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Spectral-moment constraints on electride-electron locations in the crystalline electride [Cs(18-crown-6)$_2$]

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The inverse-first moment and the first moment of the observed optical-absorption spectrum of the crystalline electride [Cs(18-crown-6)$_2$] [where (18-crown-6) is $(CH_2CH_2O)_6$] are used to determine rigorous upper and lower bounds for the absolute maximum of the single-particle probability density of a typical constituent electride electron. These bounds sufficiently bracket the contact densitites that are determined from magic-angle-spinning ^{133}Cs-NMR spectra of the pure electride and of its mix-crystals with the isomorphous sodide, [Cs(18-crown-6)$_2$Na], to indicate that the distribution of the electron most likely is located in the immediate vicinity of a cesium nucleus. Limitations on the number of ^{133}Cs-NMR absorptions in sodide-electride mix-crystals are shown to support such a location.

INTRODUCTION

The localized electride of formula [Cs(18-crown-6)$_2$] has a crystal lattice that has been described as consisting of alternate planes of (18-crown-6)-sandwich-complexed cesium cations and so-called anionic holes.[1] The (18-crown-6) designation refers to the complexant $(CH_2CH_2O)_6$, which consists of heterocyclic molecules in which six pairs of mutually bonded carbon atoms are bonded alternately to six individual oxygen atoms to form an 18-membered ring. Each complexant molecule's oxygen atoms lie in a plane and appear to be puckered toward the out-of-plane cesium cation. This gives it the appearance of a crown so that it and others like it frequently are designated as *crown ethers.* The anionic holes are located at inversion centers in the lattice and their boundaries are determined by the van der Waals surfaces of the complexant,[1,2] so that the integrity of the crystal structure does not depend on their even being occupied. Figure 1 depicts a subunit of the electride lattice that is essentially in accord with its crystal structure. By construction, the subunit encloses a net single electride electron and a net electrical charge of zero. If the small alternating displacements (±0.42 Å) of the Cs nuclei from the c axis that occur are ignored, the entire crystal lattice can be generated by appropriate displacements of the subunit. Based upon a variety of the electride's properties, Dye and his co-workers[1–4] have suggested that each electride electron has a spatial distribution located in an otherwise empty anionic hole that is surrounded by eight nearest-neighbor (18-crown-6)-sandwich-complexed cesium cations. Thereby, the resulting structure appears to be that of an essentially pure F-center salt. However, because of the impossibility of observing the electride electrons directly,[1,2] the feature of having electrons completely replace the conventional anions in a salt is uncertain and warrants caution before it is accepted.

Nevertheless, some independent theoretical support for the suggested electride electron anionic-hole location has come forth recently as the result of two independent investigations[5,6] that have dealt with the quantum-mechanical spatial distribution of the electride electrons. In both treatments, a typical one of these electrons in the vicinity of a cesium cation was reported to be subjected to an additional repulsive potential associated with the oxygen atoms of the (18-crown-6) complexant. This was regarded as providing a mechanism that diminished its probability density at the complexed cesium nucleus appreciably compared to that in a free cesium atom and, thereby, supported the suggested location. In one of the investigations,[5] in addition, an attractive potential in the vicinity of the anionic holes was reported that appeared to justify locating an electride electron there, but was accompanied by negligible probability density at the cesium nucleus. In view of the complexity of the system under consideration, however, the approximations that were required in the analyses[7,8] still warrant caution in accepting the spatial distribution suggested by Dye and his associates.

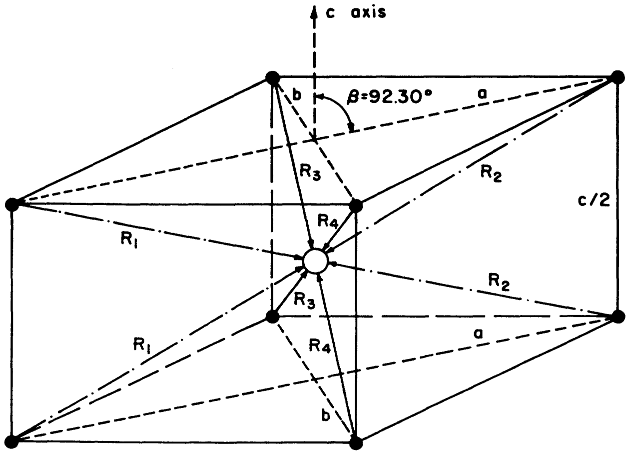

FIG. 1. Subunit of crystalline [Cs(18-crown-6)$_2$]. $a = 13.075$ Å, $b = 15.840$ Å, $c = 17.359$ Å. The central Cs site is displaced ±0.42 Å from the c axis along the b direction. $R_1 = 7.71$ Å, $R_2 = 8.01$ Å, $R_3 = 8.67$ Å, $R_4 = 9.41$ Å, anionic hole site ●, [Cs(18-crown-6)$_2$]$^+$ site ○.

Because it is extremely difficult to determine a reliable location for the spatial distribution of an electron by any direct experimental or theoretical means, an indirect method of dealing with it can be helpful. The method to be employed here uses an experimentally determined optical-absorption spectrum[9] to obtain the mean dispersion in position and the mean dispersion in momentum[10,11] of a typical electride electron, as well as an estimate of its spatial distribution with respect to its own mean location.[12] The two dispersions yield rigorous upper and lower bounds for the absolute maximum of its single-particle probability density.[13] Because of the diffuseness of the spatial distribution,[14] its location[15] will be identified here with that of this maximum. The bounds prove to be within an order of magnitude of each other for the present electride and impose experimentally determined constraints on the probability-density maximum of the electride electron's spatial distribution. From these bounds and the experimentally determined contact densities at the Cs nuclei,[4] both in pure electride and in sodide electride mix-crystals, it is concluded that a typical electride electron most likely is located in the immediate vicinity of a cesium nucleus, rather than in an anionic hole. Such a location is supported by the limited number of ^{133}Cs magic-angle-spinning (MAS) -NMR absorptions that are observed in the mix-crystals. This conclusion and the basis for arriving at it provide the motivation for this paper.

In the following section we collect several experimental facts pertaining to the system under consideration. The two bounds on the absolute maximum of the probability density of a typical electride electron are determined in the section that follows. Exhibited there is the extent to which they bracket the precisely known value of the absolute maximum of the maxentropic probability-density distribution[12] for an excess electron that has identical dispersions, thereby providing an indication of their adequacy; they are found to so bracket the observed value of the contact density at a cesium nucleus in the pure electride, that the location of the electride-electron distribution can reasonably be inferred to be in the immediate vicinity of the cesium nucleus; both the values and the limited number of cesium contact densities that are observed in co-precipitated sodide-electride mix-crystals are shown to provide independent support of the inferred location. A discussion of the results and some of their implications is given in the final section.

RELEVANT FACTS

We collect here some of the experimental evidence that has a bearing on the analysis to be employed.

(1) On the basis of the observed semiconductorlike electrical conductivity and the magnetic susceptibility of the electride,[1-4] the electride electrons appear to be weakly interacting localized entities, with a binding energy of ~ 0.9 eV.

(2) The crystal structure, determined at 216 K,[1] consists of the subunits which are adequately represented in Fig. 1. This leads to a mean electride-electron density throughout the pure electride of[4] 1.1×10^{21} cm^{-3}.

(3) The electride-electron contact density at a cesium nucleus in the pure electride,[4] deduced from its ^{133}Cs MAS-NMR spectroscopy, is 8.75×10^{21} cm^{-3}.

(4) The electride is isomorphous with the sodide,[3,4] [Cs(18-crown-6)$_2$Na], the anionic holes in the electride being the structural analogs of the Na$^-$ ions. ^{133}Cs MAS-NMR spectra of co-precipitated mix-crystals of sodide and electride yield a limited number of nuclear absorption frequencies. They correspond to electride-electron contact densities of (0, $\frac{5}{8}$, $\frac{6}{8}$, $\frac{7}{8}$, and $\frac{8}{8}$) the value in the pure electride.[2-4]

(5) As determined from the inverse-first moment of the observed optical-absorption spectrum of the electride,[9] with the use of spectral-moment theory,[10,11] the mean dispersion in position of a typical electride electron about its mean location, $\langle r^2\rangle$, is[14] 12.2 Å^2 (43, in atomic units).

(6) The first moment of the observed-optical absorption spectrum of the electride,[9] with the use of spectral-moment theory,[10,11] yields a mean dispersion in momentum $\langle p^2\rangle$ of 0.058 (in atomic units). The Heisenberg product $P=\langle r^2\rangle\langle p^2\rangle$ has a value of 2.5 (in atomic units).

SPECTRAL CONSTRAINTS ON ABSOLUTE MAXIMUM OF SPATIAL DISTRIBUTION

(i) Rigorous upper and lower bounds for the absolute maximum of the single-particle probability-density distribution of a localized electronic system have been determined recently,[13] viz.,

$$B(\text{lower})/\langle r^2\rangle^{(3/2)}\le\Gamma(0)\le B(\text{upper})/\langle r^2\rangle^{(3/2)}\ , \tag{1}$$

where the spatial origin of the distribution has been chosen to be the position of the absolute maximum density in the subunit and $\Gamma(0)$ is its value at that point. The B's were determined to be functions of the Heisenberg product. For the present purpose we can summarize the results by noting that (in atomic units)

$$B(\text{upper})=(2/\pi)P^{1/2}(P-1) \tag{2}$$

and by pointing out that the geometric mean of the bounds is numerically bounded in the range of interest here:

$$0.512\le\{B(\text{upper})B(\text{lower})\}^{1/2}\le0.540 \tag{3}$$

when

$$2.35\le P\le2.80\ . \tag{4}$$

For the present electride we can then obtain that

$$4.0\times10^{21}\le\Gamma(0)\le35\times10^{21}\ \text{cm}^{-3}\ . \tag{5}$$

(ii) To give some indication of the practical utility of the bounds and their limitations we use the precisely known absolute maximum of the maxentropic probability-density distribution for an excess electron that has the same dispersion in position and the same dispersion in momentum as an electride electron under consideration. It is[12]

$$\Gamma_{\text{mxnt}}(0)=(3/2\pi\langle r^2\rangle)^{3/2}\ . \tag{6}$$

For the present electride we obtain 7.7×10^{21} cm^{-3}. From this figure it would appear that the geometric mean of the lower and upper bounds, viz., 12.3×10^{21} cm^{-3} by Eq. (3), gives an estimate of the absolute maximum that is within a factor of 2 of the actual value.

(iii) The observed contact density at a cesium nucleus[4] in the pure electride of 8.75×10^{21} cm^{-3} is intermediate to the two bounds in Eq. (5). It would thus be consistent with the spectral facts, both optical and NMR, to regard the spatial distribution of each electride electron as simply being located in the immediate vicinity of a cesium nucleus.

Although, as suggested by Dye and his associates, a distribution located in one of the surrounding anionic holes also appears to be consistent with the spectral facts, it poses certain difficulties. For example, in order to yield the observed contact density at a cesium nucleus, additive contributions of electron density of 1.1×10^{21} cm^{-3}, on average, would have to be supplied by each of the individual electride-electron distributions in its eight anionic hole nearest neighbors. In view of the bounds of Eq. (5), each such contribution would be an appreciable fraction of the absolute maximum density of a typical electride-electron distribution. The significant overlap of the individual distributions that would result clearly conflicts with the weakly interacting characterization that has been accorded the electride electrons[1,3] on the basis of their observed magnetic behavior. Each subunit would then enclose a resulting composite spatial distribution of the electride electrons having density maxima of comparable magnitude at each of the nine sites depicted in Fig. 1, with considerably smaller densities in the intervening regions. Apart from possible coincidence, the required comparability of the densities of the electride electrons in the immediate vicinities of both the anionic holes and the cesium nuclei would remain unaccounted for. Furthermore, for each anionic-hole-localized distribution to contribute to each cesium nucleus an average density of just about the same as the mean density of[4] 1.1×10^{21} cm^{-3} and to still yield density values in the intervening regions of the subunit that must be even smaller than the mean value poses another difficulty. In addition, the large distances between a cesium and its anionic hole nearest neighbors, 8.45 Å on average, would appear to imply a considerably larger value of $\langle r^2\rangle^{1/2}$ than the spectrally determined value of 3.5 Å.

A cesium-localized electride-electron distribution clearly accounts for the spectral facts with none of the foregoing difficulties. As a consequence, the inference that the spatial distribution of each electride electron most likely is located in the immediate vicinity of a cesium nucleus rather than in an ionic hole seems entirely reasonable if not unavoidable.

(iv) The cesium locations are consistent with the results reported for the contact densities at cesium nuclei in co-precipitated sodide-electride mixtures. To see this, consider a subunit as in Fig. 1, in which N of the anionic sites are occupied by sodide ions, Na$^-$. Because of the required net electrical neutrality of the subunit, the fractional occupancy of the electride electron there must be $[1-(N/8)]$. Presuming that the normalized spatial distribution of the electride electron in the vicinity of the cesium nucleus is not affected appreciably by the presence of the sodide ions, we require the absolute density maximum there to be

$$\Gamma_{\mathrm{mix}}(0)=[1-(N/8)]\Gamma(0)\ , \qquad (7)$$

with the bounds on $\Gamma(0)$ being those in Eq. (5). Combining Eqs. (5) and (7) yields

$$4.0\times10^{21}[1-(N/8)]\mathrm{cm}^{-3}\le\Gamma_{\mathrm{mix}}(0)\le35\times10^{21}[1-(N/8)]\mathrm{cm}^{-3}\ . \qquad (8)$$

Because the observed contact densities at cesium nuclei in the sodide-electride mixtures[2-4] are related to the contact density in the pure electride precisely as in Eq. (7), for $N=0,1,2,3,8$, they also obey the inequalities implied in Eq. (8). As a result, all of the cesium-NMR contact results support the location of the electride electrons to be in the immediate vicinity of the cesium nuclei.

(v) An important aspect of the mix-crystal results is the observed restriction on the values of N. Apart from a suggestion[2,4] that the results can be accounted for in terms of a postulated superlattice in the mix-crystal in which $\frac{1}{8}$ of the anionic-hole-localized electride electrons are replaced in a regular manner by sodium anions—for which there is no supporting crystallographic evidence currently available—no good reason for such a limitation has yet been advanced. However, there is one: The increased presence, beyond a certain number, of sodium anions in a subunit having a cesium-localized distribution makes an environment for the electride electron that is unfavorable energetically.

To show how this comes about, albeit in formal terms, we will suppose that subunits containing various numbers of sodide ions exist throughout a mix-crystal. The observed semiconductorlike electrical conductivity of the pure electride means that, despite their intrinsic localization, the electride electrons there are capable of continual interchange of their locations from one subunit to another. By contrast, all the ionic species in the electride can be supposed to retain fixed locations in the lattice, as will the subunits that they determine. The same behavior can be expected in a mix-crystal. How the electride electrons are distributed among the various subunits is our immediate concern.

An electride electron that would be located in a subunit that also contained N sodide ions as nearest neighbors of the cesium nucleus there would have a mean energy $\langle E_e\rangle$ consisting of the sum of four parts: (1) $\langle T_e\rangle$ its kinetic energy; (2) $\langle V_{es}\rangle$ its net attractive energy of interaction with all the constituents of the subunit other than the sodide ions; (3) $\sum_i\langle V_{ei}\rangle$, each of the latter terms corresponding to its interaction energy with one of the sodide ions; (4) $\langle V_r\rangle$ its interaction energy with all the remaining constituents of the electride. Because of the large distances that are involved we can disregard the latter with no undue error. For the required net electrical neutrality of the subunit, each of these energies must be multiplied by the factor that reflects the fractional occupancy of the electride electron, $[1-(N/8)]$, and we obtain

$$\langle E_e \rangle = \left[\langle T_e \rangle + \langle V_{es} \rangle + \sum_i \langle V_{ei} \rangle \right] [1-(N/8)] \quad (9)$$

as an adequate approximation to the mean energy of the electron.

Since the electron is presumed to be localized in the subunit when $N=0$, we may take $\langle V_{es} \rangle$ to be negative and essentially independent of the number of sodide ions. Correspondingly, we may expect $\sum_i \langle V_{ei} \rangle$ to be positive and to increase with increasing numbers of them. Hence, we can expect that the mean potential energy of the electron will increase monotonically for small values of N, beginning with negative values that will favor the electride electron's presence in the subunit. Ultimately, positive values will arise that will promote its relocation. Depending on the values of the various energy terms, energetically favorable N in accord with the observed values can occur; all depends upon their values. An example of such behavior follows.

From the semiconductorlike behavior of the electride in paragraph (1), all energies being reckoned from the threshold value corresponding to the dissociated ground state of the electron in the pure electride, we have

$$\langle T_e \rangle + \langle V_{es} \rangle = -0.9 \text{ eV}, \quad N=0 \,. \quad (10)$$

From the mean dispersion in momentum in paragraph (6) we have

$$\langle T_e \rangle = +0.8 \text{ eV}, \quad N=0 \,. \quad (11)$$

As a result,

$$\langle T_e \rangle \approx -\tfrac{1}{2} \langle V_{es} \rangle, \quad N=0 \,. \quad (12)$$

To estimate $\langle T_e \rangle$ for nonzero N we shall assume a similar form as long as the mean kinetic energy is positive, viz.,

$$0 < \langle T_e \rangle \approx -\frac{1}{2} \left[\langle V_{es} \rangle + \sum_i \langle V_{ei} \rangle \right] , \quad (13)$$

so that then

$$\langle E_e \rangle \approx +\frac{1}{2} \left[\langle V_{es} \rangle + \sum_i \langle V_{ei} \rangle \right] [1-(N/8)] \,. \quad (14)$$

From Eqs. (10) and (11) we get

$$\langle V_{es} \rangle = -1.7 \text{ eV} \quad (15)$$

and for the sodide-electride-electron interactions we take

$$\langle V_{ei} \rangle = +(14.4/\epsilon R_i) \text{ eV} , \quad (16)$$

where ϵ is the dielectric constant for the constituents of the subunit and R_i is one of the distances in Fig. 1 (in Å).

For the purpose of illustration we shall estimate the dielectric constant to be the factor by which the ionization energy of a free cesium atom must be reduced to yield the binding energy of an electride electron in the electride, and obtain $\epsilon \approx 4.3$. For simplicity we shall consider only those locations of the sodide ions that yield the smallest repulsive energy for each N and provide, thereby, the most favorable environment for localization of the electron. Then, the (minimum) mean energies (in eV) of the localized electride electron, for $N=0$, 1, 2, 3, would be, respectively, -0.9, -0.59, -0.31, -0.11. For $N=4$ to 8, localization would not be favored since the inequality to Eq. (13) would not be satisfied. Because the system is essentially in a condition of equilibrium, only the subunits for which $N=0,1,2,3$, would thus appear to have any appreciable likelihood of retaining an electride electron as a localized entity in sodide-electride mix-crystals. Notably, these localization-favored N values are observed. In addition, all of the remaining N values that disfavor localization correspond to subunits that should exhibit no contact density at their cesium nuclei, with a resulting single nuclear absorption that also is observed. This would correspond to $N=8$ in Eq. (14). Altering the parameters will alter the energetics quantitatively, of course, but that would not appear to affect the basic reason for the limitation on N.

By contrast, electride electrons that are exclusively localized in anionic holes will experience interactions with the remaining occupants of the anionic-hole sites, viz., either electride electrons or sodide ions, that will be predominantly Coulombic because of the distances involved and will, thereby, be essentially invariant to their exact nature. As a result, the number of sodium anions that are in the subunit cannot account for the limitation.

The present agreement between results of the foregoing approximate theory and the experimental observations clearly gives added support to the location of the electride-electron distribution that we have already indicated for them. It also suggests a possibly unambiguous means for distinguishing between the cesium locations and the anionic-hole locations of the electride electrons.

DISCUSSION

The electride electrons have been treated, as in metals, *F*-center systems, and solvated-electron systems, as if they were distinct from all other electrons in the electride. No other characterization seems possible if we wish to ascribe the various spectral, electrical, and magnetic properties of the electride to those of its constituent electride electrons. However, the imposed distinction may be less serious than might first be imagined. This is because of our treatment's implicit use of the single-particle density matrix for the species to determine its mean properties, viz., its mean dispersions in position and momentum, which are single-particle properties. This density matrix implicitly incorporates all the constraints which are to be imposed on all the electrons of the system, e.g., spatial symmetry, exchange antisymmetry, spin, etc. As a consequence, the distinctness we have ascribed to the electride electrons can be viewed as assuming that they can be associated with some suitably renormalized portion of the full single-particle density matrix that embodies their unique properties.

The results obtained here have been based on just a single optical-absorption spectrum of a thin film of the electride.[9] Furthermore, a spectral-moment theory developed for infinitely dilute solutions of solvated electrons[11] has been used, even though the electride is obviously not such a system. Our justification for its use is based primarily on the model-free feature of the theory, the weak mutual interaction presumed for the electrons, and, in addition, the marked similarity of the electride's spectrum to the spectra of solvated electrons. The absorbance values of the available spectrum were determined at appropriately spaced frequencies by interpolation; beyond the reported range, they were extrapolated using a $\frac{3}{2}$-power frequency dependence in the neighborhood of the absorption threshold[16–18] and an inverse $\frac{7}{2}$-power frequency dependence asymptotically.[10] The requisite integrations to determine $\langle r^2 \rangle$ and $\langle p^2 \rangle$ were carried out with an uncertainty that we estimate to be about 5%. Clearly, the results we have obtained from its use must be regarded as tentative. More spectral evidence is necessary to establish the reliability of our conclusions. However, even if the uncertainties in the spectral moments were to differ from those estimated here by as much as fivefold, the numerical aspects of our treatment would obviously be changed but not its conclusions.

The contact densities have been identified with the spatial probability densities of the electride electrons. However, there can be effects due to induced spin which contribute to the contact density but not to the spatial probability density. In alkali-metal atoms, for example,[19] the induced contribution amounts to about one-third of the total effect. Since our treatment makes no stringent use of the actual numerical values of the densities, the conclusions we have reached are hardly likely to be changed even if the densities were to change by a factor of 2.

The use of bounds on the single-particle density of an electronic system to assess the accuracy of certain quantum-mechanical calculations is well known.[20] These have depended on the use of quantities that required further calculations, sometimes of questionable accuracy. The present treatment is one in which the requisite bounds can be determined with potentially high reliability from experiments. From the "looseness" that they manifest in respect to highly accurate densities [see the results considered in paragraph (2), above], it would be useful to have "tighter" ones that are similarly constrained experimentally.

An important aspect of the present analysis does not depend on the bounds at all: This deals with the limited number of ^{133}Cs-NMR absorptions that are observed in sodide-electride mix-crystals. Its importance lies in its potentiality to provide what appears to be an unambiguous way to discriminate between possible locations of the electride electrons. Because we have merely sketched the underlying energetic basis for the occurrence of such a limitation, a fuller statistical-mechanical treatment designed to determine the relative populations of the various subunits with electride-electron occupants and their locations would be useful. The relative intensities of the pertinent lines of the NMR spectrum would be determinable, thereby. Furthermore, the role played by subunits that would appear to have no electride-electron occupants—apart from those which would exist in the pure sodide—might be clarified. That the binding energy of a localized electron in a subunit will be lowered because of the presence of sodide ions there should be reflected in a lower semiconductor band gap for the mix-crystal than for the pure electride. It should likewise be reflected in a redshift of the optical-absorption spectrum of the sodide-electride mix-crystals. Both of these consequences seem to be amenable to experimental tests.

An important question that arises when the distributions of the electride electrons are located as we have indicated concerns the nature of the cesium entities: Are they to be regarded as *ions* or as *atoms?* Because of the diffuseness of the distribution that is involved,[14] and the relatively small binding energy of an electride electron compared to the ionization energy of an atom of cesium, viz., less than one-fourth, the cesium entity cannot properly be regarded as an atom in the electride. It has been claimed[1] that the cesium entity is an *ion in the electride,* based largely on the fact that the Cs-O distances in the electride are nearly identical with those in the sodide, as well as in other compounds involving an (18-crown-6)-complexed cesium that is presumably ionic. However, it is readily verified[21] that many diatomic molecules and their positively charged molecule-ion counterparts have interatomic distances that are within 0.1 Å of each other, and quite often less, so that the argument based on a near invariability of interatomic distances is unconvincing. Indeed, as pointed out by Slater[22] some years ago, interatomic distances are essentially independent of the nature of the bond between the atoms involved.

We suggest that the present electride be regarded as an intrinsically stable solid phase of *an electrically neutral molecule that results from the (18-crown-6)-complexed cesium cation binding an electron*: $[\mathrm{Cs(18\text{-}crown\text{-}6)_2}]^0$.

Finally, we emphasize that the most likely locations we have found for the electride electrons in the present electride are not a prototype for all crystalline electrides. There may be others, but that remains to be seen and to be shown.

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trum estimated in Ref. 5 appear not to fulfill an essential inequality required of them (Ref. 10), with the cited experimental value of the first moment being somewhat smaller than the value reported here; the radial density determined in Ref. 6 to account for the observed ^{133}Cs MAS-NMR results (Ref. 4) appears to be associated with a radial distribution that will yield a mean dispersion in position for an electride electron that exceeds that determined from the optical-absorption spectrum of the electride (Ref. 14).

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