PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Structure and dynamics of the H^0-tagged Li^+ center in KCl as studied by polarized Raman scattering

W. Joosen, J. F. Zhou,* E. Goovaerts, and D. Schoemaker
Physics Department, University of Antwerp (Universitaire Instelling Antwerpen), B-2610 Wilrijk (Antwerp), Belgium

(Received 28 January 1985)

Stabilization of a mobile interstitial hydrogen atom by a substitutional Li^+ impurity in KCl leads to a H^0Li^+ center possessing $C_{3v}\langle 111\rangle$ symmetry. A Raman line at 205 cm^{-1} is shown to be associated with this center. This line shows no isotope effect upon ^{6}Li-to-^{7}Li substitution. The behavior-type method developed recently by Zhou, Goovaerts, and Schoemaker was applied to the analysis of the polarized Raman spectra and it leads to the conclusion that the 205-cm^{-1} line originates from an E mode. The inability to produce a non-random-orientational distribution at 4.2 K with $\langle 110\rangle$-polarized light and the fact, deduced from electron-spin resonance, that the hydrogen maintains its free-atom character in the H^0Li^+ center leads to the following picture. The small Li^+ and the small H^0 are both comfortably accommodated within the same cation site and each is displaced along $\langle 111\rangle$ in opposite directions. There is no preferential molecular bond of any consequence between them. The well-established tunneling motion of the unperturbed $\langle 111\rangle$-displaced Li^+ center among its eight equivalent positions very likely persists in the H^0Li^+ center and the H^0 tags along while performing its own vibrational E mode.

I. INTRODUCTION

Recently,[1,2] the theory of the behavior-type (BT) method for the analysis of the polarized Raman spectra of defects in cubic crystals was presented. This method allows one to analyze the polarized Raman spectra of randomly or preferentially oriented defects and permits one within clearly spelled out limits to identify the symmetry of the defects and the irreducible representation to which its vibrational mode belongs.

We are applying the BT method to the Raman spectra of several classes of defects in the alkali halides, one class consisting of light and small impurities such as H^0 and Li^+. Such defects are of continuing interest because they are model defect systems possessing structural and dynamical properties, not all of which are clearly understood at present. Recently, BT results were presented for interstitial hydrogen atoms perturbed by a foreign halogen ion in a series of alkali halides.[2] The vibrational E and A_1 modes consistent with the $C_{3v}\langle 111\rangle$ symmetry of the center were identified and information about the relative magnitudes of the Raman tensor elements was obtained.

The present paper concerns a BT study of the polarized Raman spectra of a defect in KCl in which both a H^0 and a Li^+ are involved. This center was identified and studied some time ago in electron-spin resonance[3] (ESR) and the results were described in terms of a $\langle 111\rangle$-oriented $(LiH)^+$ molecule. At 128 K a rapid ($\sim 10^9$ Hz) reorientation motion among the $\langle 111\rangle$ directions was observed. A broad optical absorption band at 245 nm was also identified. We have detected a Raman line at 205 cm^{-1} which is associated with this defect (Sec. III B). Confining oneself to this essential Raman result and combining this with the conclusion derived from the ESR, namely that one is dealing with a $(LiH)^+$ molecule, one could reasonably advance the hypothesis that the 205-cm^{-1} line originates from the A_1 stretching mode of the $(LiH)^+$ molecule. However, we will show in Sec. III D through an application of the BT method that the 205-cm^{-1} line corresponds to an E mode of a $C_{3v}\langle 111\rangle$ symmetry center. This unexpected result coupled with other optical data forces one to reconsider the structure and the dynamics of this center. Briefly, it will be argued in Sec. IV that one has to abandon the $(LiH)^+$ molecule hypothesis and that one must consider a model in which both a H^0 and a Li^+ are accommodated on a single cation site without much preferential interaction between them. This is more or less reflected in the notation H^0Li^+ which will be adopted for this center. It will also be argued that the well-established tunneling motion of the unperturbed off-center Li^+ ion persists for the H^0Li^+ center.

II. EXPERIMENTAL

The Li^+- and SH^--containing KCl samples were cut from KCl crystals grown in a 5-Torr atmosphere of H_2S and from a melt containing typically 2 mol % of LiCl. Some samples came from the same boule that supplied the specimens for the ESR and optical absorption investigation.[3] The SH^- concentration was estimated to be 0.1 mol %. Two additional types of samples were employed in order to investigate isotope effects. One type of crystals was partly deuterated, i.e., it contained SD^- next to SH^-, but because the Li^+ concentration was small it yielded marginal Raman intensities. In another SH^--doped crystal the Li^+ impurity was isotope enriched: 99% of ^{6}Li compared to the natural abundancies of 93% $^7Li^+$ and 7% ^{6}Li.

The unperturbed interstitial H_i^0 centers (the U_2 centers) were produced at 15 K by an uv excitation from a deuterium lamp. The uv light passed through a 220-nm broadband interference filter before impinging on the crystal.

In this way the production of substitutional H^- centers (the *U* centers) and interstitial-type Cl_2^- centers (the *H* centers) was avoided.[4] The irradiation time was usually about 2 h. Details about the Raman scattering and optical absorption techniques can be found in Ref. 2. The ESR procedures are described in Ref. 5.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Production of H^0Li^+ as monitored by ESR

The H^0Li^+ center is produced as follows.[3] First, unperturbed H_i^0 centers are created at ~15 K by an uv excitation of a KCl:Li^+,SH^- sample. The H^0 become mobile at 90 K and some are eventually converted to H^0Li^+ centers. The conversion is optimal after about half an hour of annealing at 110 K. Because both these centers are well characterized in ESR it is convenient to use this technique to monitor the conversion process.

There is strong evidence from ESR that the conversion above 90 K of H_i^0 to H^0Li^+ is not a direct process but that it proceeds via intermediate centers which are very weakly perturbed H_i^0 centers. These centers will not be discussed here further. We only note that they decay in the 90 to 110 K region where they are partly converted to H^0Li^+. Monitoring the ESR spectrum one obtains the pulse-anneal data presented in Fig. 1. It is seen that the H^0Li^+ center decays in the 115 to 140 K region. The ESR data also show that only about 10% of the unperturbed H_i^0 are eventually converted to H^0Li^+.

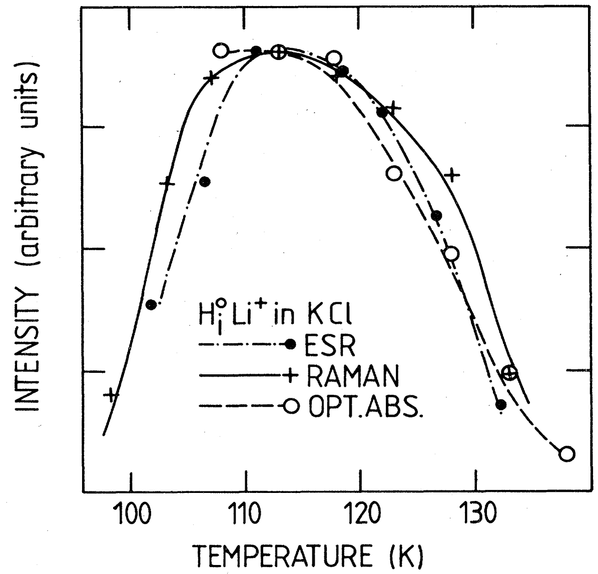

FIG. 1. Normalized pulse-anneal data based on electron-spin resonance (ESR), Raman scattering, and optical absorption measurements of the production and decay of the H^0Li^+ center in KCl:Li^+,SH^-. At each annealing point the sample was held for 10 min and the changes were recorded at 50 K in ESR, and at ~10 K in Raman scattering and optical absorption.

B. Identification of the H^0Li^+ Raman spectrum

Parallel to the ESR experiments analogous pulse-anneal measurements were performed in Raman scattering. Before uv excitation the Raman spectrum of KCl:Li^+,SH^- exhibits the SH^- stretching mode at 2953 cm^{-1} with a half width below the experimental resolution (~1 cm^{-1}), and a weak broad line at 43 cm^{-1} (Ref. 6). The latter is induced by the substitutional Li^+ ion. After uv excitation at 15 K the narrow 438-cm^{-1} T_2 mode of the unperturbed H_i^0 is easily detected.[7] A subsequent pulse anneal above 90 K shows that this peak disappears in the region 100 to 110 K, and a rather broad (~10 cm^{-1}) peak is formed at 205 cm^{-1}. For increasing temperatures from 10 up to 100 K this signal shifts to lower wave numbers ($\simeq$200 cm^{-1}) and broadens somewhat. The unpolarized Raman spectrum taken at 10 K is shown in Fig. 2. The thermal formation and decay properties of this line accurately coincide with those measured for the H^0Li^+ center measured in ESR. These results are presented in Fig. 1. We conclude that the 205-cm^{-1} line is associated with the H^0Li^+ center. Furthermore, no other Raman line connected with the same center could be detected.

The 205-cm^{-1} Raman line did not exhibit any noticeable isotope effect in going to the 99% enriched $^6Li^+$ sample. If the Li^+ impurity had been strongly participating in the corresponding vibrational mode an 8% increase, i.e., 16 cm^{-1} would have been expected for its frequency. Lithium isotope shifts about this size have been observed for the 220-cm^{-1} and 265-cm^{-1} modes of the $F_A(^7Li)$ center in KCl.[8] The complete absence of such an effect in our case strongly supports the conclusion that only the H^0 motion is responsible for the 205-cm^{-1} mode.

A considerable effort was spent to detect the D^0Li^+ Raman line in SD^-- or OD^--containing KCl:Li^+ crystals. The best KCl:Li^+,SD^-,SH^- sample at our disposal contained a lower concentration of Li^+. A weak 205-

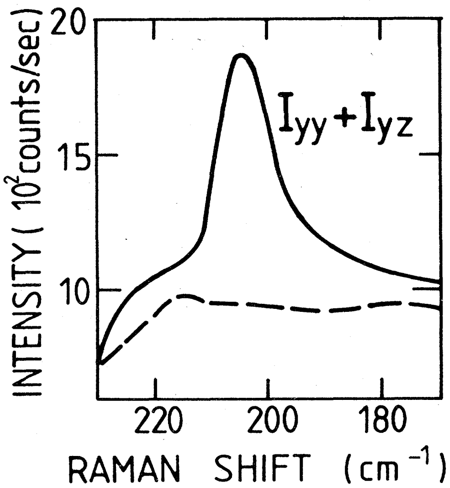

FIG. 2. Unpolarized Raman spectrum of the H^0Li^+ center in KCl:Li^+,SH^- recorded at ~10 K. The dashed line is the second-order phonon scattering before the production of H^0Li^+. The spectra have been smoothed for presentational purposes: Their statistical fluctuations in this figure and Fig. 3 amount to about 10 c/s.

cm^{-1} line of H^0Li^+ could be observed in this sample with the same formation and decay properties as given above. A careful search yielded a very weak and broader line ($\sim$20 cm^{-1}) at 170 cm^{-1}. This signal is formed after annealing at 130 K, which would be consistent with the lower mobility of deuterium compared to hydrogen atoms.[3] Nevertheless, we do not ascribe this line to the D^0Li^+ center because the Raman signal was still thermally stable up to 250 K.

C. Polarized optical excitation and absorption measurements

In the next section (Sec. III D) we will perform a behavior-type analysis of the 205-cm^{-1} Raman line. The power of this method may be enhanced if one is able to do polarized Raman scattering experiments on preferentially oriented defects.[1,2] This can often be achieved by a polarized light excitation into an absorption band provided that the centers do not reorient either by normal thermal activation or through some tunneling process. With a pulse-anneal experiment we confirmed the result obtained in Ref. 3 that the H^0Li^+ center possesses a distinct absorption band at 245 nm with a full width at half maximum of 0.5 eV.

The ESR data indicate that the H^0Li^+ center is ⟨111⟩ oriented. One does not expect to produce optical anisotropy with ⟨100⟩-polarized light excitation into the 245-nm band and indeed none was observed. This experiment yielded only an isotropic bleaching, which was confirmed both in optical absorption and in Raman scattering. Excitation with ⟨110⟩ polarized uv light should in principle produce an anisotropy but again only an isotropic bleaching was observed even after several hours of excitation. In one experiment only the long wavelength tail ($\lambda \gtrsim 250$ nm) of the absorption band, which we expect to possess the largest anisotropy, was excited with ⟨110⟩-polarized uv light. This also yielded a negative result.

It seems unlikely that the 245-nm absorption band is inherently isotropic. Its origin has not been established but very likely it can be ascribed to a charge-transfer transition from the surrounding halogen ions to the H^0 atom and/or Li^+ ion. If such a transition would only be weakly anisotropic this could account for the failure to produce an optical anisotropy with ⟨110⟩-polarized light.

Another explanation, which is one we favor, is that the H^0Li^+ center is continually reorienting among its eight possible ⟨111⟩ orientations. In fact, from the ESR analysis it was concluded unambiguously that such a thermally activated motion exists and that it becomes noticeable through line broadening above 50 K. It is possible that as the temperature is lowered this motion still goes on at 10 K where our Raman measurements were performed and it may well persist at much lower temperatures as a tunneling motion similar to the one occurring for the naked ⟨111⟩ off-center Li^+ impurity.[9] The fact that a C_{3v} symmetry is observed in Raman scattering is not in contradiction with such a motion: Nonresonant Raman scattering is virtually an instantaneous process[10] and it is much shorter than the average time the tunneling system spends in one well.

D. Behavior-type analysis of the 205-cm^{-1} H^0Li^+ mode

We will attempt to determine the nature of the 205-cm^{-1} H^0Li^+ center mode in order to learn more about the dynamics of this defect. The *behavior-type* (BT) method[1,2] will be used. The basic idea underlying this method is the following. Each dynamical mode of a defect with a given symmetry is characterized by a set of independent *intensity parameters* (IP). These IP can be obtained from the observed polarized Raman scattering intensities. For a given mode simple arithmetical relations exist between these IP and the set of relations defines the so-called *behavior-type* that is characteristic for the mode. The BT method has its limitations, which are systematically spelled out in Refs. 1 and 2. Not all the modes of all defect symmetries can be distinguished but only the so-called *representative modes* of *representative symmetry groups.* This has to do with, among other things, the fact that Raman tensors are invariant under inversion and that several symmetry groups possess the same general form for their Raman tensors. For instance, the representative symmetry group D_3 stands for the groups C_{3v}, D_3, and D_{3d}. Because we could not produce with polarized-light excitation an anisotropy in the distribution of the H^0Li^+ center orientations (see Sec. III C) the BT method will be limited to an analysis of the polarized intensities obtained from randomly oriented H^0Li^+ centers. In the terminology of Ref. 1 this corresponds to the situation where the symmetry group F_1 of the *orientating operator* is the tetrahedral group $F_1 = T$. From Tables III(a) and III(b) of Ref. 1 it can be seen that the polarized Raman intensities for randomly oriented centers are determined by at most three independent intensity parameters which are called q, r, and s. These have the following form when expressed in terms of the Raman tensor elements T_{ij}:

$$\begin{aligned} q &= kI_0N(T_{11}^2+T_{22}^2+T_{33}^2)\ , \\ r &= kI_0N(T_{11}T_{22}+T_{11}T_{33}+T_{22}T_{33})\ , \\ s &= kI_0N(T_{13}^2+T_{23}^2+T_{12}^2)\ . \end{aligned} \tag{1}$$

In these expressions k is an instrumental efficiency factor, I_0 is the intensity of the incident laser beam, and N is the number of scattering centers. The Raman tensors have been expressed in the crystal reference frame $x\,||\,[100]$, $y\,||\,[010]$, and $z\,||\,[001]$ and their explicit expressions are given in Table V of Ref. 1. Using these expressions one verifies easily that for the point groups D_3, C_{3v}, and D_{3d} only two independent intensity parameters exist for an E mode because for such a mode the following relations apply:

$$\frac{r}{q} = -\frac{1}{2}\,,\ s \neq 0\ . \tag{2}$$

This is the behavior type corresponding to an E mode of the representative symmetry group D_3 and it has been assigned the BT number 40 in Table VII of Ref. 1.

The intensity parameters q, r, and s can be determined from the polarized Raman intensities $I_{\alpha,\beta}$ measured in the traditional perpendicular scattering geometry. The symbols α and β designate the polarization directions x, y, or z of the incident and scattered light, respectively. These intensities can be measured by employing the so-

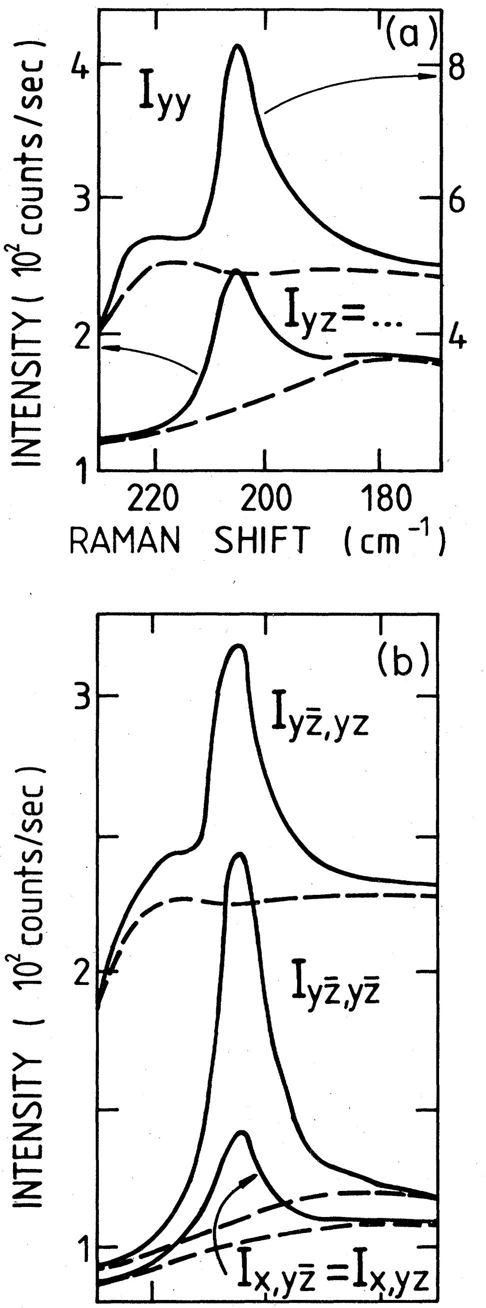

FIG. 3. Polarized Raman scattering spectra of H^0Li^+ in $KCl:Li^+,SH^-$ recorded at 10 K: (a) OGP set 1, and (b) OGP set 3. The dashed line is the second-order phonon scattering before the production of H^0Li^+. The spectra have been smoothed for presentational purposes.

called *optical geometry pair* (OGP) sets Nos. 1 and 3 presented in Fig. 2 of Ref. 1. In all OGP sets the incident laser light is parallel to the Z axis of a laboratory reference frame and the scattered light is collected along the X axis of that frame. The orientation of the crystal frame in OGP set 1 is $x||X$, $y||Y$, and $z||Z$, and the following relations hold (see Table XI of Ref. 1):

$$I_{x,y}=I_{x,z}=I_{y,z}=I_{x,yz}=I_{x,y\bar{z}}=s\ ,$$

$$I_{y,y}=q\ ,$$

$$I_{y,yz}=I_{y,y\bar{z}}=\tfrac{1}{2}(s+q)\ .$$

In OGP set 3, $x||X$ but $yz||Z$ and $y\bar{z}||Y$, and the following $I_{\alpha,\beta}$ can be measured:

$$I_{y\bar{z},y}=I_{y\bar{z},z}=\tfrac{1}{2}(s+q)\ ,$$

$$I_{y\bar{z},yz}=\tfrac{1}{2}(q-r)\ ,$$

$$I_{y\bar{z},y\bar{z}}=\tfrac{1}{2}(q+r)+s\ .$$

Some typical polarized-light Raman spectra of H^0Li^+ in KCl are presented in Figs. 3(a) and 3(b). Several sets of such measurements were performed and careful analysis of the intensities yielded the following mean result:

$$\frac{r}{q}=-0.44\pm0.14,\quad s\neq0\ . \tag{3}$$

This BT, the r/q value in particular, is within experimental error equal to the BT presented in Eq. (2), which is characteristic of an E mode of a center possessing representative symmetry D_3. It is in size and sign far away from the BT No. 39 (see Table VII of Ref. 1):

$$\frac{r}{q}=+1,\quad s\neq0\ , \tag{4}$$

which (see Table VIII of Ref. 1) stands for an A_1 mode of representative symmetry D_3. For a diatomic molecule oriented along $\langle 111\rangle$ the latter would correspond to a stretching vibration.

The representative symmetry D_3 includes C_{3v} and we conclude that if the H^0Li^+ center does indeed possess C_{3v} symmetry as indicated by the ESR results, the 205-cm^{-1} Raman line corresponds to an E mode of this center. The fact that we have not observed the A_1 Raman line of H^0Li^+ will be commented on in Sec. IV.

E. Observed versus the actual behavior type: Other possible modes and symmetries

In making the qualifying statement about the H^0Li^+ symmetry at the end of the last subsection (Sec. III D), we are implicitly relying on the assumption that Raman measurements yield the instantaneous symmetry of a defect rather than an averaged one (Sec. III C). This means the following: Suppose the H^0Li^+ is not oriented along $\langle 111\rangle$ but that it has C_{1h} symmetry, i.e., it lies well within a quadrant in a $\{110\}$ plane and makes an angle with $\langle 111\rangle$. As a result H^0Li^+ possesses three equivalent orientations with respect to a given $\langle 111\rangle$ direction. If H^0Li^+ exhibits a thermally activated jumping motion between these three orientations and if the rate of this motion is sufficiently large (larger than the g and/or hyperfine anisotropy expressed in frequency units) then one will observe in ESR an averaged spectrum possessing $\langle 111\rangle$ symmetry. However, for Raman scattering such reorientation rates (usually $\lesssim 10^9$ Hz) are slow and the instantaneous tilted C_{1h} symmetry will be observed.[10] Note that H^0Li^+ could not lie in a $\{100\}$ plane including the directions $\langle 100\rangle$ and $\langle 110\rangle$ because then the reorientation motion would out of necessity take place among all its equivalent orientations and no $\langle 111\rangle$-averaged ESR spectrum would be observed except for a cubic one.

In view of the foregoing discussion it is instructive to approach the Raman data from a more general point of view. The reasoning in Sec. III D was based on the assumption that the H^0Li^+ center possessed C_{3v} symmetry. Now we will investigate all the possible symmetries allowed by the experimentally observed BT. In the terminology of Ref. 1 we will investigate which *actual* BT are allowed by the experimentally *observed* BT under the symmetry $F_1=T$ of the orientating operator. First, one notes that BT 40 expressed by (2) allows four representative symmetries and modes, namely, $C_4[001]{:}B$, $D_3[111]{:}E$, $C_3[111]{:}E$, and $C_2[110]{:}B$ (see the T column in Table VIII of Ref. 1). Second, the experimental result (3) taken at face value could be regarded as representing another more general BT, namely,

$$q\neq 0,\;\; r\neq 0,\;\; s\neq 0\,, \tag{5}$$

meaning that the Raman spectrum is described by three independent intensity parameters. From Table VII of Ref. 1 one deduces that (5) corresponds to BT 60 which relates to the representative symmetries and modes $D_2[110]{:}A$, $C_2[110]{:}A$, and $C_1{:}A$. (See also Tables VI and X of Ref. 1.)

These eight representative symmetries based on BT 40 and BT 60 correspond to 23 actual symmetries (see Table VI of Ref. 1). Most of these actual symmetries can be eliminated by taking into account the following.

(i) A center consisting of two different impurities cannot possess inversion symmetry.

(ii) The H^0Li^+ center cannot lie in a $\{100\}$ plane including $\langle 001\rangle$ and $\langle 110\rangle$.

(iii) With two different impurities it is impossible to construct centers possessing either D_3, D_{3d}, C_3, or S_6 symmetry in cubic crystals.

The elimination procedure leaves one with the $C_{3v}[111]{:}E$ modes (from BT 40 and representative mode $D_3{:}E$) that were discussed in Sec. III D, but also with the modes $C_{1h}(110){:}A'$ (from BT 60 and representative mode $C_2[110]{:}A$), $C_{1h}(110){:}A''$ (from BT 40 and representative mode $C_2[110]{:}B$), and finally $C_1{:}A$ from BT 60 which, however, is a possible actual BT for any observed one. One notes that the two degenerate $E(x,y)$ modes of C_{3v} do indeed reduce into the $A'(x')$ and $A''(y')$ modes under C_{1h}, where y' is perpendicular to the C_{1h} reflection plane. We concluded that the more general BT approach leads to the additional possibility that the H^0Li^+ center is tilted away from $\langle 111\rangle$ in a $\{110\}$ plane and that either one of the additional $C_{1h}{:}A'$ and A'' modes could correspond to the 205-cm^{-1} line. Obviously, each of these representations reduces into $C_1{:}A$, when the defect is tilted away from $\langle 111\rangle$ in a general direction. It may not be superfluous to emphasize that on the one hand BT 40 does not allow one to discern between $C_{3v}{:}E$ and $C_{1h}{:}A''$ but that on the other hand the $C_{1h}{:}A'$ and $C_1{:}A$ possibilities are introduced through the more general BT 60. In the latter cases the effect of the tilting must be sufficiently small to permit the observation of the experimental BT 40. A careful analysis of the H^0Li^+ ESR spectra taken at very low temperatures (<10 K) where H^0Li^+ might freeze in or slow down sufficiently could possibly tell whether or not the C_{1h} configuration needs to be considered. At this point we observe that there is no compelling reason to do so. The ESR data obtained so far point to an accurate $\langle 111\rangle$ orientation for the H^0Li^+ center. The latter symmetry will be assumed in the remainder of the paper and the 205-cm^{-1} Raman line is associated with the $C_{3v}\langle 111\rangle{:}E$ mode. Even if eventually a tilted configuration would turn out to be the correct one, the essential picture of the structure and the dynamics of H^0Li^+ that we will present in the following section (Sec. IV) will remain unchanged.

IV. STRUCTURE AND DYNAMICS OF THE H^0Li^+ CENTER

We established that the 205-cm^{-1} Raman line corresponds to the degenerate $E(x,y)$ modes of the H^0Li^+ center. In these modes the H^0 atom moves in a plane perpendicular to the H^0-Li^+ axis which is parallel to a $\langle 111\rangle$ direction of KCl.

In attributing this mode exclusively to a H^0 motion we have made use of the fact that no Li isotope effect is discernible (see Sec. III B). It is not superfluous to comment on this a bit further. In Raman scattering no high-frequency Li^+ vibrational mode is observed for the unperturbed Li^+ center in KCl. It is therefore unlikely that the presence of a compact H^0 atom with its low polarizability compared to that of the surrounding Cl^- ions would enhance the derived polarizability to such an extent that this Li^+ mode would become detectable. As mentioned in Sec. III B, Li^+ modes are observed at 220 cm^{-1} and 265 cm^{-1} (Ref. 8) (with isotope effect) when $^7Li^+$ is sitting next to an F center [forming together an F_A(Li) center]. In this case, however, the Raman observability is resonantly enhanced by the F-center electronic transitions.

If one would follow the results of the ESR study[3] where a $(LiH)^+$ molecule was presented as being the essential core of the center, one could associate the observed E mode with a vibrational motion of the $(LiH)^+$ molecule with respect to the $\langle 111\rangle$ direction. However, the proton hyperfine (hf) interaction of 47.85 mT observed in ESR is isotropic and within 6% equal to the hf interaction of the free H^0 atom which is 50.50 mT. Furthermore, the hyperfine interaction of hydrogen bound to other atoms in a molecule is always at least an order of magnitude smaller than the free H^0 atom value.[11] From these facts we conclude that the hydrogen in the H^0Li^+ center retains to a very high degree its atomic character and that it does not possess a molecular bond of any substantial strength with the adjoining Li^+ ion. A theoretical calculation of the Li^+-H^0 bond strength bears this out.[12]

An important observation that must be taken into account is the inability to produce with $\langle 110\rangle$-polarized light an anisotropy in the orientational distribution of the H^0Li^+ centers even at very low temperatures (~ 10 K). This suggests (Sec. III C) that the H^0Li^+ reorientation motion among its eight $\langle 111\rangle$ orientations, whose existence is clearly established in ESR above 50 K, may still persist at liquid-He temperatures as a tunneling motion.

The picture of the structure and the dynamics of H^0Li^+ that emerges from all this is presented in Fig. 4. The small Li^+ ion ($r=0.68$ Å) and the small H^0 atom ($r=0.78$ Å) (Ref. 13) are both comfortably accommodated on the *same* cation site. They occupy off-center positions along $\langle 111 \rangle$ in opposite directions. The $\langle 111 \rangle$ off-center position of the Li^+ ion in KCl is well documented and so is its tunneling motion among the eight equivalent $\langle 111 \rangle$ off-center positions.[9] We believe it to be quite possible that the Li^+ tunneling motion persists in the H^0Li^+ center and that in doing so the light off-center H^0 performs a correlated motion, i.e., it tags along with the Li^+ ion.

While participating in this reorientation motion the H^0 performs its own vibrational E mode giving rise to the 205-cm^{-1} Raman line.

Recent electron-nuclear double resonance (ENDOR) measurements on H^0Li^+ support this picture.[14] The positions of the Li^+ ion and the H^0 atom could be determined from these data and in fact Fig. 4 has taken these results into account. The Li^+-H^0 distance is found to be 2.2 Å, which is much larger than the sum of H^0 and Li^+ radii. This makes the existence of a molecular bond of any consequence rather unlikely. In agreement with our proposed model for the H^0Li^+ center the ENDOR data place the H^0 atom near the substitutional cation site distinctly removed from the interstitial position i in Fig. 4. This is the position that the unperturbed interstitial H_i^0 center normally occupies. A reasonable criterion for deciding between a more substitutional versus a more interstitial position is to see whether or not the H^0 lies outside or inside the tetrahedron defined by the nuclei of the four Cl^- ions positioned around the interstitial site i. A projection of a tetrahedral plane is indicated in Fig. 4. It is seen in agreement with our conclusion that the ENDOR data place the H^0 clearly in a more substitutional position. From this viewpoint it is not so appropriate to describe the H^0Li^+ center as a Li^+ perturbed interstitial H_i^0 center, indicated by the notation $H_i^0(Li^+)$ in Ref. 14. To be sure, the H^0Li^+ center is produced by the trapping of a mobile interstitial H^0 atom by a substitutional Li^+ ion but in doing so the H^0 moves toward a more substitutional position sharing the cation site with the Li^+.

So far we have not commented on the fact that we could not detect in Raman scattering neither the A_1 mode of H^0Li^+ nor the isotope shifted E mode of D^0Li^+. One or several of the following reasons can be invoked to explain this.

(i) Even with optimal concentrations of the Li^+ and SH^- impurities the H_i^0 to H^0Li^+ conversion is not very efficient ($\simeq 10\%$). Consequently the H^0Li^+ signal is already quite weak, with a peak height about one third of the maximum of the second-order spectrum of KCl.

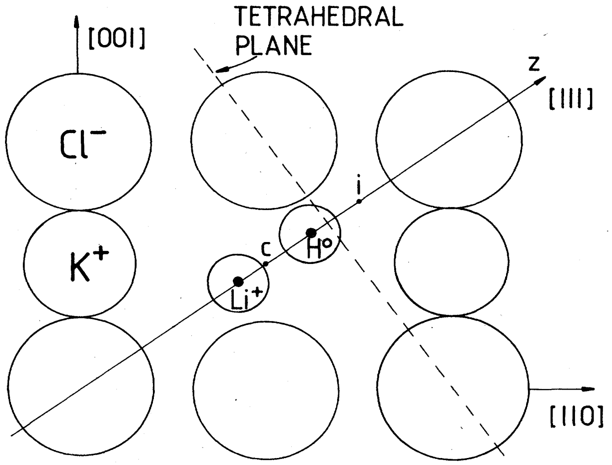

FIG. 4. Schematic model of the H^0Li^+ center shown in a $\{110\}$ plane. The tetrahedral interstitial site is indicated by i and the substitutional cation position by c. The projection of one of the tetrahedral planes defined by the four Cl^- nuclei surrounding the interstitial site i is indicated.

(ii) The D^0Li^+ Raman scattering is expected to be inherently weaker because of the smaller vibrational amplitude of D^0 compared to H^0. This is reflected in the Raman scattering cross section.

(iii) We note that the phonon spectrum of KCl cuts off at (213 ± 3) cm^{-1} (Ref. 15). The 205-cm^{-1} mode lies just inside this spectrum and can interact with a relatively low density of longitudinal optical phonons with small wave vectors. This may explain the tail at the low-wave-number side of the 205-cm^{-1} line (see Figs. 2 and 3). The E mode of the D^0Li^+ center, which would lie around 150 cm^{-1}, falls into a region of high phonon density, very near to the transverse optical branch ($\omega_{TO} \simeq 144$ cm^{-1}),[15] and strong phonon coupling could damp this mode and broaden the Raman line beyond detection. A similar argument also pertains to the A_1 mode of the H^0Li^+ if its frequency is below 205 cm^{-1}. The peak of unknown origin at 170 cm^{-1} (see Sec. III B) has a larger linewidth ($\simeq 20$ cm^{-1}) which nicely illustrates such a broadening induced by phonon coupling.

ACKNOWLEDGMENTS

The authors would like to thank J. M. Spaeth and L. O. Schwan for supplying some of the samples used in these experiments, P. Van Espen for the Li isotope analysis, and A. Bouwen for expert experimental assistance. Financial support from the Geconcerteerde Acties for W.J. and partial support from the Interuniversitair Instituut voor Kernwetenschappen (IIKW) for J.F.Z. are gratefully acknowledged. This work was supported by IIKW and the Geconcerteerde Acties (Ministerie van Wetenschapsbeleid).

---

*Permanent address: Department of Physics, Tsing Hua University, Beijing, China.

[1] J. F. Zhou, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **29**, 5509 (1984).

[2] J. F. Zhou, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **29**, 5533 (1984).

[3] L. O. Schwan, W. Geigle, and H. Paus, Z. Phys. B **35**, 43 (1979).

[4] G. Kurz, Phys. Status Solidi **31**, 93 (1969).

[5] E. Goovaerts, J. Andriessen, S. V. Nistor, and D. Schoemaker, Phys. Rev. B **24**, 29 (1981).

[6] D. Schoemaker, W. Joosen, J. F. Zhou, and E. Goovaerts, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984 (unpublished), p. 410; A. Mabud and F. Lüty, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984 (unpublished), p. 299.

[7] E. Goovaerts, L. De Schepper, A. Bouwen, and D. Schoemaker, Phys. Status Solidi A **59**, 597 (1980).

[8] B. Fritz, in *Proceedings of the First International Conference on Localized Excitations in Solids,* edited by R. F. Wallis (Plenum, New York, 1968), p. 496; A. Mabud and F. Lüty, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984 (unpublished), p. 301.

[9] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. **42**, 201 (1970).

[10] R. M. Martin and L. M. Falicov, in *Light Scattering in Solids,* edited by M. Cardona (Springer-Verlag, Berlin, 1975), pp. 83—88.

[11] See, e.g., W. Weltner, Jr., *Magnetic Atoms and Molecules* (Scientific and Academic Editions, Van Nostrand Reinhold, New York, 1983).

[12] R. N. Yardley and G. G. Balinit-Kurti, Mol. Phys. **31**, 921 (1976).

[13] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, London/Oxford, 1962), p. 338.

[14] G. Heder and J. M. Spaeth, Phys. Status Solidi B **125**, 523 (1984).

[15] J. R. D. Copley, R. W. MacPherson, and T. Timusk, Phys. Rev. **182**, 965 (1969).