)} \cdot \boldsymbol{\mu}^{(\beta)})^k, \tag{6a}$$

$$\psi_{\alpha\beta} = \phi_i^{(\alpha)}\phi_j^{(\beta)} \tag{6b}$$

for $\alpha, \beta = 1, \ldots, n$ and $k = 1, 2$. Then, for $J > 0$, the ground-state energy is given by $-J$. The ground state is n-fold degenerate for TD's, since there are n positions for which the two TD's can be parallel to each other, i.e., $E_{\alpha\alpha}^{(0)} = -J$, $\alpha = 1, \ldots, n$. The degeneracy for the TQ's is also n-fold, unless there is 180° symmetry for which each pair of vectors can be parallel or antiparallel leading to the same energy $-J$. In this case the degeneracy will be $2n$. The eigenfunctions of the ground state are $\psi_{\alpha\alpha}$ for $\alpha = 1, \ldots, n$. For TQ's with 180° symmetry we denote the eigenstate of $-\boldsymbol{\mu}_i^{(\alpha)}$ by $\bar{\phi}_i^{(\alpha)}$. The additional n degenerate states are now given by $\bar{\psi}_{\alpha\alpha} = \bar{\phi}_i^{(\alpha)}\phi_j^{(\alpha)}$ for $-\boldsymbol{\mu}_i^{(\alpha)}$ and $\boldsymbol{\mu}_j^{(\alpha)}$ antiparallel.

We are only interested in the excitation energies which arise from the splitting of the ground-state energy, since higher energies are separated by a gap of order J and J is assumed to be large. Hence those higher energies will not contribute at low temperatures. Using Eq. (5) to obtain the first-order correction to H^L, we have to diagonalize

$$H_{\alpha\beta}^{(1)} = \langle\psi_{\alpha\alpha}|H^T|\psi_{\beta\beta}\rangle = 2\delta_{\alpha\beta}\langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\beta)}\rangle \ . \tag{7}$$

The factor of 2 arises because $H^T = H_i^T + H_j^T$ for a pair. Since no tunneling occurs within the same potential well $\langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\alpha)}\rangle = 0$, and Eq. (7) is identically zero. For a TQ with 180° symmetry the first-order perturbation matrix $H^{(1)}$ contains additional elements $\langle\bar{\psi}_{\alpha\alpha}|H^T|\psi_{\beta\beta}\rangle$. If we assume no 180° tunneling for a TQ we have $\langle\bar{\phi}_i^{(\alpha)}|H_i^T|\phi_i^{(\alpha)}\rangle = 0$ and $H^{(1)}$ is again identically zero. We have thus proved that the first-order perturbation leaves the eigenvalues degenerate.

Next we do second-order perturbation theory. For simplicity we again exclude the case of 180° TQ's at first. This case becomes somewhat more complicated and will be treated later on. The second-order corrections are obtained from diagonalizing

$$H^{(2)}_{\alpha\beta} = \sum_{\gamma\neq\delta} \frac{\langle\psi_{\alpha\alpha}|H^T|\psi_{\gamma\delta}\rangle\langle\psi_{\gamma\delta}|H^T|\psi_{\beta\beta}\rangle}{E^{(0)}_{\alpha\alpha} - E^{(0)}_{\gamma\delta}} \tag{8}$$

(see, for example, Ref. 28) with $E^{(0)}_{\alpha\alpha} = -J$ from Eq. (6a). The matrix elements inside the summation are given by

$$\langle\psi_{\alpha\alpha}|H^T|\psi_{\gamma\delta}\rangle = \delta_{\alpha\gamma}\langle\phi_j^{(\alpha)}|H_j^T|\phi_j^{(\delta)}\rangle + \delta_{\alpha\delta}\langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\gamma)}\rangle \,. \tag{9}$$

This expression is nonzero only if $\langle\phi_i^{(\gamma)}|H_i^T|\phi_i^{(\delta)}\rangle \neq 0$, which means γ and δ refer to nearest-neighbor wells. Hence we can replace $E^{(0)}_{\gamma\delta}$ in Eq. (8) by $-J\cos^k\theta$, where θ is the angle between directions of orientation of nearest-neighbor wells. Since we have already shown that Eq. (9) is zero for $\gamma = \delta$, we extend the summation in Eq. (8) over all γ's and δ's and make use of closure $\sum_{\gamma\delta}|\psi_{\gamma\delta}\rangle\langle\psi_{\gamma\delta}| = 1$. Thus, $H^{(2)}_{\alpha\beta} \sim \langle\psi_{\alpha\alpha}|(H^T)^2|\psi_{\beta\beta}\rangle$ and a simple multiplication leads to

$$H^{(2)}_{\alpha\beta} = \frac{-2(\delta_{\alpha\beta}\langle H_i^T\phi_i^{(\alpha)}|H_i^T\phi_i^{(\beta)}\rangle + \langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\beta)}\rangle^2)}{J(1-\cos^k\theta)} \,. \tag{10}$$

Let p be the number of nearest-neighbor wells. Using Eq. (3), Eq. (10) becomes

$$H^{(2)}_{\alpha\beta} = \frac{-2\Delta(\Delta p\delta_{\alpha\beta} + |\langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\beta)}\rangle|)}{J(1-\cos^k\theta)} \,. \tag{11}$$

The problem of obtaining the second-order energies is now reduced to the diagonalization of the tunneling Hamiltonian H_i^T.

Next we recalculate $H^{(2)}_{\alpha\beta}$ for TQ's with 180° symmetry. In this case the $2n$ degenerate states belonging to the ground-state energy $-J$ are $\psi_{\alpha\alpha}$ and $\bar{\psi}_{\alpha\alpha}$. We proceed as follows: let the $n\times n$ matrix $H_1^{(2)}$ be given by Eq. (8), but with the states $\psi_{\alpha\alpha}$ and $\bar{\psi}_{\alpha\alpha}$ excluded from the summation over the intermediate states. Let $H_2^{(2)}$ also be given by Eq. (8) but with $\psi_{\alpha\alpha}$ replaced by $\bar{\psi}_{\alpha\alpha}$, and the states $\psi_{\alpha\alpha}$ *and* $\bar{\psi}_{\alpha\alpha}$ again excluded from the summation over the intermediate states. Since the matrix representation of the second-order perturbation matrix $H^{(2)}$ has to be symmetric and n is even, we can write

$$H^{(2)} = \begin{pmatrix} H_1^{(2)} & H_2^{(2)} \\ H_2^{(2)} & H_1^{(2)} \end{pmatrix} \,. \tag{12}$$

The only difference between $H_1^{(2)}$ defined here and in Eq. (8) are terms involving elements of the form $\langle\bar{\psi}_{\alpha\alpha}|H^T|\psi_{\beta\beta}\rangle$. Since we assume no 180° tunneling (with the only exception of 2-O TD's) these elements are zero, and the matrix $H_1^{(2)}$ is identical to Eq. (11). To obtain $H_2^{(2)}$ we repeat the same calculation as before and find that Eq. (10) is replaced by

$$H^{(2)}_{2,\alpha\beta} = \frac{-1}{J(1-\cos^2\theta)}\left(\delta_{\alpha\beta}\langle H_i^T\bar{\phi}_i^{(\alpha)}|H_i^T\phi_i^{(\beta)}\rangle + \langle\bar{\phi}_i^{(\alpha)}|\phi_i^{(\beta)}\rangle\langle H_j^T\phi_j^{(\alpha)}|H_j^T\phi_j^{(\beta)}\rangle + 2\langle\phi_j^{(\alpha)}|H_j^T|\phi_j^{(\beta)}\rangle\langle\bar{\phi}_i^{(\alpha)}|H_i^T|\phi_i^{(\beta)}\rangle\right). \tag{13}$$

We now treat two cases separately:

(i) Assume that the directions of orientation of $\boldsymbol{\mu}^{(\alpha)}$ and $-\boldsymbol{\mu}^{(\alpha)}$ are such that there are common nearest-neighbor wells. It is clear that in this case all $\boldsymbol{\mu}^{(\alpha)}$'s must be perpendicular to each other. For example, assume that each TQ can have four orientations restricted to a plane. Let us designate the orientations of $\boldsymbol{\mu}^{(\alpha)}$ by $\pm x$ and $\pm y$. Let then $\boldsymbol{\mu}^{(1)} = +x$ and $-\boldsymbol{\mu}^{(1)} = -x$. The nearest-neighbor wells lie in the directions $\pm y$. Thus $\boldsymbol{\mu}^{(\alpha)}$ and $-\boldsymbol{\mu}^{(\alpha)}$ have two nearest-neighbor wells in common. With $\langle H_i^T\bar{\phi}_i^{(\alpha)}|H_i^T\phi_i^{(\alpha)}\rangle = p\Delta^2$ and $\theta = 90^0$, Eq. (13) becomes

$$\begin{aligned} H^{(2)}_{2,\alpha\beta} = \frac{-\Delta}{J}[\, & \Delta p(\delta_{\alpha\beta} + \langle\bar{\phi}_i^{(\alpha)}|\phi_i^{(\beta)}\rangle) \\ & +2|\langle\phi_i^{(\alpha)}|H_i^T|\phi_i^{(\beta)}\rangle|]. \end{aligned} \tag{14}$$

For this case $H^{(2)}$ in Eq. (12) can be readily diagonalized using the matrices derived in Eqs. (14) and (11). The result is given in Eq. (16) in the next section.

(ii) On the other hand, for 8-O TQ's, $\boldsymbol{\mu}^{(\alpha)}$ and $-\boldsymbol{\mu}^{(\alpha)}$ have no nearest-neighbor wells in common. Evaluating Eq. (13) we find that all matrix elements are zero. Thus $H_2^{(2)} = 0$ and $H^{(2)}$ in Eq. (12) is equal to $I_2 \otimes H_1^{(2)}$. The second-order energies in this case are the same as obtained from Eq. (11), except that each energy is now doubly degenerate.

IV. LOW-ENERGY EXCITATIONS

Summarizing the result of Sec. III we have three different cases:

(i) For TD's and TQ's with no 180° symmetry the second-order energies can be obtained from diagonalizing the matrix in Eq. (11). Let λ_i be the ith eigenvalue of the tunneling Hamiltonian H_i^T defined in Eq. (3). Then the lowest excitation energies are given by

$$E_i = -J - \frac{2\Delta(p\Delta - \lambda_i)}{J(1-\cos^k\theta)} + O\left(\frac{\Delta^3}{J^2}\right) \,,\quad i = 1,\ldots,n. \tag{15}$$

(ii) For TQ's with 180° symmetry we have the same result but all energies are in addition doubly degenerate.

(iii) For TQ's with all $\boldsymbol{\mu}^{(\alpha)}$'s perpendicular to each other, $H^{(2)}$ in Eq. (12) has to be diagonalized using the matrices $H_1^{(2)}$ given in Eq. (11) and $H_2^{(2)}$ given in Eq. (14). It is straightforward to show that the energies up to order Δ^2/J are

$$\begin{aligned} E_0 &= -J - \frac{8p\Delta^2}{J} \quad (n_0 = 1), \\ E_1 &= -J - \frac{(4p-8)\Delta^2}{J} \quad (n_1 = d-1), \\ E_2 &= -J - \frac{2p\Delta^2}{J} \quad (n_2 = 2d), \\ E_3 &= -J \quad (n_3 = d) \;, \end{aligned} \tag{16}$$

where $d = 2, 3, \ldots$ is the dimensionality of the problem and $p = 2d - 2$. We have included the degeneracy n_i of the state in parentheses.

The ground state E_0 in Eq. (15) corresponds to the largest negative eigenvalue of H_i^T given by $\lambda_0 = -p\Delta$. Since λ_0 is always nondegenerate,[29]

$$E_0 = -J - \frac{4p\Delta^2}{J(1-\cos^k\theta)} + O\left(\frac{\Delta^3}{J^2}\right) \;. \tag{17}$$

Thus the lowest excitation energies in Eqs. (15) and (16) are of the order Δ^2/J for cases (i) and (iii). This is a very important result to understand. The stronger the interaction potential J, the lower the excitation energies. Thus contrary to usual expectations it is the *strongly* interacting TD's or TQ's that contribute to the low-T behavior.

For TQ's with 180° symmetry, however, E_0 in Eq. (17) is still doubly degenerate in second-order perturbation. Since the final ground state is the nondegenerate symmetric state, we expect the degeneracy to be lifted in some higher order. The degenerate eigenfunctions of E_0 are obtained by solving for the two eigenvectors of λ_0 using Eq. (12). They are

$$\psi_1 = \frac{1}{\sqrt{n}} \sum_{\alpha=1}^{n} \psi_{\alpha\alpha} \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{n}} \sum_{\alpha=1}^{n} \bar{\psi}_{\alpha\alpha} \tag{18}$$

or any linear combination of ψ_1 and ψ_2. For the final nondegenerate states we make the ansatz

$$\begin{aligned} \psi_g &= \frac{1}{\sqrt{2n}} \sum_{\alpha=1}^{n} (\psi_{\alpha\alpha} + \bar{\psi}_{\alpha\alpha}), \\ \psi_u &= \frac{1}{\sqrt{2n}} \sum_{\alpha=1}^{n} (\psi_{\alpha\alpha} - \bar{\psi}_{\alpha\alpha}) \;. \end{aligned} \tag{19}$$

Using Eq. (19) it is easy to show that third-order perturbation leads to

$$E_0 = -J - \frac{4p\Delta^2}{J\sin^2\theta} + E_{g/u}^{(3)} \;, \tag{20}$$

where

$$\begin{aligned} E_{g/u}^{(3)} = \frac{\langle \psi_{g/u} | (H^T)^3 | \psi_{g/u} \rangle}{J^2 \sin^4\theta} = {} & \frac{8}{J^2 \sin^4\theta} \\ & \times [\langle \phi_i^{(1)} | (H_i^T)^3 | \phi_i^{(1)} \rangle \pm \langle \phi_i^{(1)} | (H_i^T)^3 | \bar{\phi}_i^{(1)} \rangle] \;. \end{aligned} \tag{21}$$

Given a matrix representation for H_i^T, Eq. (21) can be easily evaluated for different geometries. For the physically important cases of 8-O TQ's and 12-O TQ's, we find that

$$E_{g/u}^{(3)} = \mp \frac{243\Delta^3}{4J^2} \quad \text{(8-O TQ)}, \tag{22a}$$

$$E_{g/u}^{(3)} = -(1 \pm 1)\frac{512\Delta^3}{9J^2} \quad \text{(12-O TQ)}. \tag{22b}$$

In the treatment up to now the interaction potential J was considered to be positive. We have shown that for large positive values of $J \gg \Delta$ the pair Hamiltonian, Eq. (5), has low-energy excitations of the order Δ^2/J given in Eqs. (15) and (16). For the 8-O and 12-O TQ's the lowest excitation energies are proportional to Δ^3/J^2 as is seen in Eq. (22). It is those low-energy excitations that determine the low-T thermal properties below $T = \Delta/k$.[27]

Our discussion in Sec. III applies to positive J only. For negative J the ground-state energy of the unperturbed Hamiltonian H^L is not necessarily given by $-|J|$ as can be seen from Eq. (6a). In general the degeneracy of the ground state is removed in first order, unless the first-order perturbation matrix, $H^{(1)}$ in Eq. (7), is zero. This is so because the largest negative eigenvalue of $H^{(1)}$ (the ground-state energy) is nondegenerate.[29] Thus, unless $H^{(1)}$ is identically zero, the lowest excitation energies resulting from large negative J will be of order Δ. Therefore it will give a negligible contribution to the thermal properties at low T ($T < \Delta/k$) compared to that from large (positive) values of J. In particular the 8-O TQ has no low-energy excitations less than Δ for negative J.

The only case not treated so far that remains to be investigated is when $H^{(1)}$ is identically zero and J is negative. For this case two important situations arise: (i) TD's with orientations having 180° symmetry. Here the excitation energies do not change if J is replaced by $-J$ as can be seen from Eq. (6a) by setting $k = 1$. Equation (15) still holds for negative J, provided J is replaced by its magnitude. (ii) 4-O TQ's, for which one can show[23,24] that the excitation energies derived in Eq. (16) ($d = 2$) are symmetric in $\pm J$.[30]

Knowing the lowest excitation energies [Eqs. (15), (16), (22)] we can now proceed to obtain the very low T thermal properties from the partition function.

V. HEAT CAPACITY FOR DILUTE TD AND TQ GLASSES AT VERY LOW TEMPERATURE

In this section we derive the low-temperature specific heat and the density of excitation energies for a system of interacting dilute TD's and TQ's. We assume that the tunneling units are randomly distributed in a nonpolar host medium. Further we assume an interaction potential of the form $J_{ij} = \pm b r_{ij}^{-3}$, where r_{ij} is the distance between two impurities and b a positive constant. The ± indicates the interaction is competing with the same probability for being negative and positive. Using the Hamiltonian in Eq. (4), we expand the free energy into a virial expansion in the impurity concentration c for sufficiently low c up to c^2. Following Ref. 23 the contributions to the heat capacity $C = C^{(1)} + C^{(2)}$ from the first and second virial coefficient are

$$C^{(1)}(\beta) = cN_0 k\beta^2 \frac{\partial^2}{\partial\beta^2}\left(\ln \mathrm{Tr}\; e^{-\beta H_i^T}\right), \tag{23a}$$

$$C^{(2)}(\beta) = \frac{\pi c^2 N_0 b k \beta^2}{3v} \int_{-J_0}^{J_0} \frac{\partial^2}{\partial\beta^2}\left(\ln \mathrm{Tr}\; e^{-\beta[H_{ij}^L(J)+H_i^T+H_j^T]} - \ln \mathrm{Tr}\; e^{-\beta[H_i^T+H_j^T]}\right)\frac{dJ}{J^2}\,, \tag{23b}$$

where N_0 is the number of sites available to the impurities in the crystal, $c = N/N_0$ the concentration, N the number of impurities, $v = V/N_0$ the volume per site, k Boltzmann's constant, $\beta = (kT)^{-1}$, $J_0 = b r_0^{-3}$ the near-neighbor interaction, and the trace (Tr) is over the eigenvalues of the quantum-mechanical operators in the exponent.

The first virial coefficient contributes the usual Schottky anomaly in the specific heat. We first consider the cases (i) and (iii) from Sec. IV. For very low T, i.e., $\exp(-\beta\Delta) \ll 1$, the contribution from $\mathrm{Tr}\exp(-\beta H_i^T)$ to the specific heat in Eq. (23b) becomes exponentially small and will be neglected. The contribution to $C^{(2)}$ from small J values vanishes exponentially as well, since those excitations are of the order of Δ. Let E_i be the lowest excitation energies given in Eqs. (15) or (16). We can approximate Eq. (23b) by

$$C^{(2)} \approx \frac{2\pi c^2 N_0 b k \beta^2}{3v} \int_0^{J_0} \frac{\partial^2}{\partial\beta^2}\left(\ln \sum_i e^{-\beta E_i}\right)\frac{dJ}{J^2}\,. \tag{24}$$

The factor of 2 indicates that there is a contribution from negative J to the specific heat for 180° TD's and 4-O TQ's, for which the integral in Eq. (23b) is symmetric in J.[31]

As examples for case (iii) we consider 4-O TQ's ($d = 2$) and 6-O TQ's ($d = 3$) in Eq. (16). For $kT \gg \Delta^2/J_0$ we let $J_0 \to \infty$ and obtain from Eq. (24)

$$C^{(2)} \approx \frac{c^2 N_0 b k^2 T}{\Delta^2 v} \times \int_0^\infty \frac{32\pi x^2(3pe^{-6x} + 8e^{-8x} + pe^{-14x})}{p^2(1 + 2pe^{-6x} + 3e^{-8x})^2}\,dx. \tag{25}$$

The numerical values of the integrals in Eq. (25) are 1.07 and 0.36 for $p = 2$ and $p = 4$, respectively. For case (i) Eqs. (15) and (24) together with $J_0 \to \infty$ yield

$$C^{(2)} \approx \frac{2\pi c b k T(1 - \cos^k\theta)}{6\Delta v} \int_0^\infty C^{(1)}(\beta)\,d\beta\,, \tag{26}$$

where we have used the definition of $C^{(1)}$ in Eq. (23a). For very low temperature $T \ll \Delta/k$, but sufficiently large concentration c, we have $C^{(1)} \ll C^{(2)}$ and the specific heat is linear in T in both cases. For $T < T_0$ and $T_0 = \Delta^2/(kJ_0)$ the specific heat is expected to drop off exponentially. This is so because the lowest excitation energy δE is determined by the largest value of J, i.e., J_0, where J_0 is the nearest-neighbor interaction. From Eqs. (15) and (16), δE is predicted to be of order Δ^2/J_0.

We next show that, except for the 8-O TQ's, the density of states $P(E)$ is approximately a constant for small excitation energies E. Equations (15) and (16) tell us that the lowest excitation energies E are proportional to J^{-1} for large J. With $P(J) \sim J^{-2}$,[32] we find that

$$P(E) = P(J)\left|\frac{dJ}{dE}\right| \approx \text{const} \tag{27}$$

for small values of E.

We next discuss the predicted low-temperature specific heat and density of states for 8-O TQ's (ii). From second-order perturbation theory we find that the lowest excitation energies E are proportional to J^{-1}. However, the ground state is still degenerate in second order. Third-order perturbation theory gives $E \sim J^{-2}$ and removes the degeneracy of the ground state. Using the perturbed eigenvalues we can calculate $P(E)$ from Eq. (27) and find that $P(E)$ is approximately constant for $E \sim J^{-1}$, whereas $P(E)$ goes like $E^{-1/2}$ for $E \sim J^{-2}$. For even lower energies $P(E)$ approaches zero, since there are no states below $kT \sim \Delta^3/J_0^2$, as can be seen from Eq. (22a). Thus the 8-O TQ is predicted to have a different behavior at sufficiently low T than the 4-O or 6-O TQ, or any of the TD's discussed previously. This is a most interesting result which could in principle be verified in a specific-heat experiment.

Finally we discuss the predicted specific heat for 8-O TQ's. The 2^d-O tunneling Hamiltonian is identical to the tunneling Hamiltonian of d 2-O tunneling Ising spins;[25] thus $\mathrm{Tr}\exp(-\beta H_i^T) = [2\cosh(\Delta\beta)]^3$ leading to the Schottky specific heat

$$C^{(1)} = 3cN_0 k[\Delta\beta\,\mathrm{sech}(\Delta\beta)]^2\,. \tag{28}$$

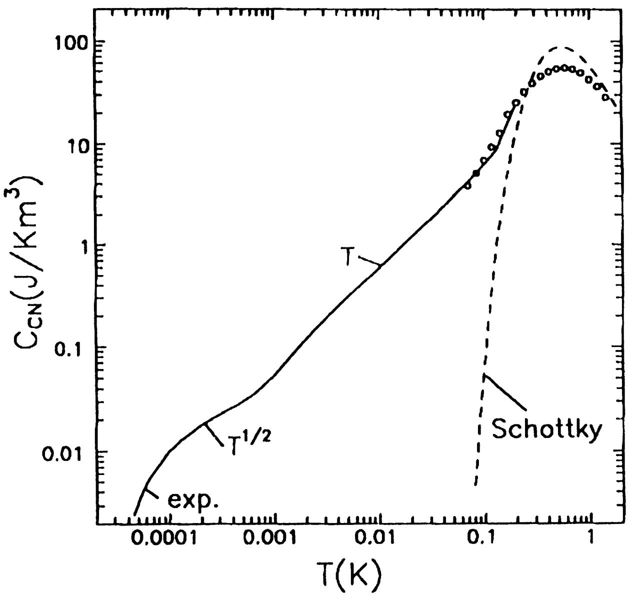

FIG. 1. Heat capacity of 340-ppm CN^- in KBr. The measured values (open circles) are taken from Ref. 10 and show the excess specific heat from the CN^- impurities without the Debye phonon specific heat. The dashed line shows the Schottky specific heat $C^{(1)}$ calculated from Eq. (28). The solid line is the predicted specific heat per unit volume obtained from the sum of $C^{(1)}$ and $C^{(2)}$. The calculation of $C^{(2)}$ was done using Eq. (24) together with the excitation energies from Eqs. (15) and (22a). We have assumed values of $\Delta/k = 0.65$ K and $J_0/k = 450$ K (Ref. 33) in agreement with Ref. 10. The specific heat is greatly enhanced by $C^{(2)}$, because $C^{(1)}$ vanishes exponentially below $T \approx 0.2$ K. From Eq. (29) the specific heat for CN^- in KBr is expected to be linear down to $T \approx 1$ mK. For even lower temperature the specific heat is described by Eq. (30). Below $T \approx 0.1$ mK the specific heat vanishes exponentially. Our perturbation calculation applies only to temperatures below 0.2 K. Previous exact calculations (Refs. 21–24) have shown that for $T \sim T_m$, $C^{(2)}$ becomes negative, which explains why the Schottky specific heat exceeds the experimental values.

Let $T_m = \Delta/(1.2k)$ be the temperature at which the maximum of the Schottky specific heat occurs. As the temperature is lowered there will be an excess specific heat from the pairs, which dominates at sufficiently low $T < T_m$, since $C^{(1)}$ becomes exponentially small. The specific heat is predicted to be approximately proportional to T, since $E \sim J^{-1}$. Using Eq. (26) we find that

$$C^{(2)} \approx \frac{\pi^3 \sqrt{2} c^2 N_0 J_0 k^2 T}{27\Delta^2} . \tag{29}$$

As T is further lowered below $T \lesssim \Delta^2/(kJ_0)$, $C^{(2)}$ changes from a linear T regime to a $T^{1/2}$ regime. The value of $C^{(2)}$ can be obtained from Eqs. (24) and (22a),

$$C^{(2)} \approx \frac{\zeta(3/2)(2-\sqrt{2})}{72\sqrt{3}} \left(\frac{\pi k}{\Delta}\right)^{3/2} c^2 N_0 J_0 T^{1/2} , \tag{30}$$

where ζ is the zeta function. At even lower temperature $C^{(2)}$ will become exponentially small, since there are no states below $T \approx 243\Delta^3/(2kJ_0^2)$, because of the finite cutoff at the near-neighbor J_0. The predicted specific heat for 340-ppm CN^- is shown in Fig. 1 together with the experimental data from Ref. 10 (open circles). The dashed line represents the Schottky specific heat, Eq. (28), which vanishes exponentially for $kT < \Delta$. The solid line is the result of a computer calculation using Eq. (24) and the excitation energies from Eqs. (15) and (22a).[33] The total specific heat due to the CN^- impurities was obtained by adding the Schottky contribution $C^{(1)}$. We expect our perturbation calculation to break down at $T \approx 0.2$ K (see caption for Fig. 1). Whereas the experimental results on 340-ppm CN^- in KBr agree with our predictions and the specific heat is greatly enhanced from its Schottky contribution, no experimental data exists at which the linear or $T^{1/2}$ region of $C(T)$ is exhibited. It would therefore be important to measure $C(T)$ for the 340-ppm sample below $0.1K$.

An alternative explanation for the low-energy excitations has been suggested by Pohl and Meissner[34] and this question has been discussed previously by Klein.[35,24] Since we deal here with very low concentrations, our work does not apply to concentrated mixed crystals discussed by Sethna and co-workers.[36]

VI. CONCLUSION

We have used second- and third-order perturbation theory to obtain low-energy excitations from pairs of *strongly* interacting tunneling dipoles (TD's) and tunneling quadrupoles (TQ's). The excitation energies obtained are used to derive the low-temperature specific heat of very dilute concentrations of TD's or TQ's. For the eight-orientational TD's and the four-orientational TQ's the results agree with previous exact evaluations of the pair excitations. However, the perturbation method developed here is simpler, and more general than previous exact solutions for some specific orientations of TD's and TQ's. For the eight-orientational TQ's we find a deviation from the linear specific heat and the constant density of states predicted for TD's and four- or six-orientational TQ's. Applying our result to the case of low concentrations ($c < 10^{-3}$) of eight-orientational TQ's (i.e., CN^- in KBr), we find that the low-temperature thermal properties are different than those of the problems treated previously.[21–24]

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[27] It is easy to show that for small interactions, i.e., $|J_{ij}| \lesssim \Delta$, the excitation energies are of the order of the tunneling matrix element Δ; hence they give no low-energy excitations below Δ.

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[29] This is a special property of *doubly stochastic (0,1)-matrices.* See, for example, H. Minc, *Nonnegative Matrices* (Wiley, New York, 1988), Theorem 4.3, p. 14 and Theorem 1.1, p. 24.

[30] Another case is the 12-O TQ. Here the exact perturbation calculation has to be carried out in order to find the lowest excitation energies for large negative values of J. We are not going to pursue this problem further, although in principle this calculation does not provide any additional difficulties.

[31] It is easy to show that the integrand remains finite in the limit $J \to 0$.

[32] This follows from $J \sim r^{-3}$ and $P(\mathbf{r}) = 1/V$, where V is the total volume.

[33] The exact values for Δ/k and J_0/k are not known. It is argued (Ref. 10) that $\Delta/k \approx 0.7$ K and J_0/k is of the order of 420 K. Note that the tunneling matrix element Δ is defined here as one-half the value used in Ref. 10.

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