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Two-level tunneling states and the constant density of states in quadrupolar glasses

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Starting from a microscopic Hamiltonian for interacting quadrupoles (QP's) randomly placed in a solid, we obtain a model for the two-level tunneling states and the constant density of states in quadrupolar glasses from fundamentals. We use perturbation theory to show that in a quenched system of strongly interacting QP's, 180° reorientational flips of single QP's give low-energy excitations. These low-energy excitations arise from our starting Hamiltonian and are described in the form of an effective two-level state (TLS) Hamiltonian. For intermediate concentrations of CN^- ions dissolved in KBr, we propose that it is the center of mass displacement of the CN^- ion that leads to a constant density of states rather than the electric dipole interaction between the cyanides, as was proposed earlier by Sethna *et al.* The physical mechanism for the glasslike low-energy excitations proposed here thus involves 180° tunneling flips with a translation of the center of mass of the tunneling unit. We then show that it is the elastic random fields experienced by the QP's that give a constant density of states and specific heat linear in temperature and logarithmic in time and that this result is not sensitive to the exact form of the QP-QP interaction or the presence of a weak electric dipole interaction. We suggest that the concepts developed for KCN-KBr mixed crystals may also help to explain the quasiuniversal low-temperature thermal properties of canonical and other quadrupolar glasses.

I. INTRODUCTION

At low temperatures amorphous materials and glasses[1] exhibit distinct anomalies in their thermal, acoustic, and dielectric properties[2,3] known to arise from the glassy state. For temperatures T below 1 K the specific heat has a component linear in T with a logarithmic time dependence. The low-T thermal conductivity is proportional to T^2 and develops a plateau around 2–10 K. The frequency dependent dielectric susceptibility $\epsilon(\omega, T)$ shows long relaxation times in addition to a $\ln T$ term in its real part. The thermal expansion coefficient is also greatly enhanced from that of its crystalline counterpart. In addition phonon echoes and saturation of the ultrasonic absorption have been observed.[4] The above properties (denoted in this paper as glasslike properties) are within the same order of magnitude for many glassy materials and are often referred to as quasiuniversal properties of glasses.[3]

To explain these anomalies, a phenomenological model was proposed[5,6] based on the assumption that glasses contain localized two-level systems (TLS's) with a random distribution of barrier heights and a random distribution of asymmetry energies. It was also proposed[5,6] that below $T \lesssim 1$ K quantum-mechanical tunneling is the primary relaxation mechanism between the two potential wells. An ad hoc assumed constant density of low-energy excitations could then explain a number of experimentally observed properties of glasses, including time dependent effects, supporting the idea of the TLS tunneling model. However, the TLS tunneling model gave no information on (i) what is the nature of the tunneling unit, and (ii) why the density of states for low energies is a constant.

In spite of the considerable effort to understand the low-temperature universal properties of canonical glasses[7] from a microscopic point of view, little progress has been made in this direction over the past 20 years. One of the difficulties was the lack of a microscopic Hamiltonian for canonical glasses. In an attempt to clarify the nature of the "glassy" state, theorists have treated, instead of canonical glasses, systems which have similar experimental properties to glasses, but for which microscopic model Hamiltonians could be formulated. Among these systems are the so-called orientational glasses (OG's) which have attracted a lot of attention over the last years.[8]

Orientational glasses (OG's) are systems in which molecules with a dipole, quadrupole (QP), or higher moment randomly occupy regular lattice sites in a crystalline solid. The impurity molecules introduce additional rotational degrees of freedom and interact with each other. For example in the prototype quadrupolar glass $(KCN)_x$ $(KBr)_{1-x}$ (x denotes the fractional concentration of CN^- ions) the cyanide molecule has a large elastic dipole moment (usually referred to as a quadrupole moment) and a relatively small electric dipole moment.[9] Below a certain freezing temperature $T_f(x)$ this special system exhibits glasslike properties for intermediate concentrations x between $x_{c1} \lesssim x \lesssim x_{c2}$, where

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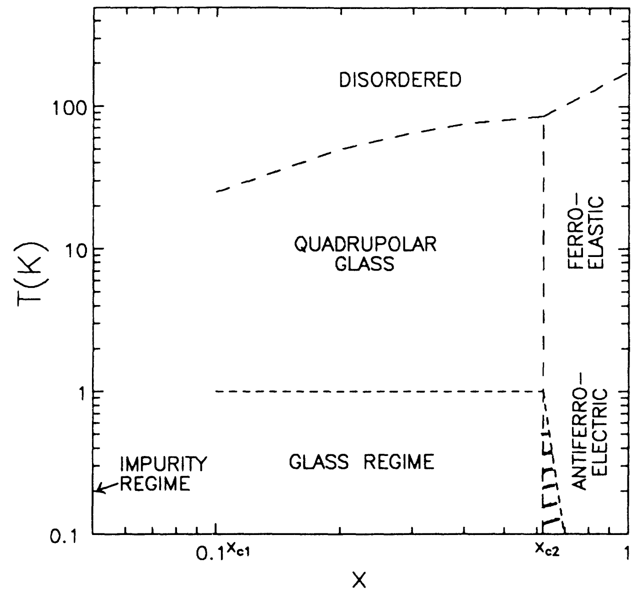

FIG. 1. Schematic concentration-temperature phase diagram for $(KCN)_x$ $(KBr)_{1-x}$ mixed crystals. Note that the glass regime and the ferroelectric regime overlap slightly. The term "disorder" refers to the directions of the elongated CN^- molecules. The value of x_{c1} is not well defined in alkali-cyanide alkali-halide crystals; $x_{c2} = 0.62$. The very dilute case ("impurity regime") has been treated previously in Refs. 44-46 and will be discussed in Sec. II B. The "glass regime" will be treated in Sec. III.

$x_{c1} \approx 0.1$ and $x_{c2} \approx 0.6$.[10-14] In this concentration range the low-temperature state is characterized by quenched orientational disorder of quasi-frozen-in cyanide QP's.[15] The "frozen-in" state[16] is referred to in the literature as orientational or quadrupolar glass phase (Fig. 1). Upon lowering the temperature below 1 K, KCN-KBr mixed crystals exhibit glasslike properties very similar to those of canonical glasses.[17,18]

A quadrupolar glass (QG) state is also observed in a broad concentration range in alkali-cyanide systems like KCN-NaCN or KCN-RbCN,[19,20] in N_2-Ar and N_2-Ar-CO mixtures[21] and in *paraortho* H_2 solutions,[22,23] to name only a few examples.[8] All these systems show very similar phase diagrams,[10,24] despite the fact that the dominant interactions between the moments may be quite different in nature: in alkali-cyanide alkali-halide crystals, like KCN-KBr or KCN-KCl, elastic dipole interaction between the cyanide ions dominates.[17,18] Elastic forces are also believed to be important in alkali-cyanide mixtures like KCN-NaCN, but there are also strong random elastic fields experienced by the cyanide molecules arising from the volume mismatch between the alkali atoms.[19,20] In the *orthopara* hydrogen mixtures o-H_2 p-H_2 electric QP interaction between the *ortho*-H_2 molecules dominates.[22,23] In N_2-Ar and N_2-Ar-CO it is the electric QP moment of N_2 and CO and nearest-neighbor-atom attraction and repulsion[21] that is believed to play an important role in the freezing process. Since the low-temperature state for intermediate concentrations is mainly determined by the dominant quadrupolar interaction forces,[24] we will denote these materials as quadrupolar glasses (QG's).

In all the systems mentioned above nonspherical molecules (CN^-, N_2, CO, o-H_2) substitute randomly host atoms or molecules (Br^-, Cl^-, Ar, p-H_2) on regular lattice sites. This allows one, at least in principle, to model such systems in terms of a microscopic Hamiltonian involving the host and impurities. A similar separation of the system into host and impurity is not obvious for canonical glasses. However, since there are no microscopic models for canonical glasses, one hopes that the study of OG's may finally yield further insight into the real glass problem.

The purpose of this paper is to give a microscopic explanation for the low-energy excitations and heat capacity of QG's and to derive the TLS model and a constant density of states from a model Hamiltonian for a glassy material. In this paper we focus on the very low-temperature and intermediate-concentration regime of QG's (the "glass regime" in Fig. 1), and we are not concerned with the glass transition[25,26] that occurs at higher temperatures or structural phase transitions of the solid.[27] We thus concentrate on the glasslike properties of QG's and not so much on the elastic spin-glass aspect of the problem which is still a subject of controversy.[28]

In our model we will start from a microscopic QG Hamiltonian describing the QP-QP interaction[25] and the interaction of the QP's with static random strain fields.[26] For example in KCN-KBr these random strains arise from the dilution of the Br^- host atoms by the randomly placed cyanide QP's,[17,26] leading to static strain fields that couple to the orientational degrees of freedom of the CN^- ions. These random fields have received a lot of attention over the last few years and their importance in connection with the glass transition seems by now well established.[17-20] Since we are only concerned with the orientational degrees of freedom of the QP's and the random fields couple linearly to the QP moment, we will denote the random fields here as random "external" fields in distinction from the "internal" quadrupolar mean field arising from the QP-QP elastic or electric interaction. Starting from a model Hamiltonian for the orientational degrees of freedom of the QP's, we derive an effective TLS Hamiltonian for the low-energy excitations using first-order perturbation theory. We propose here that the low-energy excitations responsible for the glasslike behavior arise from single QP's undergoing 180° tunneling reorientations simultaneously coupled with a small translational displacement of the tunneling unit. Such a small center-of-mass displacement of the CN^- ion is, for example, expected in KCN-KBr mixed crystals but also in other materials. We show that a specific heat linear in T and a constant density of states arises without using the effect of the weak electric dipole interaction between the QP's. The latter was an essential component of a model proposed earlier by Sethna *et al.*[29-31] In the Sethna model[29-31] the low-energy excitations were also related to 180° tunneling flips of QP's, however, in this model the *electric* dipole-dipole interaction played a crucial role in the heat capacity. Furthermore, in their model a Gaussian-distributed internal quadrupolar mean field was assumed to fit the experimental data for the specific heat.[29,30] It has been suggested that (i) there are difficulties with the Gaussian distribution which predicts a finite probability for zero fields, since the "true" internal-field distribution is believed to develop a "hole" for small fields,[32] and (ii) the specific heat of N_2-Ar-CO mixtures, which is very similar to that of KCN-KBr, is independent of the CO electric dipole moment,[21] showing that the dipole moment, at least in N_2-Ar-CO, plays no crucial role in the specific heat. Both of the above difficulties are absent in our derivation since the electric dipole moment plays no important role in our model, and a constant density of states arises from static "external" random fields. Our physical mechanism is therefore very different from that proposed by Sethna *et al.*[29–31] Since the Sethna model is widely quoted in the literature, we will discuss the differences between our model and theirs in more detail later on. Moreover, we do not make use of mean-field theory known to be very problematic in systems with random and competing interactions.[32–34] To our knowledge this is the first model which examines the effect of the static random fields on the very low-temperature thermal properties of QG's and obtains the TLS model with a constant density of states from fundamental considerations.

This paper is organized as follows. In Sec. II we give a brief introduction to orientational glasses and quadrupolar glasses in particular.[8] We also review some of our own theoretical developments for the dilute systems which could be rather rigorously established. In particular, the result that it is the *strong* interactions that give rise to *low-energy* excitations in dilute systems, will lead us to the approach proposed in Sec. III. In Sec. III we introduce our physical model in detail and derive an effective TLS Hamiltonian and a constant density of states for the low-energy excitations in KCN-KBr using perturbation theory. Finally in Sec. IV we discuss how the same ideas could apply to other systems than KCN-KBr mixed crystals.

II. QUADRUPOLAR GLASSES: BACKGROUND

In this section we focus on the low-temperature thermal properties[8] of QG's. Consider randomly substituted impurity molecules dissolved in a crystalline nonpolar host matrix. The impurities carry a dipole moment, a quadrupole moment, or both and are randomly placed on lattice sites in the crystal. In addition to their translational modes the moments have orientational degrees of freedom and interact.[35,36] Depending on the dominant interaction between the multipolar moments, one distinguishes between dipolar glasses, quadrupolar glasses, etc.[24] In all of the mixed crystals mentioned in Sec. I, the impurities were to a first approximation head-tail invariant. For our purpose the important consequence of this is (Sec. III) that the inversion symmetry of a QP opens additional relaxation channels which are absent for instance in electric dipolar glasses. These secondary or β relaxations are 180° QP flips that will give the low-energy excitations. The reason for this is that for head-tail symmetric impurities, 180° flips leave the dominant quadrupolar interaction invariant;[36] hence the system possesses a multiple degenerate ground state. A small perturbation will lift this degeneracy and give low-energy excitations. Later on in Sec. III we will suggest that it is these excitations that are intrinsically related to the glasslike behavior of QG's. Therefore we can approach the problem perturbationally and avoid many of the complications arising from the elastic spin-glass character of the problem which will not be our concern in this paper.[28]

A. Intermediate and high concentrations

The properties of the prototype quadrupolar glass KCN-KBr have been measured extensively.[8] In $(\mathrm{KCN})_x(\mathrm{KBr})_{1-x}$ mixed crystals the CN^- ions are soluble for all concentrations x from zero to unity. The principal interaction between the elongated CN^- ions is an effective elastic dipole-dipole interaction[36] referred to here as QP-QP interaction. For concentrations greater than an upper critical concentration $x_{c2} = 0.62$ and below a concentration-dependent freezing temperature $T_f(x)$, the low-T state exhibits elastic long-range orientational order.[11,12,17] For even lower temperatures an antiferroelectric ground state due to the weak electric dipole interaction between the CN^- ions is observed (Fig. 1). In this high concentration range mixed crystals show a wide variety of polymorphism.[12] It is believed that dipolar freezing, when it occurs, is decoupled from quadrupolar freezing.[15] The behavior of the highly concentrated systems ($x \lesssim 1$) is reasonably well understood.[25,37] The small electric dipole moment of CN^- in cyanide mixed crystals, and similarly of CO in N_2-Ar-CO mixtures, is believed to be unimportant for the structural properties of these materials.[15]

For intermediate concentrations $x_{c1} \lesssim x \lesssim x_{c2}$ and for $T < T_f(x)$ the QP's freeze into a state of quenched orientational disorder (Fig. 1).[12,15] In this concentration range the orientations of the QP's are characterized by dynamic disorder at high T and "frozen-in" disorder at very low T. As T decreases, the impurities which can be viewed as quasifree rotors at higher T are quenched into random directions by the dominant quadrupolar interaction forces. In this paper we are not concerned with details of the freezing-in transition[10] that occurs at higher temperatures, nor with structural phase transitions that may take place for $x > x_{c2}$.[12,37] The relaxation process associated with the orientational freezing-in of the QP moments is denoted in the literature as α relaxation.[38,39]

In addition to a strong orientational coupling between the impurities[25] elastic random fields introduced by the dilution of the host sublattice are believed to play an important role in the freezing process.[17–20] The random dilution of the host atoms (for example Br^- in KCN-KBr) by the QP's and the volume mismatch between hosts and impurities (i.e., Br^- and CN^-), is believed to generate additional static elastic fields throughout the crystal and random displacements. This effect was first postulated by Michel[26] and seems to be experimentally well established by now.[17–20] Because the impurities are randomly placed in the solid, hence find themselves in random strain environments, these elastic fields act on the QP's as if they were random "external" fields.[26] This point will be discussed in greater detail in Sec. III. Since the random fields are a direct consequence of the substitutional impurity-host disorder, their importance is expected to be most pronounced for concentrations around $x \approx 0.5$. Thus the OG state has to be viewed as a delicate balance between multipolar interaction forces on one hand and elastic random fields on the other hand.[17–20,26] This very complex behavior is also reflected in the phase diagrams which are surprisingly similar for all OG's independently of the nature of the dominant interaction.[24,26]

The influence of random fields on orientational order can be studied best in alkali-cyanide systems like $(\mathrm{KCN})_x\ (\mathrm{NaCN})_{1-x}$, where the cyanide sublattice remains undiluted.[19,20,26] Substitution of the K^+ ions by the smaller Na^+ ions, or vice versa, leads to a disturbance in the local strain environment of the cyanide QP's. In alkali-cyanide mixed crystals the generated elastic fields are believed to be even strong enough to suppress the transition to an elastically ordered state that is otherwise found for $x < x_{c1}$ or $x > x_{c2}$.[20] For example in $(\mathrm{KCN})_x\ (\mathrm{NaCN})_{1-x}$ mixed crystals an OG state with randomly frozen-in QP's is observed for intermediate concentrations $0.2 \lesssim x \lesssim 0.9$,[20] similar to the alkali-cyanide alkali-halide systems, despite the fact that the CN^- sublattice is undiluted. Thus, in alkali-cyanides local random fields can even dominate over the strong elastic CN^--CN^- interaction.[19] Experimentally it is found that the strain fields force the cyanides into preferred directions[19] with a probability distribution for the orientations which is strongly temperature dependent. For instance in KCN-KBr it is the [111] directions that are the preferred orientations of CN^- at high T, whereas it is the [100] directions that are favored at lower T.[17] The [100] orientations are also favored in KCN-NaCN at low T which is believed to be dominated by random strains.[19]

A further difficulty in the treatment of mixed crystals arises from the existence of a local crystal field potential. For example in pure KCN or NaCN the cyanide molecule is surrounded by six alkali-metal ions resulting in a local crystal field potential of octahedral symmetry.[40] The local crystal field or Devonshire potential[40] is a consequence of the repulsive Born-Mayer overlap potential acting between the ends of the CN^- dumbbell and its neighboring atoms.[25,41] The importance of the crystal field for the low-T glasslike properties of very dilute systems in which random fields play most likely no important role[41] will be discussed in Sec. II B.

For very low temperatures and concentrations $x_{c1} \lesssim x \lesssim x_{c2}$ the thermal, dielectric, and ultrasonic properties of many QG's are very similar to those found in real canonical glasses. In particular, there are strong temperature and time dependent changes in the thermal properties and long relaxation times. In this intermediate-concentration range the phenomenological TLS model[5,6] describes the very low-temperature properties of many QG's almost equally well as for canonical glasses. KCN-KBr for instance forms a static QG (Ref. 16) between $0.1 \lesssim x \lesssim 0.6$ and $T \lesssim 5$ K.[13] For temperatures below 1 K the specific heat of KCN-KBr shows a term linear[13] in T which has a logarithmic time component[13,42] that exceeds the Debye phonon specific heat $C_D \propto T^3$. As in real amorphous materials it is believed that the observed linear term in the specific heat has its origin in two-level tunneling states.[13] It is these TLS's and their density of states which will be our primary concern for the rest of this paper. There exists an additional excess nontime dependent T^3 term in the specific heat of unknown origin which is presumably not related to quantum-mechanical tunneling[13,42] and also observed in canonical glasses.

For temperatures higher than $T \approx 1$ K a crossover from tunneling phenomena to thermally activated behavior is expected to take place. Also other excitations not related to the TLS's might become more important. This change of behavior is indicated by a strong change in the thermal conductivity which changes from its T^2 variation for low T and develops a characteristic plateau[13] at $T \approx 2$–10 K in the glass phase. Furthermore, a hump in C/C_D is observed for $T \gtrsim 1$ K.[13] It has been suggested that the dominant excitations at higher T are related to librational modes of single QP's,[31] but this question has not yet been settled.[42]

The exact nature of the ground state in OG's is unknown. It has been suggested[11,28] that it is a metastable state with long relaxation times, and probably a state of broken ergodicity similar to what is expected for spin glasses.[27,28] However, there is common agreement that the site disorder together with the anisotropic QP-QP interaction leads to a multiple frustrated ground state. The role of frustration in OG's and their similarity to spin glasses has been stressed previously in connection with their glasslike behavior.[22,43] Further on we will argue that it is only the disorder in connection with the randomly placed QP's and not necessarily frustration which gives rise to the glasslike behavior in QG's at very low T. For example glasslike behavior has also been observed in KCN-KBr in the orientationally more ordered state[13] between $0.6 < x < 0.7$ (Fig. 1). Furthermore, glasslike behavior is also seen in alkali-cyanide systems like KCN-NaCN, where the CN^- sublattice remains fully occupied, and the random interaction picture in combination with a frustrated ground state is not applicable. To our knowledge glasslike behavior, i.e., the quasiuniversal properties of glasses, has not been observed in OG systems without β relaxations, e.g., in dipolar glasses. It would therefore be important to measure the very low-T properties of electric dipole glasses in the intermediate- to high-concentration range to investigate the possibility of glasslike behavior without secondary relaxations.

A mean-field approach to the statistical mechanics of OG's at higher temperatures has been developed by Michel.[26,27] Unfortunately the validity of current mean-field techniques for systems with competing and random interactions is very questionable for low temperatures,[32] i.e., well below the OG transition temperature. As a guide towards an understanding of the various processes, we now turn to the very dilute systems which are theoretically reasonably well understood. The very dilute systems have the advantage that, within certain simplifying assumptions discussed in the next section, they can be treated rigorously. However, collective effects, like the freezing-in transition, do not exist in a very dilute system, i.e., $x \ll 0.01$.

B. Dilute systems: Theoretical developments

We next discuss some of our own theoretical developments for very dilute tunneling dipole and quadrupole glasses.[44–46] In particular, our discussion here serves to clarify (i) the role of quantum-mechanical tunneling, (ii) the role of the crystalline field, (iii) the role of strong interactions. These effects are much easier understood in the dilute systems, where collective phenomena are absent and random fields can most likely be neglected.

The low-temperature thermal properties of pure alkalihalide crystals ($x = 0$) are well understood within the Debye theory of phonons. At extreme low impurity concentrations x, we can view the dipoles or QP's as isolated defects surrounded by a crystal field potential arising from the interaction of the impurity with its surrounding neighbors.[41] It has been shown that for nonspherical molecules this leads to preferred directions (potential wells) for the defect molecule. In a cubic crystal one can have 6, 8, or 12 off-center potential minima.[47–49] At sufficiently low T only the ground state in each potential well will be populated. The total wave function is then a linear combination of single-well wave functions and determined by the crystal field symmetry and the tunneling matrix element Δ. The latter is related to the quantum-mechanical overlap between the localized ground-state wave functions corresponding to different wells. Librational excitations or excitations to higher states within a single well, or Arrhenius-type excitations over the potential barriers separating the wells, can be neglected at sufficiently low T.[40,47,48] However, for higher temperatures these excitations become also important. For even higher T the nonspherical molecule approaches more and more the states of a quantized rotor. The Devonshire model[40] in which the impurities are treated as isolated defects, each sitting in a crystal field of octahedral symmetry (Fig. 2), describes this situation reasonably well and has been discussed in detail in the literature.[40,47,48]

At very low T the important degrees of freedom are tunnel reorientations between nearest-neighbor potential wells.[50] The tunneling motion between the potential wells will split the degenerate ground state of the defect into low-energy levels separated by energies typically of the order $\Delta \approx 1k_B$. This tunnel splitting is reflected by a Schottky anomaly in the specific heat. For example the CN^- ion in KCN-KBr has local potential minima along the [111] directions and therefore eight preferred directions of orientation (Fig. 2).[49] The CN^- ion can tunnel to its three nearest-neighbor potential wells.[50,51] For $(KCN)_x\ (KBr)_{1-x}$ and concentrations $x \lesssim 0.05$ (the "impurity regime" in Fig. 1), these tunnel splittings result in a specific heat anomaly of the Schottky type[13,14] with a peak at $T_m \approx 0.5$ K, where $k_B T_m$ is typically of the same order as the tunneling matrix element Δ.

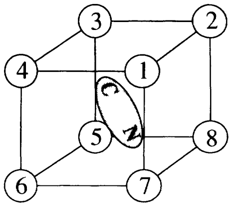

FIG. 2. Model of an isolated eight orientational tunneling QP, e.g., CN^- in KBr. The corners indicate the preferred "easy" directions of orientation corresponding to minima in the potential energy (Devonshire potential) of the cyanide QP. In a dilute system tunneling can occur, for example, from well 7 to 1, 6 or 8, i.e., between nearest-neighbor wells. The elastic energy of a cyanide QP is invariant under inversion.

For higher concentrations x of the order of a few hundred parts per million (ppm), elastic interactions between the moments become more and more important,[52] and the impurities can no longer be viewed as isolated tunneling units. Experimentally a broadening of the Schottky specific heat is observed[13,14] which cannot be explained within the Devonshire model. For example at $T = 0.08$ K the specific heat of 340 ppm CN^- in KBr is about 50 times of what one would expect from the Schottky term[14] with a single tunneling matrix element Δ. The thermal conductivity also behaves anomalously and is strongly decreased compared to that of the pure crystal.[13] In addition, dilute orientational glasses show a largely enhanced thermal expansion coefficient[14,51] and a large Grüneisen parameter,[14,51] characteristic for "glassy" systems. It must be mentioned, however, that the observed anomalies in the very dilute systems ($x \ll 0.01$) are in general distinctly different from the universal glasslike properties observed in the QG phase[13,14] around $x \sim 0.5$.

In the higher, but still dilute concentration range ($x \sim$ 200–1000 ppm), a model of isolated tunneling impurities with a single tunneling matrix element cannot explain the experimental data. Beside the increasing importance of interactions between the impurities with higher concentrations, it has been speculated[47] that a spectrum of tunneling matrix elements Δ arises from local strain fields and that this might explain the broadening of the Schottky specific heat.[53] However, it has also been estimated that the strain fields needed to explain the experimentally observed broadening in the dilute samples would have to be unphysically large.[51]

We have treated the dilute case using a virial expansion[44–46] in the impurity concentration x of the free energy arising from a quantum-mechanical model Hamiltonian. In analogy with the cluster expansions in the theory of gases, the virial coefficients involve interactions among clusters of a finite number of particles. In this model[44–46] the Hamiltonian had two noncommuting parts. A longitudinal part which describes the QP-QP interaction and a transverse part (tunneling matrix) to account for quantum-mechanical tunneling between the easy directions of orientation. The tunneling matrix was determined by the symmetry of the local crystal field surrounding the dipoles or QP's. With current techniques it is not possible to get general solutions for the statistical mechanics and the thermal properties arising from this Hamiltonian. However, if one considers only the first two virial coefficients in our low-concentration expansion, one can get corrections to the noninteracting Devonshire model (in our case the first virial coefficient) from pair interactions which contribute to the second virial coefficient. In particular, we found good agreement between specific heat measurements for dilute concentrations of Li^+ in KCl and CN^- in KBr and our calculations.[45,46]

Our exact treatment for the second virial coefficient[45] also showed that the energy spectrum is strongly modified by the interaction between the QP's. We found that, somewhat counterintuitively, the *lowest* excitation energies are determined by the *strongest* interaction. This finding, namely that strong interactions cause low-energy excitations, had very important consequences. Instead of solving for the low-energy excitations from our model exactly, we also approached the problem using second- and third-order perturbation theory[46] which greatly simplified the calculations compared to the exact solution carried out in Ref. 45. A similar perturbation approach will be used in the next section to derive an effective Hamiltonian for the low-energy excitations for a concentrated system of interacting QP's.

The virial-expansion approach used in Refs. 44–46 is expected to break down for concentrations $x \lesssim 1000$ ppm. For higher concentrations the evaluation of higher virial coefficients is needed to describe effects like frustration which becomes increasingly difficult. For example triplets enter our calculation only on the third virial coefficient level which has not been considered so far.[54] In addition, collective phenomena, like the freezing in, are difficult to describe within this virial expansion method. Furthermore, at higher concentrations new important physical phenomena occur, like for instance random strain fields which are not so important in a dilute system, but will be considered in the next section.

III. QUADRUPOLAR GLASS MODEL

In this section we treat the case of intermediate concentrations and very low temperatures ($T \lesssim 1$ K), i.e., the glass regime in Fig. 1. The major difference between our physical models for the dilute and the concentrated systems is that in the latter we will include elastic random fields into our considerations which are believed to dominate over the crystal field potential[41] in the glasslike systems for $x \gtrsim 0.1$,[17–20,26] but vanish in the limit $x \to 0$. Moreover, the tunneling motion in the dilute systems is determined by the crystal field symmetry, whereas in the more concentrated systems the crystal field is believed to play no important role in the tunneling process. We will come back to the role of the crystal field later on, but neglect it here at first.

Consider a set of N quadrupoles randomly distributed in a lattice at sites i with position $\mathbf{r}_i$. To be more specific our discussion here is presented with $(KCN)_x\ (KBr)_{1-x}$ in mind. An extension of our treatment to other systems will be given in Sec. IV. We describe the orientational coupling between the cyanides by a classical elastic QP-QP interaction.[35,36] We also include an additional interaction between the QP moments and random strain fields, generated by the replacement of the spherical host Br^- atoms by the QP's.[26] Since we neglect here the crystal field at first and emphasize the importance of random fields instead,[41] the following discussion will not apply to dilute or highly concentrated systems. Consider a zeroth-order QG Hamiltonian $\mathcal{H}^{(0)}$ of the form

$$\begin{aligned}\mathcal{H}^{(0)} &= \mathcal{H}_Q + \mathcal{H}_R \\ &= -\sum_{i<j}^{N} K_{ij}^{\alpha\beta\gamma\delta} Q_i^{\alpha\beta} Q_j^{\gamma\delta} - \sum_{i=1}^{N} H_i^{\alpha\beta} Q_i^{\alpha\beta}\ , \qquad (1)\end{aligned}$$

where Q_i is an elastic second rank QP tensor,[35,36] H_i the local strain field at site i arising from the elastic random fields,[26] N the number of QP's, and $\alpha, \beta, \gamma, \delta = 1, 2, 3$ denote tensor coordinates. We used the summation convention to sum over superscripts. K_{ij} is the strength of the interaction which for an elastic dipole (QP) falls off like r_{ij}^{-3} and like r_{ij}^{-5} for electric QP's;[55] r_{ij} is the distance between a pair of QP's located at sites i and j. The QP-QP pair interaction can take either plus or minus sign with the same probability and depends on the vector connecting site i and j.[36] The interaction is therefore random due to the site randomness of the QP's and competing. Our zeroth-order Hamiltonian $\mathcal{H}^{(0)}$ in Eq. (1) thus consists of two different parts: an "elastic spin glass" Hamiltonian $\mathcal{H}_Q$ and a random field Hamiltonian $\mathcal{H}_R$.

The second part of the Hamiltonian in Eq. (1), $\mathcal{H}_R$, arises from the coupling of the orientational degrees of freedom of a QP to random strain fields.[41] $\mathcal{H}_R$ is always an elastic interaction generated by the random fluctuations in the local strain environment of the cyanide QP's.[41] Since the QP's couple linearly to the random strain fields which are not correlated with the rotational excitations of the QP's, these elastic random fields act like random *external* fields, in distinction from the *internal* fields which arise from the elastic QP-QP interaction in $\mathcal{H}_Q$.[26] Presumably it is the $\mathcal{H}_R$ part of the Hamiltonian which prevents an elastic spin-glass transition to occur at higher temperatures.

The QG Hamiltonian introduced in Eq. (1) describes only the orientational degrees of freedom of the QP's. We have neglected translational degrees of freedom in our model Hamiltonian which gives rise to additional terms in the Hamiltonian. Our point of view here is that it is the orientational degrees of freedom of the QP's that are intrinsically related to the TLS's and the glasslike behavior and that translational modes play no important role for the low-energy excitations at very low temperatures. A derivation of an OG Hamiltonian starting from microscopic potentials between the host and impurity molecules was given by Michel.[26] However, since the details of the impurity-host interactions are in general unknown, a formulation of an appropriate OG Hamiltonian using a lattice-dynamical approach still seems to be an elusive task (see also Ref. 56). A recent review on the theoretical aspects of this still controversial subject is given in Ref. 28. Since our following discussion will not be sensitive to details of the quadrupolar interaction, the model Hamiltonian in Eq. (1) is sufficient for our purpose.

A. Perturbation approach

A natural approach to the statistical mechanics arising from a Hamiltonian of the form Eq. (1), would be via mean-field theory. However, it is by now a well-known fact that current mean-field techniques not only lead to quantitatively but also to qualitatively incorrect answers, if applied to systems with random and competing interactions.[32–34] The failure of standard mean-field techniques in these systems is one of the major theoretical problems in spin-glass theory and has been discussed intensively in the spin-glass literature.[32–34] We therefore choose here an approach that avoids introducing mean fields, however at the same time, restricts us to the very low-T regime.

Previous calculations have shown that, at least in the dilute systems,[44–46] the low-energy excitations come from strongly interacting QP's. The lowest excitation energies could then be obtained from a virial expansion in the QP concentration using perturbation theory on the ground state of a pair Hamiltonians,[46] with the tunneling Hamiltonian (crystal field) acting as a perturbation.[57] We use here the same perturbation argument and assume at first that the orientational coupling between the QP's is sufficiently strong to allow us to treat $\mathcal{H}^{(0)}$ in Eq. (1) as an unperturbed or zeroth order Hamiltonian. We think that this assumption is well justified by experiments and our own work on dilute systems. The low-energy excitations of the system can then be obtained by doing perturbation theory on the ground-state energy, say E_0, of the unperturbed Hamiltonian $\mathcal{H}^{(0)}$. For N head-tail symmetric QP's this ground state is 2^N-fold degenerate. A small perturbation will lift the degeneracy and the energy levels will fan out[58] as indicated in Fig. 3. The low-energy excitations arise therefore from 180° rotational flips of the QP's, as was proposed earlier by Sethna *et al.*[29–31] Since these low-energy splittings are small compared to higher excited levels (E_1, E_2,... in Fig. 3) of $\mathcal{H}^{(0)}$, we can describe them in an effective Hamiltonian[58] derived later on in this section. This effective Hamiltonian will give us the TLS Hamiltonian. The higher excited levels of $\mathcal{H}^{(0)}$ are not known and are not necessary for our purposes. The low-T thermal properties of the system can then be obtained from this new effective TLS Hamiltonian and not from the original QG Hamiltonian, Eq. (1), which is a significant simplification of the problem. Clearly the approach proposed here works only for systems which have a secondary relaxation process associated with the head-tail symmetry of the impurities and would fail, for instance, for a dipole glass.

In order to do perturbation theory on the ground state of $\mathcal{H}^{(0)}$, we will introduce a second part $\mathcal{H}^{(1)}$, in our total Hamiltonian $\mathcal{H}$. The different parts contributing to $\mathcal{H}^{(1)}$ in our model will be discussed below. Thus, for the moment we make the following ansatz

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} , \qquad (2)$$

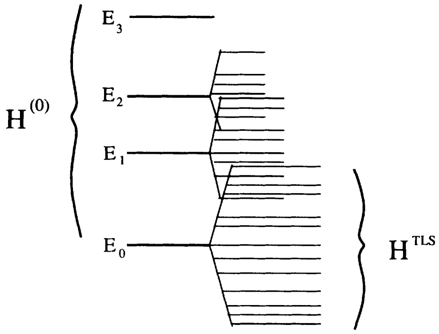

FIG. 3. Fanning out of energy levels of the 2^N-fold degenerate ground state of a system of N interacting QP's. E_0 denotes the ground-state energy of $\mathcal{H}^{(0)}$ in Eq. (1), E_1 is the first excited level, etc. The whole set of 2^N low-lying excitation energies will be described by an effective TLS Hamiltonian. Note that the fanned-out levels may overlap.

with $\mathcal{H}^{(0)}$ given in Eq. (1) and $\mathcal{H}^{(1)} \ll \mathcal{H}^{(0)}$. We emphasize that we do perturbation theory to distinguish our approach from a mean-field treatment.

Contrary to our approach here that *strong* interactions between the QP's are important, it has also been proposed that the low-energy excitations might arise from *weakly* interacting QP's and that in this case frustration might play an important role for the glasslike low-energy excitations.[43] Since the system is in a quasifrozen-in state, it has been argued[43] that only a small number of completely frustrated QP's (namely the ones that see basically no quadrupolar fields) can relax at very low T.[59] These QP's would almost behave like the isolated impurities in a highly dilute system. In the proposed scenario[43] 180° relaxations of tunneling QP's play no important role, only "higher" excitations E_1, E_2, E_3,... of $\mathcal{H}^{(0)}$ (Fig. 3). It has also been suggested that excitations not related to the rotational motion of single or groups of QP's might be the microscopic origin[11] of the low-energy excitations in QG's and tunneling might play no important role whatsoever. However, none of these models could successfully explain a constant density of low-energy excitations which is characteristic for all glassy materials at very low temperatures.

B. Crystal field

To a first approximation we assume that the strain QP tensor Q_i in Eq. (1) is symmetric and that the QP's are elongated (Fig. 2) with their principal axes pointing in direction $\boldsymbol{\mu}_i$, where $\boldsymbol{\mu}_i$ is a unit vector, and i labels the position $\mathbf{r}_i$ of the QP in the solid. Let the axis of the ith QP in the ground state be along direction $\mathbf{n}_i$, where $\mathbf{n}_i$ is also a unit vector. For a head-tail symmetric impurity the two states $\mathbf{n}_i$ and $-\mathbf{n}_i$ are degenerate under inversion and will be represented by their wave functions $|\psi_i^+\rangle$ and $|\psi_i^-\rangle$, respectively. Using the fact that in the ground state $\psi_i^{\sigma_i}$ ($\sigma_i = \pm$) are two degenerate eigenstates of $\boldsymbol{\mu}_i$, we have

$$\boldsymbol{\mu}_i \psi_i^{\sigma_i} = \sigma_i \mathbf{n}_i \psi_i^{\sigma_i} \ , \quad \sigma_i = \pm \ ,$$

and (3)

$$\langle \psi_i^{\sigma_i} | \psi_j^{\sigma_j} \rangle = \delta_{ij} \delta_{\sigma_i \sigma_j} \ ,$$

where δ denotes the Kronecker δ function. The total ground-state wave function of N quadrupoles in this special representation is given by

$$\psi^{(\sigma)} = \prod_{i=1}^{N} \psi_i^{\sigma_i} \quad \text{with} \quad \sigma_i = + \text{ or } -$$

and (4)

$$\mathcal{H}^{(0)} \psi^{(\sigma)} = E_0 \psi^{(\sigma)},$$

where σ denotes the whole set of quantum numbers $(\sigma_1, \ldots, \sigma_N)$.

We will now obtain a new effective Hamiltonian, denoted here as $\mathcal{H}^{\mathrm{TLS}}$, for the fanned out low-energy excitations of E_0 (Fig. 3). In first-order perturbation theory the matrix elements of $\mathcal{H}^{\mathrm{TLS}}$ are given by $\mathcal{H}^{(\sigma\nu)} = \langle \psi^{(\sigma)} | \mathcal{H}^{(1)} | \psi^{(\nu)} \rangle$ with the zeroth-order wave functions of $\mathcal{H}^{(0)}$ from Eq. (4) and $\mathcal{H}^{(1)}$ being the perturbation in Eq. (2). Note that the order of perturbation theory in which the degeneracy of E_0 will be lifted is determined by the physical process involved in a 180° QP flip. If we view this as a one-step tunnel process (Sec. III D) over an effective angular elastic potential barrier arising from the Hamiltonian, Eq. (1), the degeneracy is lifted in first-order perturbation. It should be mentioned, however, that if the random fields are strong enough to "fix" the quadrupolar axes in, say the [100] directions, as is believed to be the case in some of the alkali-cyanide systems,[19] the tunnel relaxation would be a two-step tunnel process over one intermediate state. This case would require a second-order perturbation calculation as for the dilute system.[60] Since the dominant interaction in KCN-KBr is believed to be the elastic QP-QP interaction, we continue here with first-order perturbation theory. The mathematical treatment of the concentrated system is therefore somewhat simpler than the dilute case, where the octahedral symmetry of the crystal field potential demanded a higher-order perturbation calculation.[46]

We next examine the different parts of $\mathcal{H}^{(1)}$ that will contribute to $\mathcal{H}^{\mathrm{TLS}}$ in our model. The rotational motion of molecules in solids is often coupled with a center-of-mass displacement of the defect molecule. Such an effect is not described by the quadrupolar Hamiltonian in Eq. (1) which takes only the orientational degrees of freedom of the QP's into consideration. Consider, for example, a small one-dimensional displacement of a "frozen-in" QP along its long axis $\mathbf{n}_i$. For these translational degrees of freedom the ends of the elongated QP's will also experience strong repulsive forces (the Born-Mayer repulsive potential[25]) from their nearest-neighbor atoms in addition to the harmonic potential. It has been shown[61] that in the presence of such an additional repulsive potential, the harmonic modes can become unstable which then leads to new equilibrium positions displaced from the center.[61,62] Thus, the same physical mechanism which manifests itself as a crystal field in the dilute samples, might also lead to the experimentally observed off-center displacement of the defects in the higher-concentration range.

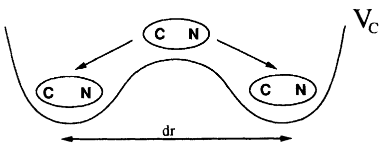

FIG. 4. A two-dimensional cut through the crystal field potential in Fig. 2, showing two off-center equilibrium positions for an orientationally "frozen-in" QP. In the intermediate concentration range the crystal field potential V_C is believed to be strongly disturbed by the presence of random elastic fields, leading to an asymmetry energy for the QP.

A small center-of-mass displacement is formally described by introducing an effective crystal field potential V_C with off-center potential wells, like in the very dilute systems. Since the crystal field is believed to be small compared to the elastic interaction, we treat the crystal field potential as a perturbation. For an orientationally frozen-in QP, an anisotropic but symmetric crystal field[41] with off-center potential wells, for example, in the [111] directions (Fig. 2), leads to two new off-center equilibrium positions along the QP axis $\mathbf{n}_i$ (Fig. 4). This point of view is quite different from that in the literature, where the influence of the crystal field is usually neglected for higher concentrations. Since the random and crystal fields have different physical origins,[41] the crystal field potential (V_C in Fig. 4) will become distorted by the presence of random strain fields. It has been mentioned before that due to the random placement of the defects, the resulting elastic random fields are believed to be strongly inhomogeneous in the glassy concentration regime, i.e., $H_i = H(\mathbf{r}_i)$, where $\mathbf{r}_i$ denotes the lattice position in the solid, and H_i is the elastic field at site i, Eq. (1). If we consider not only 180° rotational motion but also a small translational displacement $d\mathbf{r}_i$ (Fig. 4), the asymmetry energy ε_i between the two states $|\psi_i^+\rangle$ and $|\psi_i^-\rangle$ becomes

$$\varepsilon_i \approx Q_i^{\alpha\beta} (\nabla_{\mathbf{r}_i} H_i^{\alpha\beta}) \cdot d\mathbf{r}_i \ , \tag{5}$$

where $\nabla_{\mathbf{r}_i} H_i^{\alpha\beta}$ is the strain gradient at site i introduced by the fluctuations in the random strain environment. Since the QP tensor Q_i depends on $\mathbf{r}_i$ and $\mathbf{n}_i$, and hence $Q_i = Q(\mathbf{n}_i, \mathbf{r}_i)$ and $Q(\mathbf{n}_i, \mathbf{r}_i) = Q(-\mathbf{n}_i, \mathbf{r}_i)$, first-order perturbation theory yields an effective asymmetry energy of the form

$$\mathcal{H}_R^{\mathrm{TLS}} = -\tfrac{1}{2} \sum_{i=1}^{N} \varepsilon_i \sigma_i^z \ , \tag{6}$$

where we have used a pseudospin notation in which σ_i^z denotes the z component of the Pauli spin matrix. Thus, we have related the asymmetry energies of the TLS's to inhomogeneous random fields via Eqs. (5) and (6).

C. Electric dipole interaction

In addition to their large QP moment, the cyanide ion possesses a relatively small electric dipole moment. Next we consider the effect of a weak electric dipole interaction which will also be treated as a perturbation.

Let $\mathcal{H}_D$ be the classical dipole-dipole Hamiltonian

$$\mathcal{H}_D = p^2 \sum_{i<j} r_{ij}^{-3} \left[\boldsymbol{\mu}_i \boldsymbol{\mu}_j - 3(\mathbf{e}_{ij}\boldsymbol{\mu}_i)(\mathbf{e}_{ij}\boldsymbol{\mu}_j) \right] ,$$
$$\mathbf{e}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij} , \tag{7}$$

where p is the magnitude of the electric dipole moment and $\boldsymbol{\mu}_i$ a unit vector along the direction of the electric dipole. Evaluation of $\mathcal{H}_D^{(\sigma\nu)} = \langle \psi^{(\sigma)} | \mathcal{H}_D | \psi^{(\nu)} \rangle$ with the wave functions from Eq. (4) yields an effective electric dipole-dipole contribution of the form

$$\mathcal{H}_D^{\mathrm{TLS}} = - \sum_{i<j} J_{ij} \sigma_i^z \sigma_j^z , \tag{8}$$

where J_{ij} is now a "quenched" random variable given by

$$J_{ij} = -p^2 [\mathbf{n}_i \mathbf{n}_j - 3(\mathbf{e}_{ij}\mathbf{n}_i)(\mathbf{e}_{ij}\mathbf{n}_j)]/r_{ij}^3 . \tag{9}$$

The random character of J_{ij} results from the site randomness of the QP's on the one hand and orientational randomness of the frozen-in axes $\mathbf{n}_i$ on the other hand. Provided that the freezing of the axes $\mathbf{n}_i$ is purely random, one could in principle derive a probability distribution function for the random couplings J_{ij} from Eq. (9).

In the Sethna model[29–31] the asymmetry energy ε_i between the two states $|\psi_i^+\rangle$ and $|\psi_i^-\rangle$ was related to the internal electric field, i.e., $\varepsilon_i = \sum_j J_{ij} \sigma_j^z$ in Eq. (8). In order to obtain a linear specific heat, as is observed experimentally, the distribution function of asymmetry energies, say $D(\varepsilon, T)$, must be sufficiently "flat" and finite on energy scales of the order $k_B T$ around $\varepsilon = 0$. In their model[29–31] the value of $D(0, T)$ which is crucial for obtaining a linear specific heat was obtained from the tail of a shifted Gaussian distribution.[29,30] However, substantial deviations of the "internal" electric fields from a mean-field theory predicted Gaussian distribution are expected for small fields (energies) ε in the limit $T \to 0$ (as usual we measure fields in units of energy). Spin-glass theory predicts that for an infinite-range interaction a "hole" in the distribution function $D(\varepsilon, T)$ develops at the origin when T approaches zero and that most likely $D(\varepsilon, 0) \propto \varepsilon$.[33] According to numerical calculations by Sethna *et al.*[31] a "hole" also develops for a short-range interaction. Thus based on Eq. (8), we believe that the electric dipole moment will not contribute a linear term to the specific heat and will not lead to a constant density of states, contrary to what has been suggested previously.[29–31] Furthermore, the specific heat and low-energy excitations in QG's do *not* seem to depend on the presence of an additional electric dipole moment, as specific heat measurements for N_2-Ar-CO and N_2-Ar have clearly indicated.[21] We will come back to the N_2-Ar problem in Sec. IV.

However, a small electric dipole moment makes it possible to follow the reorientations of the electric dipoles, i.e., the QP's, dielectrically.[63,64] The importance of the strong elastic coupling between the QP's can also be seen from deviations of the static electric susceptibility from Curie-type behavior[65] which would be expected in a system of noninteracting QP's.

For completeness we include here an external electric field $\mathbf{E}$ to our Hamiltonian. From $\mathcal{H}_E^{(\sigma\nu)} = -\langle \psi^{(\sigma)} | \sum_i \mathbf{E} \cdot (p\boldsymbol{\mu}_i) | \psi^{(\nu)} \rangle$ and by use of Eq. (3), we obtain

$$\mathcal{H}_E^{\mathrm{TLS}} = -\tfrac{1}{2} \sum_{i=1}^{N} \xi_i \sigma_i^z , \tag{10}$$

where the projection $\xi_i = 2p\,\mathbf{E} \cdot \mathbf{n}_i$ is a random variable because of the orientational randomness of the frozen-in axes $\mathbf{n}_i$ in the ground state.

D. Tunneling and time dependence

Dielectric loss experiments[63–65] at higher T have shown that the β relaxations in QG's exhibit Arrhenius-type of behavior and that they may involve 180° reorientations of QP's over a Gaussian-distributed orientational potential barrier.[63–65] We adopt here a similar point of view[29,30] and assume that the relaxation process between the two wells involves a 180° reorientation of a QP rather than a simple displacement jump. We also assume that for very low T quantum-mechanical tunneling rather than thermal crossover is the primary relaxation mechanism between the two wells, as experiments on dilute systems have demonstrated. The physical mechanism proposed here for the glasslike low-energy excitations in QG's thus involves 180° tunneling flips in connection with a small center of mass displacement, as indicated in Fig. 5.

In order to introduce quantum-mechanical tunneling, we must assume a finite overlap between the two single-

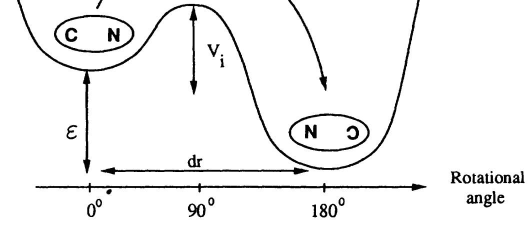

FIG. 5. Tunneling relaxation via a 180° reorientational flip. In our model the asymmetry energy ε is related to inhomogeneous elastic random fields in connection with the off-center motion of a QP. The major contribution to the angular potential barrier V_i is provided by the elastic fields arising from the Hamiltonian, Eq. (1), and not the crystal field V_C in Fig. 4. At very low T the assumed relaxation mechanism is quantum-mechanical tunneling through the potential barrier.

well wave functions $|\psi_i^+\rangle$ and $|\psi_i^-\rangle$, denoted as tunneling matrix element $\Delta_i = -2\langle\psi_i^-|\mathcal{H}^{(0)}|\psi_i^+\rangle > 0$ (the factor of -2 is introduced for convenience). This is so because the major contribution to the angular potential barrier through which the QP has to tunnel (V_i in Fig. 5) comes from the strong elastic fields in Eq. (1). Using the standard TLS model ansatz,[66] we can express the tunneling Hamiltonian in the form

$$\mathcal{H}_T^{\mathrm{TLS}} = -\tfrac{1}{2}\sum_{i=1}^{N}\Delta_i\sigma_i^x \ , \tag{11}$$

where σ^x denotes the x component of the Pauli spin matrix. In the 180° tunneling model[30] the tunneling matrix element for QP's with moment of inertia I tunneling through a 180° angular potential barrier of height V_i (Fig. 5), is approximated by an expression of the form

$$\Delta_i \approx 2\hbar\omega\exp(-4\sqrt{2IV_i}/\hbar) \ . \tag{12}$$

A distribution of attempt frequencies ω is usually neglected in the TLS model, since Δ_i depends only strongly on the distribution of barrier heights V_i. The time dependent probability $\Gamma_i(t)$ for a QP to tunnel within time t, is then given by[30]

$$\Gamma_i(t) = 1 - \exp(-\Delta_i t/2\hbar) \ , \tag{13}$$

i.e., only QP's which experience sufficiently small elastic fields can relax on experimental time scales and contribute to the low-T thermal properties. Thus, to explain the experimentally observed time dependencies, the probability distribution $P(V,T)$ of barriers V_i in Eq. (12) is needed (Sec. III F).

In the Sethna model[29–31] the distribution of barrier heights $P(V,T)$ was provided by the "internal" quadrupolar mean field arising from the first part in Eq. (1), i.e., $V_i^{\alpha\beta} = \sum_j K_{ij}^{\alpha\beta\gamma\delta}Q_j^{\gamma\delta}$. If in the simplest approximation only the most favorable path for a 180° reorientation is considered, the potential barrier V_i can be described by a scalar quantity as indicated in Fig. 5, with the tunneling matrix element Δ given by Eq. (12). The distribution of barrier heights $P(V,T)$ was obtained by Sethna by fitting the experimentally measured high-T dielectric-loss data[63–65] to a Gaussian distribution assuming a single-particle Debye-Arrhenius model for the relaxation.[29,30,63] Using an *ad hoc* introduced temperature dependent width, the Gaussian distribution was then extrapolated to low temperatures to obtain the desired distribution $P(V,T)$ near $T = 0$.[29,30,63] Again, the question about the true nature of $P(V,T)$ is closely related to the internal field distribution problem in spin glasses and substantial deviations from the mean-field predicted Gaussian distribution are expected for low T and small internal fields V.[32,33] In particular, it is believed that $P(V,0) \propto V$ for small values of V, if random fields are not considered.[32] This would lead to time dependencies for the linear specific heat considerably different from the observed logarithmic form.[32] Since it is the small field part of the distribution which gives the time dependencies, special attention has to be paid to this crucial point (Sec. III F).

In our case there are two additive parts to the effective orientational barrier V_i arising from Eq. (1). An "internal" part from the QP-QP interaction $\mathcal{H}_Q$ that was already considered previously by Sethna *et al.*,[29–31] and the "external" static fields H_i that arise from the random strain fields in $\mathcal{H}_R$ and were not considered before. Both the random "external" fields and the "internal" quadrupolar fields contribute to V in our model. Thus the probability for the effective rotational barrier $P(V,T)$ which reflects the sum of both fields could be finite for small fields and not develop a hole, otherwise expected for a "pure" elastic spin glass Hamiltonian $\mathcal{H}_Q$.[32] The experimentally found distribution of effective elastic fields[63–65] with a nonzero probability for small fields, is thus rendered more understandable from our model.[32]

E. TLS tunneling Hamiltonian

Our effective TLS Hamiltonian $\mathcal{H}^{\mathrm{TLS}}$ for the low-energy excitations in Fig. 3 is now given by the sum of Eqs. (6), (8), (10), and (11). Collecting all parts in one Hamiltonian, we arrive at the following effective low-T glass Hamiltonian:

$$\mathcal{H}^{\mathrm{TLS}} = -\tfrac{1}{2}\sum_{i=1}^{N}[(\varepsilon_i+\xi_i)\sigma_i^z + \Delta_i\sigma_i^x] - \sum_{i<j}J_{ij}\sigma_i^z\sigma_j^z \ . \tag{14}$$

A theoretical approach to the statistical mechanics arising from the full Hamiltonian, Eq. (14), was developed in Ref. 67, including also an additional TLS-phonon coupling. A phonon-TLS coupling is needed to obtain for instance thermal conductivity. The dominant long-wavelength phonons at very low T that contribute to the thermal conductivity are believed to scatter resonantly from the TLS's and to be only weakly coupled.[13,68] These phonons could in principle be introduced perturbationally in our model, like in the TLS model. In fact a strong coupling between the phonons and the TLS's in Eq. (14) would introduce a new non-negligible TLS-TLS interaction, as was pointed out in Ref. 69. This would lead to an inconsistency with the TLS model[69] which assumes *a priori* only weak or no interactions between the TLS's. Since in our case a strong phonon coupling was already incorporated in the first part of the Hamiltonian, $\mathcal{H}_Q$ in Eq. (1), with an effective coupling strength K_{ij} (the elastic QP interaction is a phonon-mediated interaction),[36] the same problem does not arise in our discussion. It is the strong interaction between the QP's which "freezes out" effective TLS's which can then be treated in a weak coupling approximation to obtain, for example, the thermal conductivity. This would explain the paradoxical fact that a model of weakly interacting units (the TLS model) describes the (low-T) properties of a strongly interacting system of QP's so well.

We next derive the TLS Hamiltonian and the density of states. Instead of treating the full Hamiltonian, Eq. (14), it is sufficient for us to consider a much simpler case. The major simplification arises from neglecting the electric dipole-dipole term in Eq. (14). The reason for this is twofold: (i) the electric dipole moment is small and is known to depend highly on the dilution factor (for example ferroelectric order is only observed in highly concentrated systems), (ii) specific heat measurements for N_2-Ar-CO mixtures have already demonstrated that the small electric dipole moment of CO makes an insignificant contribution to the low-energy excitations.[21] It seems very unlikely that the glasslike properties in KCN-KBr and N_2-Ar-CO should arise for two different reasons in two systems which are so much alike. For simplicity we will therefore neglect the electric dipole interaction in our following discussion and treat a "pure" QG instead.

With no external electric field and the above simplifications, the TLS contribution in Eq. (14) becomes

$$\mathcal{H}^{\mathrm{TLS}} = -\tfrac{1}{2}\sum_{i=1}^{N}(\varepsilon_i\sigma_i^z + \Delta_i\sigma_i^x) \ , \qquad (15)$$

with yet unknown distributions of asymmetry energies ε_i and tunneling matrix elements Δ_i. Diagonalizing Eq. (15) leads to the well-known result[66]

$$\mathcal{H}^{\mathrm{TLS}} = -\tfrac{1}{2}\sum_{i=1}^{N} E_i\sigma_i^z \ , \qquad (16)$$

where

$$E_i = \sqrt{\varepsilon_i^2 + \Delta_i^2} \qquad (17)$$

is the energy of the TLS.

F. Density of states

Next we derive the density of states and time dependent specific heat for KCN-KBr. In the 180° tunneling model[30] the excess heat capacity arising from $\mathcal{H}^{\mathrm{TLS}}$ in Eq. (16), can be obtained from the expression

$$C(T,t) = Nk_B \int_0^\infty d\varepsilon\, D(\varepsilon) \int_0^\infty dV\, P(V,T) \times \Gamma(\Delta,t)\, \left((\beta/2)\sqrt{\varepsilon^2+\Delta^2}\,\mathrm{sech}[(\beta/2)\sqrt{\varepsilon^2+\Delta^2}]\right)^2 \ , \qquad (18)$$

where $\beta = (k_B T)^{-1}$, $D(\varepsilon)$ is the distribution of asymmetry energies, Eq. (5), $P(V,T)$ the distribution of barrier heights arising from the Hamiltonian, Eq. (1), Δ the tunneling matrix element in Eq. (12) and $\Gamma(\Delta,t)$ the tunneling probability, Eq. (13). Values for the attempt frequency $\omega = 8.3 \times 10^{13}$ Hz and the moment of inertia $I = 2.65 \times 10^{-46}\ \mathrm{kg\,m^2}$ of a cyanide molecule dissolved in KBr which enter the calculation of Δ through Eq. (12) were given in Ref. 30. For the above choice of parameters numerical calculations have shown that Δ can be neglected compared to ε in Eq. (18). Thus the double integral decouples, yielding a time dependent linear specific heat in T of the form[30]

$$C(T,t) = (\pi^2/6)Nk_B^2 D_0 A(t)\, T \ , \qquad (19)$$

where

$$A(t) = \int_0^\infty dV\, P(V,T)\, \{1 - \exp[-\Delta(V)t/2\hbar]\} \ . \qquad (20)$$

In deriving Eq. (19) we have assumed that the density of asymmetry energies in Eq. (5), denoted here as $D(\varepsilon)$, is a constant for small energies, i.e., $D(\varepsilon) \approx D(0) = D_0$. The above expression for the specific heat fits the experimental data for $(\mathrm{KCN})_{0.5}\ (\mathrm{KBr})_{0.5}$ remarkably well, as has been pointed out previously.[30,42]

A constant density of states D_0 follows from our model in a very natural way. Since the directions of orientation of the QP's are fixed in the ground state, the distribution of asymmetry energies results from a distribution of random fields H_i in Eq. (5). Since H_i is the sum of elastic fields created by the randomly replaced host atoms (which are not correlated with the orientational degrees of freedom of the QP's) acting at site i, we can use the law of large numbers to justify a Gaussian distribution for ε (the same can be found by doing a numerical calculation). The important result, namely $D(\varepsilon) \approx D_0$ for small energies ε, follows now from an estimate of the width of this distribution:[70] the strength of the QP-QP nearest-neighbor elastic interaction, denoted as K_0, has been estimated previously to be of the order of 400 K in dilute KCN-KBr crystals.[14,45,46,51] It is believed that the elastic fields are of a similar order of magnitude as the quadrupolar interaction. Using K_0 as a rough estimate of the strength of the interaction and assuming a rotational amplitude that is of appreciable size compared to the interatomic spacing, our numerical calculations show that the resulting distribution for the asymmetry energy ε is sufficiently flat on energy scales of the order of $k_B T \ll K_0$, and that $D_0 = (\pi\sigma^2/2)^{-1/2} \gtrsim 1/(k_B \times 400\,\mathrm{K})$, where σ is the second moment of the distribution. Calculations by Sethna *et al.*[29,30] have shown that a value of $D_0 = 1/(k_B \times 314\,\mathrm{K})$ in Eq. (19) provides the best fit to the experimental data for $(\mathrm{KCN})_{0.5}\ (\mathrm{KBr})_{0.5}$,[13] in agreement with our estimate. However, these authors concluded that D_0 reflects the asymmetry energy due to the electric dipole moment of CN^- in Eq. (8) which is very different from our viewpoint.

Time dependencies enter the 180° tunneling model[29,30] via the time integral in Eq. (20). Using a shifted Gaussian distribution for $P(V,T)$, suggested by high-T susceptibility measurements,[63–65] a computer calculation leads to a specific heat that varies approximately logarithmic in time and that fits the experimental data rather well.[30] However, different forms of $P(V,T)$ have been suggested by theorists (see for example the discussion in Ref. 32). This discrepancy has been a serious problem in the 180° tunneling model, because it was the value of $P(V,T)$ in the limit $V, T \to 0$ that played a very crucial role in the heat capacity and density of states.

The same difficulty does not arise in our case for two reasons: (i) The distributions of asymmetry energies $D(\varepsilon)$ and barrier heights $P(V,T)$ are independent in our model. Thus we get a linear specific heat in T and constant density of states without resorting to the exact analytical form of $P(V,T)$. (ii) The time factor in Eq. (20) that determines the order of magnitude of the specific heat is *not* very sensitive to the value of $P(V,T)$ at $V = 0$ and $T = 0$ when the random external fields are taken into account. As a numerical calculation shows, both a shifted Gaussian for $P(V,T)$ (Ref. 30) and a $P(V,0) \propto V$ (Ref. 32) lead to results that agree very well with experimental findings for fifty percent CN$^-$ dissolved in KBr. We think that this result is physically reasonable since we do not expect that the specific heat arises merely from tunneling quadrupoles with zero barrier heights (Fig. 5), but from the small-field tail of the distribution.

For completeness, the total low-temperature specific heat of KCN-KBr is now given by

$$C = C_D T^3 + (\pi^2/6) N k_B^2 D_0 A(t) T \ , \qquad (21)$$

where the first part reflects the phonon contribution to the specific heat. There is also an additional nontime dependent contribution to the specific heat arising from $\mathcal{H}^{(0)}$, Eq. (1), which has not been included in our discussion. This term is not related to quantum-mechanical tunneling and becomes more important at higher T because it reflects "higher" rotational excitations of QP's (E_1, E_2,... in Fig. 3) than the 180° flips that gave the low-energy excitations. Indeed, here only a more detailed knowledge of the elastic field distribution $P(V,T)$ for small fields would enable us to calculate the thermal properties arising from $\mathcal{H}^{(0)}$ alone.[71] It could be speculated that this additional contribution to the specific heat might have a low-temperature tail that is related to the excess T^3 term observed in the heat capacity of almost all disordered materials.[13] However, it has also been argued that librational excitations of single QP's could be the origin of this term.[31,42]

IV. DISCUSSION

The physical model that we suggested to explain the glasslike excitations in QG's at very low temperatures involved strongly interacting QP's, random strains, and a crystal field potential, in connection with quantum-mechanical tunneling. Since all these effects have been observed in QG's and seem to play important roles, we think that we have a good justification for our proposed physical mechanism. Furthermore, we had previously shown[44,45] that a pair of strongly interacting QP's each tunneling in a local crystal potential has low-energy excitations. Using a similar perturbation argument[46] (Sec. III A), the same approach carries over to a system of N interacting tunneling QP's. By carefully distinguishing between "internal" and "external" fields for the orientational degrees of freedom of the QP's, we could avoid a conflict with the yet unsolved internal-field distribution problem[33] that also arises in the theory of spin glasses, and derive a constant density of states.

One of our fundamental assumptions in this paper was to separate the total Hamiltonian into a QP-QP Hamiltonian[36] and a QP-random-field Hamiltonian of the form Eq. (1). A calculation of this QG Hamiltonian starting from realistic microscopic potentials between the host and impurity atoms or molecules would therefore be a highly desirable task. One major step in this direction is the work of Michel *et al.*[25–27] Numerical arguments for modeling QG's in terms of a defect Hamiltonian were also given by Grannan *et al.*[31] However, the latter authors argued that glasslike behavior arises from the first part $\mathcal{H}_Q$ of the Hamiltonian, Eq. (1), in connection with the electric dipole moment of the defects and did not consider local fields in their discussion, like the proposed random fields and crystal fields which were crucial in our derivation.

It has also been suggested[69] that a semiclassical description like the one in Eq. (1) is not valid and that a quantum-mechanical strong coupling calculation emphasizing the role of the phonon coordinates would be necessary to obtain glasslike properties. While we admit that this is the right procedure, we do consider our QP-QP interaction as the renormalized one. The resulting strong effective orientational coupling between the QP's which also manifests itself, for example, in the OG transition is however an experimentally well-established fact. Furthermore, our mechanism for the glasslike low-energy excitations does not depend on the details of the QP-QP interaction which enters the calculation indirectly via the distribution of barrier heights $P(V,T)$ in Eq. (20) and leads to time dependencies. As mentioned earlier in Sec. III F, almost any sensible choice for $P(V,T)$ leads to reasonable agreement with the experimentally observed heat capacity because of the presence of random "external" fields.

Our physical mechanism which leads to the TLS tunneling model is not directly related to the presence of frustration or long-range order among the QP's. However, the perturbation approach in Sec. III demanded a clear separation between the ground-state energy E_0 and higher excited levels $E_1, E_2, \ldots$ (Fig. 3), i.e., sufficiently strong orientational couplings between the QP's. A second necessary ingredient for our model was fluctuations in the local strain environment in which the tunneling takes place. Both conditions are satisfied in QG's for intermediate concentrations ($x \sim 0.5$), but not in the highly concentrated ($x \lesssim 1$) and very dilute systems ($x \ll 0.1$).

Whereas the orientational coupling is strongest for $x = 1$, the effects of random fields are expected to be most pronounced around $x \approx 0.5$. As the concentration of the QP's is lowered below $x \approx 0.5$, the effective QP-QP interaction becomes weaker and the orientations of the QP's are no longer frozen into their random directions. Other quadrupolar excitations different from 180° flips become more likely, leading to an increased overlap of the fanned-out energy levels $E_0, E_1, \ldots$ in Fig. 3. In addition, fluctuations in the local random environment of the QP's vanish as they become more and more diluted; hence the importance of random strain fields diminishes. Simultaneously the importance of the crystal field increases which finally completely dominates over the elastic random fields in the very dilute limit.[44–46] The net result is that dilution destroys the glassy state. On the other hand for higher concentrations interactions between the QP's becomes more and more important. As the system orders elastically (or even electrically), the appropriate internal fields become less random. The broad distribution functions, which are crucial to obtain a linear specific heat, are no longer flat but approach δ functions in the ordered state. The QP's can no longer relax via tunneling on experimental time scales, since the low-field tail in the distribution $P(V,T)$ is missing. As the host-impurity disorder vanishes, so does the asymmetry energy. In either case the glasslike behavior results from a delicate balance between random fields and quadrupolar interactions. Since both effects are coupled with the impurity concentration, the density of states and heat capacity is expected to have a nontrivial concentration dependence.

A. N_2-Ar-CO mixtures and the glass problem

In our work we considered the properties of QG's for the case when, according to our understanding, the electric dipole interaction plays no or little role in the very low-temperature glasslike properties. Since glasslike properties have also been found in QG's like N_2-Ar and N_2-Ar-CO, independently of the CO electric dipole moment,[21] one might wonder if our mechanism applies to these systems as well. However, it has also been suggested that quadrupolar order might be important in niobium-doped systems like $KTa_{(1-x)}Nb_xO_3$, where, in contrast to the alkali-halide alkali-cyanide crystals, a strong electric dipole moment is present.[72] Again, we think it would be most interesting to measure the very low-T properties of systems in which the electric dipole interaction dominates to see if these systems behave glasslike at very low T.

The TLS asymmetry energy in our model was related to the center-of-mass displacement associated with a 180° tunneling flip of a QP. Such a small displacement of the cyanide ion is expected, for instance, in KCN-KBr which in principle could have its origin in the asymmetrical shape of the CN^- molecule.[73] However, in N_2-Ar-CO mixtures in which the N_2 has a symmetrical shape, the off-center position would have to come from the repulsive interaction as is discussed further on. Furthermore, large rotational amplitudes are also observed in a wide variety of other materials. Earlier we have suggested that the off-center motion of CN^- in KCN-KBr mixed crystals is a result of the elongated shape of the QP's and the repulsive potential acting between the ends of the CN^- dumbbell and its neighboring atoms. An off-center displacement of interstitial atoms or molecules due to strong repulsion between host and impurity is also a well-established fact in metals[62] (however, here the repulsive forces are different in nature). Recently it has been argued[74] that the observed radiation effects of interstitial iron atoms ^{57}Fe in α-Zr provide unambiguous proof that the iron atom occupies off-center octahedral sites. The experimental data indicate that the Fe atoms can perform local jumps in an octahedral "cage" that is formed within the hcp host lattice with off-center equilibrium positions lying at the corners of the cage displaced from the center of symmetry[74] (for example along the corners of the cube in Fig. 2). Off-center potential wells are also believed to exist in various other OG systems. For example it has been speculated[75] that NH_4 tetrahedra in the electric dipolar glass $(NH_4I)_x$ $(KI)_{1-x}$ occupy off-center positions of about 0.1–0.3 Å. An off-center motion of Li^+ was also observed in the dipolar glass LiCl-KCl.[51] However, in dipolar glasses the dominating electric dipole moment is not invariant under inversion, and thus does not give glasslike low-energy excitations. The self-induced lowering of symmetry[76] of defects (here by going off-center) is a well-known effect which also arises in connection with the Jahn-Teller effect.[76] Since it is the off-center displacement that gives the asymmetry energy and constant density of states in our derivation, and not the electric dipole moment of CO, this could explain why the specific heat of N_2-Ar-CO mixtures is glasslike, irrespective of the CO electric dipole concentration.[21]

We now want to make some speculative comments about the reason for the constant density of states and the nature of the tunneling unit in *canonical glasses.* The major problem in modeling canonical glasses is that no clear distinction between lattice and defects can be made on experimental or theoretical grounds. However, let us assume that canonical glasses contain defects. Assume that (i) these defects interact via elastic strains, and that (ii) they also experience elastic random fields from the random structure of the amorphous solid. Then a description of the defects in terms of a model Hamiltonian like the one in Eq. (1) would be in place, and the mechanism suggested here for the glasslike low-energy excitations could apply to the real glass as well. Similar physical ideas have been suggested by experiments on vitreous silica. In this context the work of Buchenau *et al.*[77] deserves some special attention. These authors concluded from their experiments[77] that the relaxation processes in vitreous silica, although at higher T, can be interpreted as collective reorientations of SiO_4 tetrahedra in combination with a jump width dr of approximately 0.5 Å. Whereas we have no explanation for the formation of these SiO_4 defects in canonical glasses, we suggest that the TLS model might be placed in the same theoretical framework as our discussion for the quadrupolar glass presented till here. Since positions and strain environments of the SiO_4 tetrahedra are random, our proposed mechanism for the glasslike excitations could apply here as well.

V. CONCLUDING REMARKS

We have proposed a new physical mechanism to explain the microscopic origin of the two-level tunneling systems in quadrupolar glasses and their constant density of low-energy excitations. Even though the quadrupole (QP) axes in our model are effectively frozen-in at very low T, the head-tail symmetric QP's maintain their mobility to perform 180° tunneling flips. A 180° tunneling reorientation of a QP coupled with a small center-of-mass displacement then yields isolated two-level states (TLS's), responsible for the glasslike behavior. This tunneling motion takes place in a local crystal field environment which is, however, disturbed by the presence of random elastic fields from the substitutional host-impurity disorder on the lattice. Since the TLS asymmetry energy results from the sum of *external* random fields (as far as the orientational degrees of freedom of the QP's are concerned), we can use the law of large numbers to derive a Gaussian distribution for the asymmetry energies. This distribution, rather than having a "hole" for small fields, will have a finite probability and therefore give a constant density of states. Furthermore, the physical mechanism for the low-energy excitations proposed here, does not depend on details of the QP-QP interaction, nor do we have to use mean-field theory, known to be very problematic in systems with random and competing interactions. Our model seems to be sufficiently universal to account for the linear low-temperature specific heat in other quadrupolar glasses, like N_2-Ar-CO mixtures, too. We remark that similar ideas to the ones developed here are suggested by experimental work on vitreous silica. However, the identification of the tunneling unit in canonical glasses still remains one of the foremost problems in glass science to be solved.

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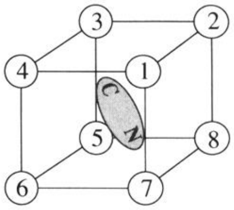

FIG. 2. Model of an isolated eight orientational tunneling QP, e.g., CN$^-$ in KBr. The corners indicate the preferred "easy" directions of orientation corresponding to minima in the potential energy (Devonshire potential) of the cyanide QP. In a dilute system tunneling can occur, for example, from well 7 to 1, 6 or 8, i.e., between nearest-neighbor wells. The elastic energy of a cyanide QP is invariant under inversion.