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Scaling relations and orientation of CN^- impurities in alkali halide and silver halide crystals

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The confined-oscillator scaling model gives the stretching frequencies ν_0 of isolated CN^- impurities in alkali halide and silver halide crystals and ν_3 of CN^- molecules sandwiched between satellite impurity cations in terms of (1) the kind of neighbor-ion species, (2) the axial space availability, and (3) the position of neighbor ions relative to the host lattice.

I. INTRODUCTION

The cyanide molecular ion CN^-, substituted at anion sites in alkali halide (AX) crystals, represents a simple model system for studying the influence of a host crystal matrix on properties of an impurity molecule. A striking example is the dependence of the fundamental CN^- stretching frequency ν_0 on the lattice constant a of the host crystal[1] as indicated by the linear scaling relations in Fig. 1 from the data in Table I. The overall feature in Fig. 1 is a decrease of ν_0 with increasing a. Such a frequency dependence of the confined molecule's vibration on space availability in the surrounding matrix implies the model of a squeezed anharmonic oscillator for CN^- in an AX host.[2] Closer inspection of Fig. 1 shows that the ν_0 data from the KX and RbX (X = Cl,Br,I) hosts fall along a common straight line whereas the data from the NaX and CsX hosts fall along two separate lines. The separate line of the CsX data may be easily attributed to the different cesium chloride ($B2$) structure of the CsX crystals in contrast to the rocksalt ($B1$) structure of KX and RbX. However, the deviating behavior in the NaX hosts (also of $B1$ structure) is surprising.

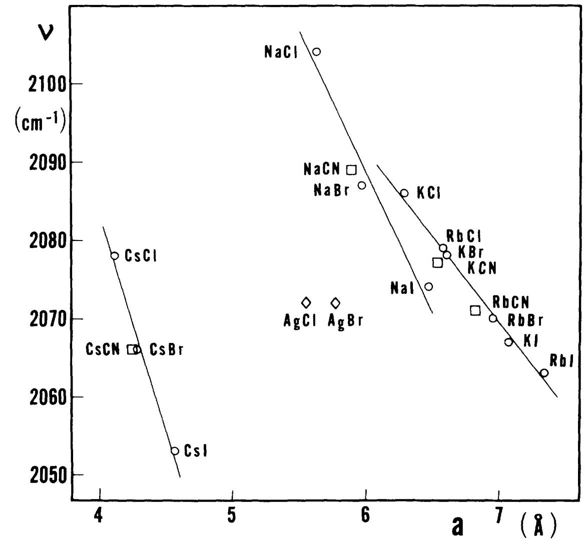

FIG. 1. Observed fundamental stretching frequency ν_0 of CN^- molecules in alkali halide (circles) and silver halide hosts (diamonds) and in alkali cyanides (squares) vs lattice constant a of the host crystal.

The irregularity of ν_0 in the NaX hosts, which has received little attention so far, must be a consequence of the observed dependence of the molecular orientation on the host cation species, namely a ⟨100⟩ orientation of CN^- in NaX in contrast to a ⟨111⟩ orientation in KX and RbX.[3–6] Viewed with regard to the axial host neighbor distance, such orientational behavior of the confined CN^- molecule in NaX hosts seems counterintuitive. In order to minimize axial compression one would expect that the CN^- molecule in an AX host of $B1$ structure would prefer the possibly longest distance, $s=a\sqrt{3}$, between opposite cation neighbors in a ⟨111⟩ direction rather than the possibly shortest distance, $s=a$, between opposite cation neighbors in a ⟨100⟩ direction. The disagreement between expected and observed CN^- orientations indicates a peculiarity among the interatomic forces that favors a closer proximity between CN^- and Na^+ than the trend of the more repulsive interaction between CN^- and the larger cations, K^+ and Rb^+, implies.

It is, of course, the minimum total energy that determines the atomic configuration of the CN^--host complex. It will therefore require total-energy calculations to explain the ⟨100⟩ orientation of CN^- in NaX in contrast to the ⟨111⟩ orientation in KX and RbX. To point out

TABLE I. Fundamental vibrational stretching frequency ν_0 (in cm^{-1}) of substitutional CN^- molecules in alkali halide host crystals at $T=100$ K, in alkali cyanides at room temperature, and in silver halides at $T=22$ K (top values) (Refs. 1, 2, and 14) and lattice constant a (in Å) of the host crystals at room temperature (bottom values) (Ref. 22).

	Cl	Br	I	CN
Na	2104	2087	2074	2089
	5.63	5.97	6.47	5.89
K	2086	2078	2067	2077
	6.29	6.60	7.07	6.53
Rb	2079	2070	2063	2071
	6.58	6.85	7.34	6.82
Cs	2078	2066	2053	2066
	4.12	4.29	4.57	4.25
Ag	2072	2072		
	5.55	5.77		

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the difficulties involved, we note that atomistic calculations of AX:CN$^-$ complexes using Born-Mayer potentials[1,7] have had only limited success so far because of considerable uncertainties in the potential parameters facing the high-accuracy requirement in determining the minimum-energy configuration.

While an explanation of the dependency of CN$^-$ stretching frequencies ν_0 on both the host-cation species and the host-lattice spacing in terms of microscopic calculations is beyond the scope of this study, the linear scaling relations in Fig. 1,

$$\nu_0(AX{:}\mathrm{CN}^-)=m(A^+)a(AX)+b(A^+)\ , \qquad (1)$$

with host-lattice constant $a(AX)$ and host-cation-dependent slope $m(A^+)$ and intercept $b(A^+)$,[8] (1) draw attention to this remarkable problem, (2) predict approximate stretching frequencies of CN$^-$-Na$^+$ impurity complexes in KX and RbX hosts, and (3) provide insight into the neighbor distances of CN$^-$ in NaX, CsX, and AgX hosts.

II. CN$^-$ WITH Na$^+$ NEIGHBORS IN KX AND RbX HOSTS

When KX crystals are double-doped with small amounts of KCN and NaX, both isolated CN$^-$ impurities (with $\langle 111\rangle$ orientation and stretching frequencies ν_0) and additional CN$^-$-Na$^+$ impurity complexes are formed in the KX hosts. The CN$^-$ and Na$^+$ ions of the latter complexes are nearest neighbors (NN's) residing substitutionally at KX lattice sites with CN$^-$ oriented toward Na$^+$, i.e., in a $\langle 100\rangle$ direction.[9] Thus it appears that the orientational effect which Na$^+$ ions exert on CN$^-$ molecules in NaX hosts carries over to the KX matrix by the mere presence of one Na$^+$ neighbor to a CN$^-$ molecule in a KX host. Because of the polar character of CN$^-$ there are two stretching frequencies of these complexes, ν_1 and ν_2, according to the two possible $\langle 100\rangle$ configurations, K$^+$-CN$^-$-Na$^+$ and Na$^+$-CN$^-$-K$^+$, which typically[9,10] differ by a few wave numbers, $\nu_2-\nu_1\approx 5$ cm^{-1}. Another molecular stretching frequency, ν_3, arises when a CN$^-$ molecule in a KX host is sandwiched between *two* Na$^+$ satellite impurities in $\langle 100\rangle$ orientation, Na$^+$-CN$^-$-Na$^+$.

We now want to extend the scaling behavior in Fig. 1 to obtain hypothetical CN$^-$ stretching frequencies of impurity complexes in KX hosts, ν^*(KX:CN$^-$:Na$^+$), based on three model assumptions. Two general assumptions are that these frequencies are determined by (1) the species of axial NN cations and (2) the space availability s defined as the distance between the opposite, axial cation neighbors of CN$^-$. We restrict our confined-oscillator scaling model to those cases where the axial NN's are actually absolute NN's to CN$^-$ such as Na$^+$ neighbors of $\langle 100\rangle$-oriented CN$^-$ molecules in KX hosts (and A^+ neighbors of $\langle 111\rangle$-oriented CN$^-$ in CsX hosts, to be discussed below). The reason for this restriction is that the axial neighbor distance is not the only neighbor distance affecting the CN$^-$ stretching frequency if there are nearer absolute neighbors than the axial NN's. This is the case, for example, for $\langle 111\rangle$-oriented CN$^-$ in KX where the stretching vibration of CN$^-$ is not only impeded by the axial K$^+$ neighbors (being absolute third neighbors to CN$^-$) but also by X^- neighbors in $\langle 110\rangle$ directions (being absolute second neighbors to CN$^-$).

While the purpose of Fig. 1 is to reveal systematic dependences of the fundamental stretching frequencies ν_0 on the host lattice constant a, Fig. 2 relates to the confined-oscillator scaling model in showing stretching frequencies of CN$^-$ molecules or complexes in their dependence on the axial space availability s. Since $s=a$ in the case of the NaX:CN$^-$ systems, the line relating to the ν_0 (NaX:CN$^-$) data is the same in Figs. 1 and 2. On the other hand, because of the above-mentioned restrictions, the KX:CN$^-$ and RbX:CN$^-$ systems are beyond the present model and are therefore not included in Fig. 2.

For the KX:CN$^-$:Na$^+$ systems under consideration we make a third, specific model assumption, namely that the impurity Na$^+$ ions are substitutionally incorporated at (ideal) cation sites in the KX crystals. For later reference let us call this assumption the "on-lattice residence" of satellite impurities. From the three model assumptions we expect ν_3^*(KX:CN$^-$:Na$^+$) values to scale according to Eq. (1) like the fundamental stretching frequency of an isolated, $\langle 100\rangle$-oriented CN$^-$ molecule in a NaX crystal, ν_0(NaX:CN$^-$), but with a space availability of the lattice constant of the actual KX host, $s=a$(KX). Such extrapolated ν_3^*(KX:CN$^-$:Na$^+$) frequencies, scaled with Eq. (1) (or, equivalently, with Figs. 1 or 2) are listed in Table II. They deviate, for KX=KCl and KBr, about twice as much from the fundamental frequencies ν_0 (KX:CN$^-$) than the average values ν_{12}(KX:CN$^-$:Na$^+$)=$(\nu_1+\nu_2)/2$ of the measured[9,10] stretching frequencies ν_1 and ν_2 that

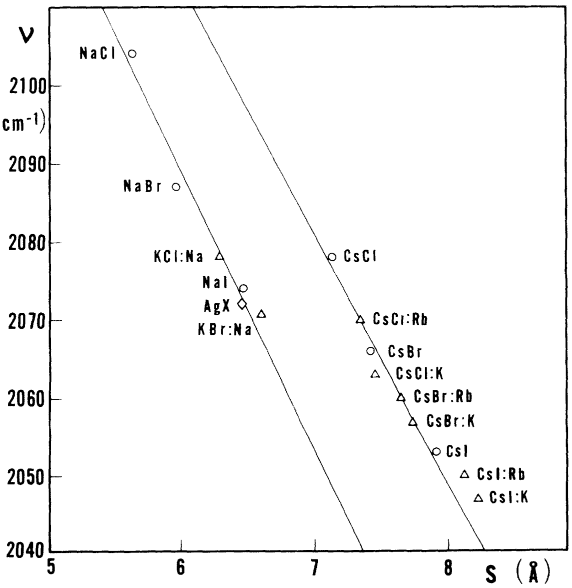

FIG. 2. Observed fundamental stretching frequency $\nu_0(AX{:}\mathrm{CN}^-)$ of isolated CN$^-$ molecules (circles, labeled AX) vs axial space availability $s=d(A^+\text{-}A^+)$ and stretching frequency $\nu_3(AX{:}\mathrm{CN}^-{:}A'^+)$ of A'^+-CN$^-$-A'^+ impurity complexes (triangles, labeled $AX{:}A'$) in alkali halide hosts vs space availability $s=d(A'^+\text{-}A'^+)$.

TABLE II. Observed and scaled stretching frequencies (in cm^{-1}) of CN^- molecules in alkali halides (AX). The frequency $\nu_{12}=\frac{1}{2}(\nu_1+\nu_2)$ is averaged over ν_1 from A^+-CN^--Na^+ complexes and ν_2 from Na^+-CN^--A^+ complexes in the AX hosts. The frequency ν_3 arises from Na^+-CN^--Na^+ complexes in AX hosts.

Isolated molecule in ⟨111⟩	Experiment ν_0	Impurity complex in ⟨100⟩	Scaling ν_{12}^*	ν_3^*	Experiment ν_{12}	ν_3
KCl:CN^-	2088[a]	KCl:CN^-:Na^+	2083	2079	2085[a]	2078[a]
KBr:CN^-	2078	KBr:CN^-:Na^+	2073	2068	2075[b,c]	2069[c]
KI:CN^-	2067	KI:CN^-:Na^+	2059	2051		
RbCl:CN^-	2079	RbCl:CN^-:Na^+	2074	2068		
RbBr:CN^-	2070	RbBr:CN^-:Na^+	2064	2058		
RbI:CN^-	2063	RbI:CN^-:Na^+	2052	2041		

[a] References 10 and 20.
[b] References 9 and 21.
[c] Reference 10.

arise when CN^- is sandwiched between a Na^+ impurity and a K^+ host ion. A renewed inspection of the KCl:CN^-:Na^+ and KBr:CN^-:Na^+ absorption spectra[10] has indeed revealed, besides the prominent ν_0, ν_1, and ν_2 peaks, a smaller, previously unidentified absorption peak at a frequency $\nu_3 \approx \nu_3^*$ for which an empirical relation,

$$\nu_3(KX{:}CN^-{:}Na^+)-\nu_0(KX{:}CN^-) \approx 2[\nu_{12}(KX{:}CN^-{:}Na^+)-\nu_0(KX{:}CN^-)]\ , \quad (2)$$

holds. We therefore assign the experimental frequency ν_3 to the stretching vibration of a CN^- molecule sandwiched between two Na^+ impurities in a KX host. When the experimental ν_3 (KX:CN^-:Na^+) data from the two known cases (X=Cl,Br) (Ref. 10) are plotted in Fig. 2 vs the space availability $s(KX{:}Na^+\text{-}CN^-\text{-}Na^+)=a(KX)$, we indeed see a continuation of the linear scaling of the $\nu_0(NaX{:}CN^-)$ data vs $s=a(NaX)$, which supports the model assumptions.

The scaled ν_3^* values in Table II permit estimates of average stretching frequencies ν_{12}^* if we assume that the presence of *one* axial Na^+ neighbor to a ⟨100⟩-oriented CN^- molecule in a AX host (A=K,Rb) would create about half as much a deviation from the fundamental stretching frequency $\nu_0(AX{:}CN^-)$ than the deviation caused by the presence of *two* axial Na^+ neighbors,

$$\nu_{12}^*(AX{:}CN^-{:}Na^+)-\nu_0(AX{:}CN^-) =\tfrac{1}{2}[\nu_3^*(AX{:}CN^-{:}Na^+)-\nu_0(AX{:}CN^-)]\ . \quad (3)$$

The proposed relation of hypothetical ν_{12}^* and ν_3^* values with ν_0 in Eq. (3) is, of course, a reversal of the empirical relation of experimental ν_{12} and ν_3 data with ν_0 in Eq. (2).

Since isolated CN^- impurities take on ⟨111⟩ orientations in both KX and RbX hosts, we extend the analogy that CN^--Na^+ complexes will take on ⟨100⟩ orientations not only in KX but also in RbX hosts. Correspondingly scaled ν_3^* (RbX:CN^-:Na^+) and extrapolated ν_{12}^*(RbX:CN^-:Na^+) values, based on the three model assumptions and Eq. (3), are listed in Table II.

III. CN^- WITH A^+ NEIGHBORS IN CsX HOSTS

Double doping of CsX crystals with small quantities of CNX and AX (A=K, Rb) introduces, besides isolated CN^- molecules (with ⟨111⟩ orientation and fundamental stretching frequency ν_0), additional, ⟨111⟩-oriented CN^--A^+ complexes in the CsX hosts.[11,12] The stretching frequency of the Cs^+-CN^--A^+ complex is denoted by ν_1, the one of A^+-CN^--Cs^+ by ν_2, and the one of A^+-CN^--A^+ by ν_3. The averages of measured ν_1 and ν_2 data,[11] $\nu_{12}=\frac{1}{2}(\nu_1+\nu_2)$, are listed in Table III. The ν_3 values in Table III are taken from small peaks in the corresponding absorption spectra[11]—peaks that have obtained little attention previously. Again, an empirical relation, analogous to Eq. (2), is found,

$$\nu_3(CsX{:}CN^-{:}A^+)-\nu_0(CsX{:}CN^-) \approx 2[\nu_{12}(CsX{:}CN^-{:}A^+)-\nu_0(CsX{:}CN^-)]\ . \quad (4)$$

When no ν_3 peak was noticible in the absorption spectrum an estimated value, derived with Eq. (4) from ν_0 and ν_{12} data, is listed (marked in Table III with a dagger).

We now want to search for systematic features among the $\nu_3(CsX{:}CN^-{:}A^+)$ data that are compatible with the confined-oscillator model (dependence on the species of axial neighbors A^+ and on space availability s). From Fig. 1 we recall that, for a given axial space availability $s=a\sqrt{3}$, the fundamental stretching frequencies ν_0 of isolated, ⟨111⟩-oriented CN^- molecules in KX and RbX hosts have the same qualitative dependence on the species of axial neighbors, be it K^+ or Rb^+. By analogy we expect the same kind of behavior when K^+ or Rb^+ are axial neighbors to CN^- in a CsX host. We therefore assume the same qualitative influence from $A^+=K^+$ or Rb^+ neighbor species on the frequency $\nu_3(CsX{:}CN^-{:}A^+)$.

In order to relate also to the cases with axial Cs^+ neighbors to a CN^- molecule it is reasonable to assume furthermore that the same qualitative influence from K^+ and Rb^+ neighbor species extends to the species of the large-sized Cs^+ neighbors. This is in contrast to the different influence from the species of the small-sized Na^+ neighbors noted above. Since the data in Table III

TABLE III. Observed and scaled stretching frequencies (in cm^{-1}) of CN^- molecules with $\langle 111 \rangle$ orientation in cesium halides (CsX). Values marked with a dagger are extrapolated from experimental data with Eq. (4). The frequency $\nu_{12} = \frac{1}{2}(\nu_1 + \nu_2)$ is averaged over ν_1 from $\mathrm{Cs}^+\text{-}\mathrm{CN}^-\text{-}\mathrm{A}^+$ complexes and ν_2 from $A^+\text{-}\mathrm{CN}^-\text{-}\mathrm{Cs}^+$ complexes in the CsX hosts with impurities $A = \mathrm{Rb,K,Na}$. The frequency ν_3 arises from $A^+\text{-}\mathrm{CN}^-\text{-}A^+$ complexes in CsX hosts.

Host and impurities	ν_0	Experiment[a] ν_{12}	ν_3	Scaling ν_{12}^*	ν_3^*
$\mathrm{CsCl:CN^-}$	2078				
$\mathrm{CsCl:CN^-:Rb^+}$		2074	$2070^\dagger$	2074	2070
$\mathrm{CsCl:CN^-:K^+}$		2070	2063	2072	2067
$\mathrm{CsCl:CN^-:Na^+}$				2063	2048
$\mathrm{CsBr:CN^-}$	2067				
$\mathrm{CsBr:CN^-:Rb^+}$		2064	2060	2064	2060
$\mathrm{CsBr:CN^-:K^+}$		2062	2057	2062	2057
$\mathrm{CsBr:CN^-:Na^+}$				2053	2038
$\mathrm{CsI:CN^-}$	2054				
$\mathrm{CsI:CN^-:Rb^+}$		2052	$2050^\dagger$	2050	2045
$\mathrm{CsI:CN^-:K^+}$		2051	$2048^\dagger$	2048	2042
$\mathrm{CsI:CN^-:Na^+}$				2037	2020

[a] Reference 11.

show, for a given halide species X, that $\nu_3(\mathrm{Cs}X\mathrm{:CN^-:K^+}) < \nu_3(\mathrm{Cs}X\mathrm{:CN^-:Rb^+}) < \nu_0(\mathrm{Cs}X\mathrm{:CN^-})$, it follows that the axial space availability of these complexes must be $s(\mathrm{Cs}X\mathrm{:K^+\text{-}CN^-\text{-}K^+}) > s(\mathrm{Cs}X\mathrm{:Rb^+\text{-}CN^-\text{-}Rb^+}) > s(\mathrm{Cs}X\mathrm{:Cs^+\text{-}CN^-\text{-}Cs^+})$. This finding rules out that K^+ or Rb^+ neighbors to a CN^- molecule in a CsX host reside at Cs^+ sites. Instead the K^+ or Rb^+ impurity neighbors are found to be farther from CN^- than (nearest) Cs^+ host neighbors despite their smaller ionic radii, $r(\mathrm{K}^+) < r(\mathrm{Rb}^+) < r(\mathrm{Cs}^+)$. Overall, this behavior establishes a common trend of preferred large distances between the central CN^- molecule and axial K^+ or Rb^+ neighbors, both in CsX hosts, as considered here, and in KX and RbX matrices, discussed above, which causes the $\langle 111 \rangle$ instead of $\langle 100 \rangle$ orientations of CN^- in the KX and RbX hosts.

Since our former assumption of on-lattice residence of satellite impurities cannot hold here, the question arises which specific model assumption about the space availability $s(\mathrm{Cs}X{:}A^+\text{-}\mathrm{CN}^-\text{-}A^+)$ makes the frequencies $\nu_3(\mathrm{Cs}X\mathrm{:CN^-}{:}A^+)$ join the scaling behavior of the fundamental frequencies $\nu_0(\mathrm{Cs}X)$ vs $s = a(\mathrm{Cs}X)\sqrt{3}$ in Fig. 2. To this end we consider a linear $X^-\text{-}A^+\text{-}\mathrm{CN}^-\text{-}A^+\text{-}X^-$ ion configuration, aligned in $\langle 111 \rangle$ orientation, with the central CN^- molecule, the A^+ satellite impurities, and X^- anions of the CsX host. Before we turn to the axial neighbor distance $d(\mathrm{CN}^-\text{-}A^+) = s/2$, which represents (half of) the space availability of the confined CN^- molecule, let us first concentrate on the distance $d(A^+\text{-}X^-)$ between the subsequent neighbors. Each $A^+ = \mathrm{K}^+$ or Rb^+ impurity ion seeks, on the one hand, a large distance from the central CN^- molecule and, on the other hand, a "natural" distance from its neighboring X^- anion of the CsX host. It seems reasonable to expect that such a "natural" distance would be similar to the NN distance $D(A^+\text{-}X^-)$ of an isolated A^+ impurity in a CsX host. Let us therefore make the specific model assumption that the distance $d(A^+\text{-}X^-)$ between subsequent neighbors of CN^- in CsX be the same as the neighbor distance of an isolated $A^+ = \mathrm{K}^+$ or Rb^+ impurity in a CsX host, $d(A^+\text{-}X^-) = D(A^+\text{-}X^-)$. Using a radial force constant model,[13] the quantity $D(A^+\text{-}X^-)$ and consequently the space availability can be expressed in terms of the lattice constants of pure CsX and AX crystals,

$$s(\mathrm{Cs}X{:}A^+\text{-}\mathrm{CN}^-\text{-}\mathrm{A}^+) = \tfrac{1}{8}[11a(\mathrm{Cs}X)\sqrt{3} - 3a(AX)] , \quad (5)$$

as derived in the Appendix. For later reference we want to call the present assumption on the location of satellite impurities A^+ around CN^- molecules in CsX hosts "off-lattice residence."

In Fig. 2 we see that a plot of the $\nu_3(\mathrm{Cs}X\mathrm{:CN^-}{:}A^+)$ data from Table III vs the assumed space availability from Eq. (5) is largely in line with the scaling behavior of ν_0 (CsX) vs $s = a(\mathrm{Cs}X)\sqrt{3}$. The reasonable agreement supports the present assumption of off-lattice positions of A^+ neighbors to CN^- molecules in CsX hosts. There is, however, some scattering of the triangle points, particularly from the CsI hosts, about the straight line in Fig. 2 which may indicate that the situation is more complicated than the specific model assumptions on off-lattice residence of the A^+ satellite impurities.

In order to complete the survey of CN^- molecules in CsX hosts let us apply the confined-oscillator scaling model to the case of Na^+ satellite impurities. By the two general model assumptions, the stretching frequency depends on the kind of neighbor ions and on space availability. To be consistent with the case of Na^+ satellites in KX and RbX hosts we adopt again the specific model assumption that the Na^+ satellites reside at on-lattice sites. Reading stretching frequencies of axial $\mathrm{Na^+\text{-}CN^-\text{-}Na^+}$ complexes off the left line in Fig. 2 at the corresponding values of space availability, $s(\mathrm{Cs}X\mathrm{:Na^+\text{-}CN^-\text{-}Na^+})$

$=a(CsX)\sqrt{3}$ and, we then obtain frequency estimates $\nu_3^*(CsX{:}CN^-{:}Na^+)$ using the analog of Eq. (3), estimates $\nu_{12}^*(CsX{:}CN^-{:}Na^+)$ as listed in Table III.

IV. CN^- IN AgX HOSTS

Impurity CN^- molecules in AgCl and AgBr hosts have been observed[14] to have the *same* value for the fundamental stretching frequency $\nu_0(AgCl{:}CN^-)=\nu_0(AgBr{:}CN^-)$, in the different hosts (see Fig. 1). A $\langle 100\rangle$ orientation of the defect has been conjectured but remains to be confirmed.[14] Because of the strong deviation of the $\nu_0(AgX{:}CN^-)$ data from the scaling behavior of $\nu_0(AX{:}CN^-)$ data with host-lattice constants (see Fig. 1), an assignment of the CN^- orientation in AgX is by no means obvious. The deviation is likely to be a consequence of the peculiar interatomic forces in the silver halides where a strong dominance of van der Waals (vdW) attraction over short-range (SR) repulsion causes the unusual small lattice constants $a(AgX)$.[15] This is in contrast to the more familiar dominance of SR repulsion over vdW attraction in the alkali halides which gives rise to hard-sphere behavior of the ions and the consequent additivity of ionic radii to the NN distance, $d_0(A^+\text{-}X^-)=r(A^+)+r(X^-)$.

An indicator for the dominance of vdW attraction or SR repulsion between two ions is given by the ions' orbital moments.[16] For the present purpose it suffices to regard the ratio of each ion's electron number and size as a crude indicator for the vdW/SR dominance. Because of the much smaller electron number, $N_e(CN^-)=14<N_e(Br^-)=36$, but a very similar size of the CN^- molecule[17] compared to Br^-, $\frac{1}{2}L(CN^-)=1.97$ Å$\simeq r(Br^-)=1.95$ Å, no dominance of vdW attraction over SR repulsion but rather the opposite relation with subsequent "hard-ion" behavior can be expected for interacting CN^- and Ag^+ ions. Adding $\frac{1}{2}L(CN^-)$ to the hard-sphere radius $r(Ag^+)=1.26$ Å we get a neighbor distance $d(CN^-\text{-}Ag^+)=3.23$ Å. We therefore make the specific model assumption of a constant, transferable "bond length", $d(CN^-\text{-}Ag^+)=3.23$ Å, between CN^- and nearest Ag^+ neighbors. This gives, with the definition $s=2d$, a hypothetical space availability $s^*(Ag^+\text{-}CN^-\text{-}Ag^+)=6.46$ Å.

Inserting the value $s^*=6.46$ Å into the scaling relation for $\langle 100\rangle$-oriented CN^- molecules in AX hosts of the $B1$ structure (left line in Fig. 2), gives a hypothetical stretching frequency $\nu_0^*(AgX{:}CN^-)=2073$ cm^{-1}. The close agreement with the measured frequency, $\nu_0(AgX{:}CN^-)=2072$ cm^{-1}, supports the conjectured $\langle 100\rangle$ orientation of CN^- in AgX hosts and suggests the following interpretation for the same ν_0 value in both AgCl and AgBr hosts: When two Ag^+ ions axially sandwich a CN^- molecule, then the Ag^+ neighbors seek close proximity to CN^-, similar to Na^+ neighbors, but with a constant neighbor distance determined by hard-ion behavior, $d(CN^-\text{-}Ag^+)=3.23$ Å, regardless of the otherwise "soft" AgX host lattice.

If the special model assumption of constant $Ag^+\text{-}CN^-$ bond length extends to Ag^+ satellite impurities in AX hosts, then hypothetical stretching frequencies $\nu_3^*(AX{:}CN^-{:}Ag^+)=\nu_0(AgX{:}CN^-)=2072$ cm^{-1} for $Ag^+\text{-}CN^-\text{-}Ag^+$ complexes in any AX host, can be predicted. Let us finally extend the same scenario to corresponding Cu^+ satellites. Adding $\frac{1}{2}L(CN^-)$ to the hard-sphere radius[18] $r(Cu^+)=1.06$ Å, we get a neighbor distance $d(CN^-\text{-}Cu^+)=3.03$ Å and a space availability $s^*(Cu^+\text{-}CN^-\text{-}Cu^+)=6.06$ Å. Scaling again with the line of the $\nu_0(NaX{:}CN^-)$ data in Fig. 2 we predict $\nu_3^*(AX{:}CN^-{:}Cu^+)=2087$ cm^{-1} for $Cu^+\text{-}CN^-\text{-}Cu^+$ complexes in any AX host.

V. REMARKS

In order to keep the confined-oscillator scaling model reasonably simple, some secondary effects have been ignored which should be mentioned briefly. One secondary effect is a slight, but systematic dependence of the fundamental stretching frequency ν_0 on the anion species X^- of the host lattice. Close inspection of Figs. 1 and 2 shows that the data points from bromide hosts, $X^-=Br^-$, always fall below the straight lines. The degree of scattering of the ν_0 data about those straight lines is comparable to that of the ν_3 in Fig. 2. The systematic deviation of the ν_0 data from straight lines could possibly arise from relaxation effects. Since the lattice constants of the alkali cyanides ACN (in their high-temperature phase where the CN^- molecules rotate almost freely) are close to the lattice constants of the alkali bromides, $a(ACN)\simeq a(ABr)$, the axial length of a CN^- molecule is comparable to the diameter of a Br^- ion. Thus a CN^- impurity appears oversized in a ACl host and undersized in a AI host but rather fitting in a ABr host.[19] No relaxation effects from anion size mismatch, $r(Cl^-)<\frac{1}{2}L(CN^-)<r(I^-)$, are accounted for by the present model.

Relaxation effects are also ignored for axial neighbor cations to CN^- by making the special model assumptions that these cations reside either at on-lattice sites, or at off-lattice sites due to Eq. (5), or at constant bond-length positions.

VI. CONCLUSION

Alerted by the different scaling behavior of the fundamental stretching frequency ν_0 of isolated CN^- molecules in NaX hosts on the one hand and in KX and RbX hosts on the other hand, we distinguish qualitatively between two trends, namely that Na^+ neighbors prefer close proximity to CN^-, whereas the larger A^+ neighbors ($A=$K,Rb) prefer large separation from CN^-. The proximity preference of Na^+ ions gives rise to the observed $\langle 100\rangle$ orientation of both CN^- in NaX hosts and $CN^-\text{-}Na^+$ complexes in KX and RbX hosts. On the other hand the separation preference of the larger A^+ neighbors gives rise to the observed $\langle 111\rangle$ orientation of CN^- in KX and RbX hosts and is in qualitative agreement with the assumption of off-lattice positions of K^+ and Rb^+ satellite impurities to CN^- molecules in CsX hosts. An experimental test of such off-lattice sites, e.g., with extended x-ray absorption fine structure spectroscopy, would be interesting.

The qualitative trends are incorporated in the confined-oscillator scaling model for stretching frequencies of CN^- impurities. The model is applicable if the axial NN's of a CN^- molecule are actually its absolute NN's. Thus the model holds for the cases of (a) $\langle 100\rangle$-oriented CN^- with Na^+ and Ag^+ neighbors in NaX, KX, RbX, and AgX hosts and (b) $\langle 111\rangle$-oriented CN^- with Na^+, K^+, Rb^+, or Cs^+ neighbors in CsX hosts but it excludes the cases of (c) $\langle 111\rangle$-oriented CN^- with A^+ neighbors in AX hosts ($A=\mathrm{K,Rb}$).

The confined-oscillator scaling model makes two general assumptions, namely that the CN^- stretching frequency is determined by (1) the species of axial NN cations to CN^- and (2) the axial space availability s. A third, specific model assumption is that NN Na^+ ions reside at on-lattice sites whereas K^+ or Rb^+ satellite impurities in CsX hosts reside at off-lattice sites, given by Eq. (5), while Ag^+ satellites maintain constant bond lengths, determined by hard-ion behavior.

The three model assumptions permit predictions of stretching frequencies $\nu_3^*(AX{:}\mathrm{Na}^+\text{-}\mathrm{CN}^-\text{-}\mathrm{Na}^+)$ for $AX=\mathrm{K}X$, RbX hosts and $\nu_3^*(\mathrm{Cs}X{:}\mathrm{Na}^+\text{-}\mathrm{CN}^-\text{-}\mathrm{Na}^+)$ by scaling from $\nu_0(\mathrm{Na}X{:}\mathrm{CN}^-)$ data as well as $\nu_3^*(\mathrm{Cs}X{:}A^+\text{-}\mathrm{CN}^-\text{-}A^+)$ ($A=\mathrm{K}$, Rb) by scaling from $\nu_0(\mathrm{Cs}X{:}\mathrm{CN}^-)$ data. Circumventing complications from the polarity of the CN^- molecule, we consider the average stretching frequency $\nu_{12}=\frac{1}{2}(\nu_1+\nu_2)$ for CN^- sandwiched by different neighbor cations. Combined with an empirical relation between ν_0, ν_{12}, and ν_3, Eqs. (2), (3), and (4), the scaling procedure yields hypothetical ν_{12}^* frequency averages. In the cases where experimental data from double-doped systems are available the predicted ν_3^* and ν_{12}^* values agree closely with the measured ν_3 and ν_{12} data. Exceptions with somewhat larger discrepancies exist for data from CsI hosts. This may indicate that the off-lattice residence of A^+ satellite impurities in CsX hosts is more complicated than the specific model assumption employed here. Comparisons of the predicted ν_{12}^* and ν_3^* values in Tables II and III with the averages of ν_1 and ν_2 and with ν_3 data from future experiments in the remaining cases of double-doped systems would provide a test of the confined-oscillator scaling model.

Fundamental stretching frequencies of CN^- impurities in silver halides have been observed to show no dependence on the host-lattice constant $\nu_0(\mathrm{AgCl{:}CN}^-)=\nu_0(\mathrm{AgBr{:}CN}^-)$, and to deviate from the scaling of ν_0 of the $AX{:}\mathrm{CN}^-$ systems. We explain these features with hard-ion behavior of CN^- and the NN Ag^+ ions, while the other Ag^+ and X^- ions in the AgX host show "soft-ion" behavior as is characteristic for silver halides. A scaling relation supports the conjectured $\langle 100\rangle$ orientation of CN^- in AgX hosts. New experiments with $AX{:}\mathrm{CN}^-{:}\mathrm{Ag}^+$ systems should indicate whether Ag^+ satellites maintain constant $\mathrm{CN}^-\text{-}\mathrm{Ag}^+$ bond lengths also in AX hosts or whether they reside at AX on-lattice sites. Analogous information about Cu^+ satellites could be obtained from $AX{:}\mathrm{CN}^-{:}\mathrm{Cu}^+$ experiments.

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APPENDIX

We derive the NN distance $D(A^+\text{-}X^-)$ of an isolated impurity A^+ ion at a cation lattice site in a CsX host using the radial force constant model of Shih *et al.*[13] This model has successfully predicted NN distances of impurity atoms and ions in hosts of zinc-blende and rocksalt structures. In applying the model to the present host of CsCl structure we consider a rigid cubic cell with A^+ at one corner, designated as the origin (0,0,0) and seven Cs^+ ions at the remaining corners of the cell. The edge length of the cell is the lattice constant of a pure CsX crystal, $a(\mathrm{Cs}X)$. Inside the cell, at a variable position $(\frac{1}{2}+v,\frac{1}{2}+v,\frac{1}{2}+v)$ along the space diagonal, resides the anion X^-. The radial force-constant model expresses in harmonic approximation the elastic energy E of the cell in terms of a spring constant k and deviations Δ of NN distances from an ideal AX or CsX crystal, $E=\sum\frac{1}{2}k\Delta^2$.

There are eight contributions to E due to interaction pairs of X^- with the eight cations at the corners of the cell. The contribution from the $A^+\text{-}X^-$ pair is accounted through the size difference between the A^+ impurity and a replaced Cs^+ ion, expressed in terms of NN distances $D_0(\mathrm{Cs}^+\text{-}X^-)=\frac{1}{2}a(\mathrm{Cs}X)\sqrt{3}$ and $D_0(A^+\text{-}X^-)=\frac{1}{2}a(AX)$ of ideal CsX and AX crystals, respectively, together with the displacement $u=v\sqrt{3}$ of the X^- anion along the $\langle 111\rangle$ axis, which combine to $\Delta(A^+\text{-}X^-)=D_0(\mathrm{Cs}^+\text{-}X^-)-D_0(A^+\text{-}X^-)+u$. The distance deviation associated with the Cs^+ ion at the (1,1,1) corner is $\Delta(X^-\text{-}\mathrm{Cs}^+)=-u$. The deviation associated with the Cs^+ ion at the (1,1,0) corner, and equivalently at the (1,0,1) and (0,1,1) corners, is, to first order, $\Delta(X^-\text{-}\mathrm{Cs}^+)\approx -u/3$. Similarly, we get for Cs^+ at (1,0,0), as well as at (0,1,0) and (0,0,1), $\Delta(X^-\text{-}\mathrm{Cs}^+)\approx u/3$. The elastic energy of the cell is found to be minimal, $dE/du=0$, when X^- is displaced along $\langle 111\rangle$ by $u=\frac{3}{8}[D_0(A^+\text{-}X^-)-D_0(\mathrm{Cs}^+\text{-}X^-)]$.

With u being expressed through ideal-crystal lattice spacings, we combine terms to obtain the NN distance of an isolated A^+ ion in a CsX host,

$$\begin{aligned} D(A^+\text{-}X^-) &= D_0(A^+\text{-}X^-)+\Delta(A^+\text{-}X^-) \\ &= [3D_0(A^+\text{-}X^-)+5D_0(\mathrm{Cs}^+\text{-}X^-)]/8\ . \end{aligned}$$

Turning now to the $X^-\text{-}A^+\text{-}\mathrm{CN}^-\text{-}A^+\text{-}X^-$ ion configuration in a CsX host, and equating the distance $d(A^+\text{-}X^-)$ of that configuration with $D(A^+\text{-}X^-)$ of an isolated A^+ impurity in CsX as derived above, we obtain for the distance between the CN^- molecule and an A^+ satellite

$$\begin{aligned} d(\mathrm{CN}^-\text{-}A^+) &= d(\mathrm{CN}^-\text{-}X^-)-d(A^+\text{-}X^-) \\ &= a(\mathrm{Cs}X)\sqrt{3}-D(A^+-X^-)\ . \end{aligned}$$

Here it is assumed that the X^- anions reside at lattice sites of the double-doped CsX host. With the definition of space availability, $s(\mathrm{Cs}X{:}A^+\text{-}\mathrm{CN}^-\text{-}A^+)=2d(\mathrm{CN}^-\text{-}A^+)$ we get, in terms of lattice constants,

$$s(\mathrm{Cs}X{:}A^+\text{-}\mathrm{CN}^-\text{-}A^+)=\tfrac{1}{8}[11a(\mathrm{Cs}X)\sqrt{3}-3a(AX)]\ ,$$

denoted as Eq. (5) in Sec. III.

[1] G. R. Field and W. F. Sherman, J. Chem. Phys. **47**, 2378 (1967).

[2] D. Durand, L. C. Scavarda do Carmo, and F. Lüty, Phys. Rev. B **39**, 6096 (1989).

[3] F. Lüty, Phys. Rev. B **10**, 3677 (1974).

[4] H. U. Beyeler, Phys. Rev. B **11**, 3078 (1975).

[5] D. Durand and F. Lüty, Phys. Status Solidi B **81**, 443 (1977).

[6] A. Diaz Gongora and F. Lüty, Phys. Status Solidi B **85**, 693; **86**, 127 (1978).

[7] B. G. Dick, Phys. Status Solidi B **141**, 61 (1987).

[8] The parameters in Eq. (1) are (in cm^{-1}/Å units) $m(\mathrm{Na}^+)=-37$, $m(\mathrm{K}^+)=m(\mathrm{Rb}^+)=-23$, $m(\mathrm{Cs}^+)=-56$ and (in cm^{-1} units) $b(\mathrm{Na}^+)=2314$, $b(\mathrm{K}^+)=b(\mathrm{Rb}^+)=2233$, $m(\mathrm{Cs}^+)=2308$.

[9] R. C. Spitzer, W. P. Ambrose, and A. J. Sievers, Phys. Rev. B **34**, 7307 (1986).

[10] M. Feege, Master's thesis, University of Paderborn, 1988.

[11] W. von der Osten and F. Lüty, Phys. Rev. B **35**, 7684 (1987).

[12] M. Schrempel, W. Gellermann, and F. Lüty, Phys. Rev. B **45**, 9590 (1992).

[13] C. K. Shih, W. E. Spicer, W. A. Harrison, and A. Sher, Phys. B **31**, 1139 (1985).

[14] D. Samiec, Master's thesis, University of Paderborn, 1990.

[15] M. Bucher, Phys. Rev. B **30**, 947 (1984).

[16] M. Bucher, Phys. Rev. B **35**, 5985 (1987).

[17] Subtracting the Pauling ionic radius of alkali ions from the nearest-neigbor distances of alkali cyanides in their high-temperature phase (where the CN^- molecules rotate almost freely) gives the axial half-length of the dumbbell-shaped cyanide molecule as $\frac{1}{2}L(CN^-)=1.97$ Å.

[18] M. Bucher, Phys. Rev. B **27**, 5919 (1983).

[19] A consequence of the close agreement in ion size, $\frac{1}{2}L(CN^-)\simeq r(Br^-)$, is a close agreement in space availability, $s(ACN)\simeq s(ABr{:}CN^-)$, resulting in the close agreement of the CN^- stretching frequencies ν_0 from ACN crystals with those of isolated CN^- impurities in ABr hosts, $\nu_0(ACN)\simeq\nu_0(ABr{:}CN^-)$, shown in Fig. 1.

[20] A larger temperature variation than for other $AX{:}CN^-$ systems exists among the KCL:CN^- data with $\nu_0=2086$ cm^{-1} at $T=100$ K from Ref. 1 and $\nu_0=2088$ cm^{-1} at $T=2$ K from Ref. 10. Other $T=2$ K values are ν_1 (KCl:CN^-:Na^+)$=2086$ cm^{-1} (assumed overlap of ν_0 and ν_1 absorption peaks) and ν_2(KCl:CN^-:Na^+)$=2082$ cm^{-1}.

[21] ν_1(KBr:CN^-:Na^+)$=2078$ cm^{-1} and ν_2(KBr:CN^-:Na^+) $=2072$ cm^{-1} from Ref. 9 and also measured by H. Brinkmann (private communication).

[22] R. W. G. Wyckhoff, *Crystal Structures,* 2nd ed. (Wiley, New York, 1963), Vol. 1, p. 86.