Librational motion of the $H_A(\mathrm{Li}^+)$ center in KCl†

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It is shown from the analysis of some subtle features of the ESR spectra that the Cl_2^- axis of the $H_A(\mathrm{Li}^+)$ center in KCl:Li$^+$ which makes a 26° angle with a ⟨100⟩ direction, does not lie exactly in a {110} plane at 4.2 K, but lies outside it by about 1.5°. Such a geometry implies the existence of a librational motion over a 3° angle. The behavior of the ESR lines both as a function of temperature and under ⟨110⟩ uniaxial stress indicates that such a motion exists, and that it is very likely a tunneling motion at 4.2 K with a rate of about 1×10^7 Hz.

In the course of the $H_A(\mathrm{Li}^+)$-center investigations in KCl : Li$^+$ [1–3] it was observed that there are small differences between the ESR spectra taken at 4.2 K and those taken at or above 16 K (Ref. 4) (but below 29 K above which the lines broaden[2]). These differences are quite noticeable in the lines of the $\theta = 31.3°$ spectrum observed when $\vec{H} \parallel [110]$, where θ is the angle between the magnetic field $\vec{H}$ and the Cl_2^- internuclear axis z''. The ESR spectra are shown in Figs. 1(a) and 1(b). However, no detectable differences in the line positions, line shapes, and linewidths are found for the $\theta = 26°$ ($\vec{H} \parallel \langle 100\rangle$) and $\theta = 28.7°$ ($\vec{H} \parallel \langle 111\rangle$) spectra taken at 4.2 and 16 K. The latter spectra can be found in Refs. 1 and 2.

The $\theta = 31.3°$ lines at 4.2 K [Fig. 1(b)] show a loss of resolution, an asymmetric broadening, and a small difference in position when compared to the 16-K spectra [Fig. 1(a)]. This is clear when one compares the lowest or the highest lines of Fig. 1(b) with the corresponding lines at 16 K in Fig. 1(a). In spite of these differences the analysis of the ESR spectra yielded at both temperatures, the same geometric structure for the $H_A(\mathrm{Li}^+)$ center.

However, the above observations can be explained by assuming that at liquid-helium temperatures the Cl_2^- axis lies out of the (011) plane by a small (1° to 2°) angle. The situation is sketched in Fig. 2. Indeed, such a small displacement ($\leq 2°$) out of the (011) plane will not affect the $\theta = 26°$ ($\vec{H} \parallel [100]$) and $\theta = 28.7°$ ($\vec{H} \parallel \langle 111\rangle$) ESR spectra but it will split the $\theta = 31.3°$ ($\vec{H} \parallel [110]$) spectrum into two spectra characterized by $\theta_1 = 31.3° + \epsilon$ (the $1B$-2 direction in Fig. 2) and $\theta_2 = 31.3° - \epsilon$ (the $1A$-2 direction in Fig. 2), where ϵ is a small ($< 2°$) angle. Thus the observed broadening and asymmetry of the lines in the $\vec{H} \parallel [110]$ ESR spectrum is ascribed to a superposition of these two slightly different $\theta = 31.3°$ spectra. Furthermore, the tipping of the Cl_2^- axis out of the (011) plane breaks the equivalence of the two Cl nuclei Nos. 3 and 4 which are responsible for the nonresolved superhyperfine structure (shf) of the $H_A(\mathrm{Li}^+)$ ESR lines.[1] This too may have some influence on the shape and width of the EPR lines. Finally, because the $H_A(\mathrm{Li}^+)$ center changes geometry under ⟨100⟩ uniaxial stress,[3] random internal stress of this type may also contribute to a broadening of the ESR lines. An estimate of the difference in the first-order hf parameter K between the $\theta_1 = 31.3° + \epsilon$ and $\theta_2 = 31.3° - \epsilon$ spectra gives a value of 1–1.5 G. This corresponds to a value for ϵ between 1° and 1.5° ($K \approx 84$ G).

A distinct out of the (011) plane position implies an equivalent equilibrium position on the other side of the (011) plane. One expects that the Cl_2^- when sufficiently activated, will jump between those two

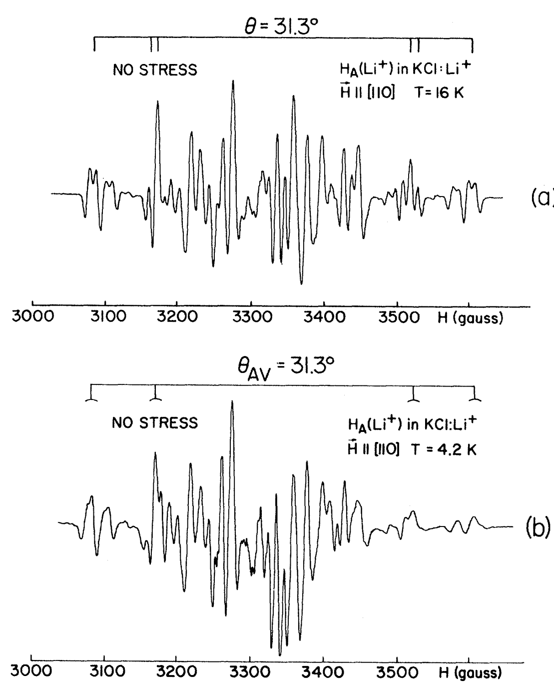

FIG. 1. $\vec{H} \parallel [110]$ ESR spectra of the $H_A(\mathrm{Li}^+)$ center in KCl, (a) at 16 K and (b) at 4.2 K.

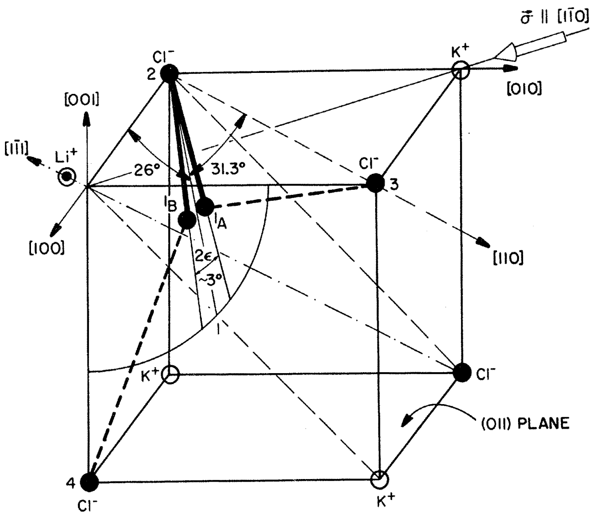

FIG. 2. Two possible out of (011) plane positions of the $H_A(Li^+)$ center at 4.2 K. In the librational motion the Cl_2^- axis z'' librates between the two directions $1A$-2 and $1B$-2.

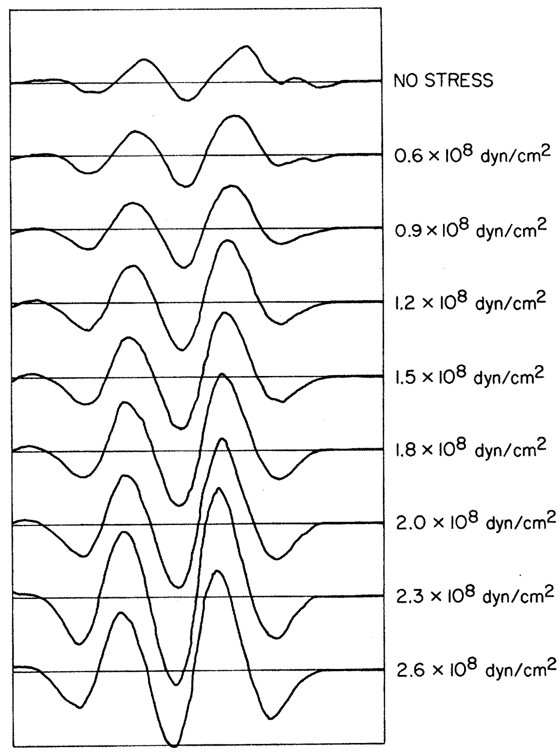

FIG. 4. Effect of $\vec{\sigma} \parallel [1\bar{1}0]$ uniaxial stress at 4.2 K on the high-field line of the $\theta = 31.3°$ spectrum of Fig. 1.

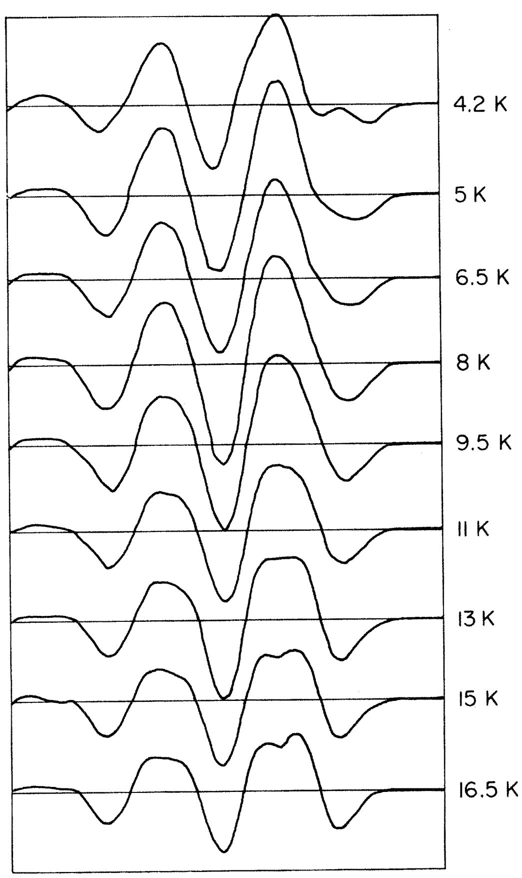

FIG. 3. Temperature dependence of the highest line of the $\theta = 31.3°$ spectrum of Fig. 1 between 4.2 and 16.5 K.

positions. Such a motion has the characteristics of a librational motion (LM) with a librational angle of about $2 \times 1.5° = 3°$. The temperature dependence of the $\theta = 31.3°$ lines as shown in Fig. 3 indicates that such a LM does indeed exist. As the temperature is raised above 4.2 K the line shape changes until at 16 K it reaches a stable shape. As described in detail in Ref. 1 this shape is consistent with hf interaction with nuclei Nos. 3 and 4 (Fig. 2) which are geometrically equivalent with respect to the Cl_2^- axis [assumed to be exactly in the (011) plane], but which are inequivalent with respect to the $\vec{H} \parallel [110]$ external magnetic field.

The spectra in Fig. 3 are interpreted as arising from motional averaging caused by the LM. The averaging is complete at ~16 K, and since the averaging is over a field interval of a few G one estimates that the librational frequency at 16 K is of the order of about 5×10^7 Hz. The spectra of Fig. 3 also indicate that this LM is probably a tunnelling motion at 4.2 K. If, for the sake of making an estimate, one assumes that the libration rate has a linear temperature dependence, one estimates that the LM tunnelling rate at 4.2 K is of the order of, or smaller than, 1×10^7 Hz. This is at least two orders of magnitude larger than the restricted-interstitial-motion (RIM) tunnelling rate at 4.2 K which was estimated[2] to lie in the interval between 10^2 and 10^5 Hz.

The existence of a librational tunnelling motion suggests that it should be possible to populate one librational state, at the expense of the other by means of uniaxial stress along a suitable direction. Fig. 2 shows that the two librational orientations $1A$-2 and $1B$-2 are nonequivalent with respect to $\vec{\sigma} \parallel [1\bar{1}0]$ uniaxial stress. One expects that under such a stress one of these two orientations will build up at the expense of the other.

The $\vec{\sigma} \parallel [1\bar{1}0]$ stress experiments were performed and they can indeed be explained from this point of view. They are shown in Fig. 4. The $\vec{\sigma} \parallel [1\bar{1}0]$ uniaxial stress was applied at 4.2 K and the $\theta_{av} = 31.3°$ spectrum (more precisely, the $\theta_2 = 31.3° - \epsilon$ and the $\theta_1 = 31.3° + \epsilon$ spectra) was monitored through its highest field line. Several things are observed in Fig. 4. First one notes that the absolute intensity of the line is enhanced by the $[1\bar{1}0]$ stress. This is caused by the effect of the $\langle 110\rangle$ stress on the RIM,[5] which is a tunnelling motion. This is of no consequence for the discussions in this paper and it will be described fully in a forthcoming paper.

Second, one notes that the structure on the high-field side of the upper line in Fig. 4, which we believe belongs to the $H_A(Li^+)$ line in the $1A$-2 direction, disappears with stress. The line that remains at slightly lower fields becomes progressively more symmetric and well defined as the magnitude of the stress is increased. The latter line we ascribe to $H_A(Li^+)$ in the $1B$-2 direction, which, because of its larger angle with $\vec{H} \parallel [110]$, possesses a slightly smaller hyperfine separation than H [illegible] in direction $1A$-2. Thus, we conclude that [illegible] [110] uniaxial stress builds up the librational orientation $1B$-2 at the expense of the other librational orientation $1A$-2.

The tipping of the Cl_2^- axis out of the (011) plane is so small (~1.5°) for the $H_A(Li^+)$ center in KCl, that it can be neglected for all practical purposes. However, for the $H_A(Li^+)$ center in NaF : Li^+ this tipping is quite pronounced: Plant and Mieher[6] established that the F_2^- axis of this $H_A(Li^+)$ center makes a $\epsilon = 16.8°$ angle with the (011) plane (the angle with [001] is 33.9° in this case). By means of uniaxial stress measurements at 4.2 K we were able to establish recently[7] that besides a RIM-type tunnelling motion this center too possesses a librational tunnelling motion with respect to the (011) plane. The librational angle is $2\times 16.8° = 33.7°$ for this $H_A(Li^+)$ in NaF : Li^+.

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[1]D. Schoemaker and J. L. Kolopus, Phys. Rev. B 2, 1148 (1970).

[2]D. Schoemaker and E. L. Yasaitis, Phys. Rev. B 5, 4970 (1972).

[3]D. Schoemaker, Phys. Rev. B 9, 1804 (1974).

[4]For recent surveys of interstitial centers in alkali halides, see M. N. Kabler, in *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972); and N. Itoh, Cryst. Lattice Defects 3, 115 (1972).

[5]D. Schoemaker, Bull. Am. Phys. Soc. 18, 305 (1973).

[6]W. Plant and R. L. Mieher, Phys. Rev. B 7, 4793 (1973).

[7]D. Schoemaker, International Conference on Color Centers in Alkali Halides, Sendai, Japan, 1974 (unpublished).