FULLERENES AND ATOMIC CLUSTERS

Paraelectric resonance of centers with icosahedral symmetry

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The paraelectric resonance spectrum of non-central impurity ions situated in crystal fields of icosahedral symmetry is predicted. A multiwell potential is considered that corresponds to the displacement of the ions from the center of symmetry toward the vertices of the icosahedron, the faces of a dodecahedron, and the pentagonal faces of a fullerene molecule. The effective Hamiltonian of endohedral complexes in external electric fields with arbitrary orientation is obtained, its eigenvalues are found, and the line intensities of different transitions between the tunneling levels are calculated. © 1997 American Institute of Physics.

1. The discovery of fullerenes and the creation of fullerite crystals based on them1–3 have opened up many areas of study in various fields of science, including solid-state physics. Interest has also arisen in objects described by symmetry groups whose elements include rotations by an angle that is a multiple of \(2 \pi / 5 = 72^\circ\), such as \(C_5, C_{5v}, D_5, D_{5h}\), \(Y, Y_h\) (especially the latter two). Here attention has been drawn not only to the unique structure and symmetry of these new formations, but also to the unusual properties of such materials. For example, it has been shown that when atoms of other elements are introduced into their structure, semiconducting, metallic, or even superconducting properties may be induced. It has turned out to be possible to directly introduce atoms (molecules) of elements belonging to different groups of the Periodic Table (including the lanthanides and even uranium4–6). Such formations have come to be called endohedral fullerenes and the notation \(M@C_{60}\) has been introduced, where \(M\) is the enclosed atom (ion) or group of atoms and \(N\) is the number of atoms of carbon in the fullerene molecule. This notation was introduced to distinguish these compounds from ordinary compounds where the elements are neighbors (in the case of fullerenes this means attached from the outside).

The large diameter of the fullerene cavity (in the case of \(C_{60}\) it is \(\sim 7.1\) Å) points to the possible appearance of a noncentrality effect, as was observed earlier in crystals with local symmetry below icosahedral7–9. This effect involves a displacement of the potential energy minimum of the interaction of the trapped atom with the fullerene cage from the center of the latter. Usually the noncentrality effect arises when the radius of the enclosed atom is small in comparison with the radius of the cage. The above arguments are confirmed by concrete calculations. For example, in Ref. 10 the equilibrium positions \((r_{\text{min}})\) of a large group of atoms (ions) enclosed in \(C_{60}\) were calculated, and it was shown that for many of them \(r_{\text{min}} \neq 0\); i.e., they are not located at the center of the \(C_{60}\) cage. In particular, \(r_{\text{min}} \approx 1.3\) Å for \(Li^+\). These results for \(Li^+\) have been confirmed by independent calculations.\(^{11}\) Independent calculations for \(Na^+\) were performed in Refs. 12 and 13. They showed that \(r_{\text{min}} \approx 0.7\) Å. For comparison we point out that \(r_{\text{min}} = 0\) in the case of heavier ions \((K^+, \text{Ref. } 14)\) and atoms of the noble gases\(^{15–17}\). To this we may add that the fullerene \(C_{20}\) and one of the higher fullerenes \(C_{180}\) possess icosahedral symmetry.\(^{18}\)

Along with the fullerenes, clusters have been studied consisting of atoms of other elements of the Periodic Table and possessing different symmetry, including icosahedral.\(^{19–21}\) Jinlong et al.\(^{22}\) considered the icosahedral cluster \(M@Co_{12}\) consisting of twelve cobalt atoms inside which are located atoms of various elements of the iron group: from Ti to Ni. They showed that in all the atoms except Ti, Mn, and Co, having a closed shell inside the cluster, a displacement from the center is allowed.

The creation of condensed materials from endohedral fullerenes and other clusters opens up new possibilities for solid state physics. In particular, as was noted by Cioslowski and Nanayakkara,\(^{23}\) the introduction into fullerenes of polar molecules (LiF, LiCl, NaF, NaCl) with permanent dipole moments may be a basis for creating a new class of ferroelectric crystals. Wang et al.\(^{10}\) pointed out the possibility of a new class of high-temperature superconductors with a specific electron–phonon bond based on endohedral fullerenes (in contrast to already-tested doped fullerenes, where the impurity is introduced between the fullerenes\(^3\)).

The effect of noncentrality is accompanied by the presence of several \((n)\) energetically equivalent equilibrium positions. In the case of impurity atoms (ions) these positions are displaced from the center along the symmetric directions. In the case of dipole molecules (ions) both displacements and a dipole orientation of these directions are possible. Because of overlap of the potential wells and of the wave functions of the particle moving in them, the particle executes interwell tunneling and the \(n\)-fold degenerate term splits. The characteristic system of tunneling energy levels arising in this way leads to various phenomena, including paraelectric resonance (PER)\(^{7,8,24}\) which when used as a method allows one to directly examine noncentrality effects.

Noncentrality effects and PER in particular were observed earlier in various alkali-halide crystals with a wide variety of impurity ions and impurity polar molecules and in
quartz, rutile, and other materials. Most of the theoretical and experimental studies were performed on alkali-halide crystals, distinguished by high local symmetry ($O_h$) at the impurity sites. This gives a basis to suppose that high symmetry is a favorable factor for the appearance of noncentrality effects. In this regard, note that icosahedral symmetry is the highest point symmetry group, which together with calculations of shifted equilibrium positions gives reason to expect to observe noncentrality effects.

The aim of the present work is to elucidate the conditions for the most favorable observation of these effects and to develop a technique for their interpretation. The present work investigates the spectrum of PER centers located in a crystal field with icosahedral symmetry arising as a consequence of different configurations of the atoms (icosahedron, dodecahedron, fullerene).

2. Earlier studies of high-symmetry systems showed that the noncentral ions are displaced along symmetric directions of the types $[111]$, $[100]$, and $[110]$, i.e., toward vertices, centers of faces, or edges. In this light, and also taking into account the given calculations of $r_{\text{min}}$ (Ref. 13), we studied displacements along symmetric directions; specifically we considered a 12-well potential simultaneously corresponding to displacements of noncentral ions toward the vertices of an icosahedron, the face centers of a dodecahedron, and the centers of the pentagonal faces of the fullerene molecule. All of these figures belong to the symmetry group $Y_h$, the characters of the irreducible representations (IR) of which are given in Table I (Ref. 25).

For the reducible representation $\Pi_{12}$ we obtain the expansion

$$\Pi_{12} = \Pi_g + F_{1u} + F_{2u} + H_g ,$$

indicating the nature and number of the tunneling levels.

Let us consider resonance transitions in the system of levels (1) in the absence of an external dc electric field $E_0$, i.e., field-free PER. In PER, transitions take place induced by an ac electric field $E$ which transforms according to the irreducible representation $F_{1u}$. An analysis of the direct products of the irreducible representations of the group $Y_h$ (Ref. 26) leads to the allowed transitions indicated in Fig. 1a. The transitions are caused by the electric field whose field intensity vector is arbitrarily oriented in space.

Paraelectric resonance is often obtained by sweeping the external dc electric field $E_0$ through resonance. The field, for convenience of analysis of the spectra, is oriented along the symmetry directions so that some elements of the point symmetry group are preserved. For example, in the case of centers of cubic symmetry the direction $E_0$ is usually chosen along $[100]$, $[110]$, and $[111]$ axes, as a result of which the local symmetry is lowered from $O_h$ to $C_{4v}$, $C_{2v}$, and $C_{3v}$, respectively. In the case of icosahedral symmetry we choose as the symmetry directions of the electric field the directions from the inversion center toward the vertices, face centers, and edges of the various figures. Table II indicates the symmetry groups arising for such directions of the external field. The existence of two point groups in one cage in the case of fullerene is connected with the two types of faces and edges. The upper symbols correspond to a pentagonal face and the edge joining a pentagonal face and a hexagonal face, and the lower symbols correspond to a hexagonal face and the edge joining two hexagonal faces. Table III presents data on the nature of the level splittings under the action of the field $E_0$. Here the numbers indicate how many times the irreducible representation indicated in the column heading (together with the corresponding subgroup) is contained in the irreducible representation of the group $Y_h$. It is clear from Table III that to consider the selection rules in an arbitrary case it is sufficient to take account of each irreducible representation of any point subgroup not more than twice. Results of the calculations are shown in Fig. 2. The arrows in the figure indicate the allowed electric dipole transitions. The indices on the arrows denote the directions of the components of the