Effects of pressure on the V_K center in KCl

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The effects of isotropic pressure on the relaxation and optical-absorption spectra of Cl_2^{-} in KCl are presented. This study is based on an extended Mott-Littleton relaxation calculation for KCl: Cl_2^{-} as a function of lattice constant using the HADES program. The calculations show relatively little effect of pressure on the properties of the V_K center (Cl_2^{-}) until the lattice constant drops below ~ 3.0 Å. Below this value of the lattice constant, there are substantial changes in the relaxation effects and optical spectrum predicted. Comparisons with normal $MCl:Cl_2^{-} V_K$ centers and hybrid $KX:Cl_2^{-} V_2$ centers are also presented. We conclude that in KCl, the optical and spin-resonance spectra should show a clear change in their pressure dependence beyond a threshold. This threshold is not related to the phase transition in crystal structure.

I. INTRODUCTION: LATTICE RELAXATION NEAR A SELF-TRAPPED HOLE

Our present paper is concerned with the effects of pressure on self-trapped holes (V_K centers). We shall show that the local lattice distortion changes in a striking manner once the lattice parameter has been reduced beyond a certain value. This, in turn, should lead to clear changes in the shifts with pressure of optical and spinresonance spectra at a threshold pressure. This threshold is not related to the pressure-induced phase transition in crystal structure.

A systematic theoretical investigation of the selftrapped hole in NaCl-type alkali halides has been presented by the authors¹ which involves an extensive Mott-Littleton relaxation calculation using the HADES program.² This study reported the lattice relaxation and optical properties for the alkali halide $MX:X_2^-$ systems and employed the normal (0 K) lattice constants a_0 to characterize the parent MX crystal. In the present paper we report parallel studies on the lattice relaxation and optical spectra for the V_K center in KCl as a function of the lattice constant a_0 . Varying the lattice constant corresponds to the application of an isotropic hydrostatic pressure on the crystal. The purpose of this study is to examine details of the ion relaxation and changes in the anticipated V_K -center absorption spectra under these circumstances.

Our previous calculations employed methods developed and implemented by Lidiard and Norgett to study the relaxation about defects in ionic crystals.³ This technique comprises a refinement of the Mott-Littleton procedure with considerable development of the appropriate numerical methods to permit rather large numbers of ions to be explicitly relaxed. In this approach a region I is defined (full details are given in Ref. 1) and lattice ions in this region are explicitly relaxed until the forces acting fall below a small threshold; the surrounding region II is relaxed within a harmonic approximation to insure adequate consideration of long-range polarization effects.

This very useful technique is exhaustively described in a recent monograph⁴ and is now receiving much attention in a diverse range of applications. In the present calculations the alkali halide potentials developed by Catlow, Diller, and Norgett⁵ for the X^--X^- , M^+-M^+ , and M^+ - X^- interactions used earlier¹ are again used. A useful discussion of these particular potentials is given by Catlow, Diller, and Norgett,⁵ and are further discussed by Catlow et al.,6 Catlow, Dixon, and Mackrodt,7 and by Eggenhoffner, Fumi, and Murthy.⁸ Stoneham⁹ gives a full compilation of the specific potentials employed here for the parent KCl crystal. The remaining potentials required are the Cl_2^- potential function and the $Cl^--Cl_2^-$ and K^+ - Cl_2^- potentials. The present calculations continue to employ the *ab initio* potential curve for Cl₂⁻ due to Tasker *et al.*¹⁰ and the modified (and simple) forms for the $Cl^{-}-Cl^{1/2}$ potentials. The weak link in the present relaxation calculations is the representation of the $Cl^--Cl_2^-$ and K^+ - Cl_2^- potentials. A more-detailed discussion of this limitation, also applicable here, is given earlier.¹

The HADES calculations with a variable lattice constant are very straightforward and present no new problems over the range of a_0 values employed. No attempt was made to consider anisotropic distortions such as under uniaxial stress, which change the lattice symmetry, although application of pressure along particular axes, e.g., along the (110) V_K center axis, would be particularly interesting in view of these calculations and those of Gillan.¹¹ The normal NaCl-type structure is maintained throughout the calculations although it is desirable to construct a "matching" curve from the high-pressure CsCl-type structure. There was no attempt to explore dependence of the relaxation calculation on the size of region I, vis-à-vis the lattice constant, but it is felt that the present generous size of region I is adequate to absorb all pertinent relaxation changes when hydrostatic pressure is applied. The related study of hybrid V_K -center systems, e.g., Cl_2^- in other alkali halides $(MY:X_2^-)$ is consistent with these assumptions.¹²

System LiClb

NaCl^b

KCl

KCl

KCl

KCl

KCl^b

KCl

RbCl^b

KBr^c

ΚI^c

2.95

3.00

3.05

3.10

3.15

3.259

3.262

3.489

3.116

z 0 (Å)	V/V ₀ (%)	$R_0(V_K)$ (Å)	$R_c(V_K)^{a}(\text{\AA})$	$R_s(V_K)$ (Å)	E_D (eV)	Madelung potential a anion site A/a_0
2.539		3.166	2.674	2.732	5.464	9.911
2.789		3.944	2.638	2.725	5.197	9.023

2.548

2.598

2.603

2.602

2.602

2.600

2.586

2.605

2.609

2.630

2.716

2.716

2.711

2.701

2.705

2.710

2.705

2.698

TABLE I. Summary of (KCl;Cl₂⁻) V_K -center results as a function of lattice constant a_0 and related results for V_K centers with Cl₂⁻. (All calculation (196 ions) and the cu

^a The lattice constant for KCl at 0 K is given by a_0 (3.116 Å is the normal value at 1 atm). The other lattice constants are simi	larly
defined. The separations $R_c(V_K)$ and $R_s(V_K)$ are the core and shell distances in Cl_2^- ; $R_0(V_K)$ is the normal lattice separation	on of
$X^{-}-X^{-}$ in the NaCl-type structure for the a_0 given. The normal R_e distance in the Cl ₂ ⁻ molecular ion is 2.71 Å according to ca	alcu-
lations of Tasker, Balint-Kurti, and Dixon (Ref. 10).	

^bThese results for $MCl:Cl_2^-$ are taken from earlier work by Cade, Stoneham, and Tasker (Ref. 1).

^cThese results for KX:Cl₂-hybrid V_K centers are taken from work by Cade, Stoneham, and Tasker (Ref. 12).

4.172

4.243

4.313

4.384

4.406

4.455

4.609

4.613

4.934

II. SYSTEMATICS OF POLARIZATION AND DISTORTION

0.85(-15)

0.89(-11)

0.94(-6.2)

0.98(-1.5)

1.04(+4.3)

1.0(0)

The basic results of these relaxation calculations are summarized in Table I and Fig. 1. The range of lattice constants employed corresponds to isotropic pressures up



FIG. 1. Relaxed core $R_c(V_K)$ and shell $R_s(V_K)$ distances for the $Cl_2^- V_K$ center as a function of lattice constant, a_0 . All distances in Å. \triangle , normal $MCl:Cl_2^- V_K$ centers (Ref. 1); \bullet , KCl:Cl₂⁻ (δa_0) V_K centers; \bigcirc , hybrid KX:Cl₂⁻ V_K centers (Ref. 12). Alkali halides indicated (LiF, NaCl, etc.) on the abscissa scale correspond to equilibrium a_0 values.

to 30 kbar and includes the transition pressure for KCl (19.7 kbar) for the NaCl (B1) to CsCl (B2) transition. Our present results refer only to the NaCl structure. We note that, for NaCl at least¹³ there is good evidence that the potentials work well even when the crystal is strongly compressed. We have also included, for reference and comparison, results for Cl_2^- (V_K center) in the normal alkali halides, $MCl:Cl_2^-$, and for two hybrid results,¹² KBr:Cl_2⁻ and KI:Cl_2⁻, which involve the chloride molecular ion and involve a range of lattice constants, a_0 . There is relatively little experience in relaxation calculations in which the fundamental lattice constant is varied, and it may be necessary to consider redetermination of the potential parameters from new compressibility and dielectric data. However, these new problems may become important only at the extreme limits of pressure-the lattice constants employed here for KCl:Cl₂⁻ are already bracketed by a_0 for the other (normal and hybrid) V_K -center results given in Table I. In general, one might expect that the pressure increase will exert more influence on the diffuse negative ion than on the small, compact cations^{14,15} and have the greatest influence on the diatomic molecular anion, Cl_2^- . In this sense, the optical spectra of V_K centers might be particularly sensitive to effects of pressure.

The relaxation of ions near the defect, Cl_2^- , for the KCl:Cl₂⁻ system still follows the general pattern described in Ref. 1 (Fig. 3) when a_0 is varied; we focus here only on relaxation of class 1 (V_K) anions and class 2 cations (M^+) . The relaxed separations, $R_c(V_K)$ for the cores and $R_s(V_K)$ for the shells, for the V_K -center molec-

8.530

8.388

8.251

8.118

8.076

7.989

7.722

7.715

7.213

5.137

4.998

4.837

4.660

4.60

4.472

4.259

4.099

3.566

ular ion as a function of lattice constant for $KCl:Cl_2^-$ are given in Fig. 1. We compare three sequences of systems with variable lattice constant: KCl:Cl2⁻ (with variation in a_0); the MCl:Cl₂⁻ sequence (with M = Li, Na, K, and Rb); and the sequence $KCl:Cl_2^-$, $KBr:Cl_2^-$, and $KI:Cl_2^-$. All three sequences contain the normal $KCl:Cl_2^-$ (with $a_0 = 3.116$ Å) system. It is apparent that $R_c(V_K)$ and $R_s(V_K)$ for KCl:Cl₂⁻ versus change in a_0 does not follow the behavior of the corresponding values for the $MCl:Cl_2$ sequence, in which the smaller a_0 is accomplished by a decrease in the size of the cation, M^+ . We do not have results for KF:Cl₂⁻, but it is possible that the sharp decrease in $R_c(V_K)$ and $R_s(R_K)$ with pressure in KCl:Cl₂⁻ may be comparable in nature to the hybrid, $KX:Cl_2^-$, systems in which the decrease in a_0 is associated with the smaller host anion.

The values of $R_c(V_K)$ and $R_s(V_K)$ show a dramatic decrease below a threshold value of a_0 . This threshold corresponds to a pressure approaching that needed to drive the B1-to-B2 phase change in KCl. When the V_K center is formed, the Cl⁻-Cl pair involved move substantially inwards (up to 50%) from the normal Cl⁻-ion positions, i.e., the Cl⁻-Cl⁻ separation is substantially shortened; thus lattice relaxation is primarily to accommodate the smaller size of the resultant Cl_2^- molecular anion. When the lattice constant a_0 is decreased, the Cl_2^- ion is not appreciably affected until the $Cl_2^- \cdot M^+$ and $Cl_2^- \cdot Cl^$ repulsive potentials exceed the Cl_2^- repulsive potential. This occurs at a separation appreciably greater than $R_0(V_K)$ (Table I), which is the normal Cl⁻-Cl⁻ distance in the NaCl-type lattice. The relative decrease is quite noticeably greater for $R_s(V_K)$ than for $R_c(V_K)$ as might be expected.

The conjugate nearest-neighbor K^+-K^+ distance normally increases in the relaxation relative to the separation in the normal lattice (also R_0), and this increase is larger in terms of *percent* change as the pressure is increased (i.e., an increase from 26.8% to 28.3% for the a_0 values included here). It should be noted, however, that the absolute distance between the conjugate K^+-K^+ pair does decrease as the lattice parameter falls (the distance in units of the lattice parameter actually increases). The precise relaxations of the V_K center and of the ions near the V_K center are quite sensitive to the two $Cl_2^- - M^+$ and $Cl_2^{-}-X^{-}$ potentials which are least well established, and as a_0 decreases these potentials assume even greater importance. There is a good case for a quantum-mechanical treatment of more than just the Cl₂⁻ molecular ion in a few representative geometries.

It should be noted that the defect energy, E_D (eV), is sensitive to any decrease in a_0 . Thus in going from the normal lattice separation $a_0=3.116$ to 2.95 Å the energy to form the V_K -center defect in KCl increases by approximately 10%. This is comparable with changes in the defect energy when a_0 is decreased either by a smaller cation in the MCl:Cl₂⁻ sequence or by a smaller anion in the KX:Cl₂⁻ hybrid sequence. In Fig. 2 the defect energies given in Table I are plotted as function of a_0 ; it is apparent that the defect energy for the KCl:Cl₂⁻ (a_0) sequence will fit very well on the line for the KX:Cl₂⁻ hybrid sequence (without KF:Cl₂⁻).



FIG. 2. Defect energy for $\operatorname{Cl}_2^- V_K$ centers, $E_D(eV)$, as a function of lattice constant a_0 . \triangle , normal $M\operatorname{Cl}:\operatorname{Cl}_2^- V_K$ centers (Ref. 1). \bullet , $\operatorname{KCl}:\operatorname{Cl}_2^-$ (δa_0) V_K centers; \bigcirc , hybrid $\operatorname{K}X:\operatorname{Cl}_2^- V_K$ centers (Ref. 12).

III. STABILITY AND OPTICAL TRANSITIONS

In the earlier V_K -center studies of alkaline earth fluorides¹⁶ and of caesium halides,¹⁷ the stability of the self-trapped hole (i.e., as X_2^{-}) relative to the hole in its lowest-energy state in the valence band of an undistorted crystal (i.e., X^0 at a usual X^{-} lattice site) is discussed. In all cases, the self-trapped hole is clearly the more stable system. The key (approximate) expression used was

$$-E_D(a_0) + \frac{1}{2}E_v(a_0) - A/a_0 \le 0 , \qquad (1)$$

where $E_D(a_0)$ is the calculated defect energy for the V_K center given in Table I. As usual, E_v is the width of the valence band in the undistorted crystal¹⁸⁻²⁰ and A/a_0 is the Madelung potential at the anion (with the explicit dependence on a_0 shown). The self-trapped hole is stable (Table II) if the above expression is negative as indicated. When a_0 is decreased, E_D increases (Table I) and the last term also increases since A is fixed; therefore the relative stability of the V_K center is dominated by the more sensitive dependence on a_0 . The behavior of $\frac{1}{2}E_v$ with a_0 is indicated in Table III following Ref. 18.

How is the optical spectrum of the V_K center $(Cl_2^$ here) affected by the reduction of a_0 ? The pertinent results are given in Table IV and Fig. 3; again other results are included for comparison. It will be recalled¹ that the relaxed values of $R_c(V_K)$ obtained by the HADES calculation (Table I) are used with the theoretical potential curves for free Cl_2^- molecular anions of Tasker, Balint-Kurti, and Dixon¹⁰ to estimate the corresponding electronic absorption peaks, ΔE_{π} , ΔE_g , and ΔE_{σ} . The latter quantities are defined in Ref. 1 and no account is included of the influence of the host (relaxed) lattice on the potential curves of the Cl_2^- impurity. This approach is consistent with almost all previous experimental and theoreti-

	$E_D(a_0) + A/a_0 (eV)$		$\frac{1}{2}E_v(a_0) (eV)$		
LiCl	4.447	1.8ª	2.5 ^b	2.25 ^c	1.8 ^d
NaCl	3.826	1.5ª	1.55 ^b	2.05 ^c	1.5 ^d
KC1	3.476	1.2 ^a	1.15 ^b	1.35 ^c	1.2 ^d
RbCl	3.463	1.1 ^a	0.8 ^b	1.15 ^c	1.1 ^d

TABLE II. Stability of small polaron (V_K center) for alkali chlorides, MCl. All cases refer to the equilibrium bulk value of a_0 .

^aFrom Ref. 18, assuming that "width" means "full width."

^bFrom Ref. 19.

^cFrom Ref. 20, quoting here their values for half of the full width (rather than half of their quoted full widths at half maximum).

^dFrom Ref. 21.

cal approaches for the V_K center. This basic rationale is summarized by Tasker and Stoneham.²² The actual numbers assembled in Table II are obtained from an analytic form given in the Appendix which has been fitted to the theoretical numbers.¹⁰ (This accounts for minor discrepancies in excitation energies for the $MCl:Cl_2^-$ system compared with those given earlier¹ where an estimate was given directly from the plotted ΔE_i curves.) Our attention here is on trends, as the absolute numbers (which are somewhat too large) are discussed in detail in Ref. 12. Near the equilibrium separation at one atmosphere, $a_0 = 3.116$ A, there is practically no affect on the spectrum as a_0 decreases, i.e., as the pressure is increased by 10-15 kbar. However (see Fig. 3), one notes a sharp blue shift for all transitions when a_0 is less than ~ 3.00 A. This latter behavior, in the present context, may be traced to the strongly repulsive potential curves of the excited states of Cl_2^- and their increasing importance as $R_c(V_K)$ (and a_0) becomes smaller. The nonconformity of the KCl:Cl₂⁻ (δa_0) results with the normal MCl:Cl₂⁻ sequence is apparent and as before, the hybrid KX:Cl2⁻ V_K -center systems appear compatible with results as a_0 is reduced in KCl. However, as a_0 becomes smaller the influence of the host on the excited states may become more important and the picture of the V_K center behaving as an essentially free Cl₂⁻ molecule trapped in the crystal needs further consideration. It is also possible that the above changes in the spectrum would not be observed due to the B1-to-B2 phase transition, and instead as the pressure is increased a more discontinuous change in the spectrum may occur, characteristic of the CsCl:Cl₂⁻ type of V_K center.

There appear to be no published experimental studies of the effects of pressure on the optical and ESR spectrum of the V_K center for a single material. There is abundant optical and ESR spectra for a common V_K center with variable a_0 , but solely by comparison of different crystalline substances. It is likely that pressure-dependent spectroscopy of $KCl:Cl_2^-$ is feasible in light of the extensive studies of Drickamer and colleagues and others of various optical spectra under the influence of applied high pressure. There are a number of experimental studies of the effects of high pressure on the optical and ESR spectra of the F center in alkali halides which may imply the scope

a_0 (Å)	Comment	$E_D(a_0) + A/a_\sigma$ (eV)	$\frac{1}{2}E_V(a_0)$ (eV)	Stabilization energy $(eV)^d$	F ^e
2.95	Value of a for which the rapid change in V_K spacing starts	3.393	0.75 ^a 1.04 ^b 1.34 ^c	2.64	4.52
3.116	Normal equilibrium value	3.476	0.58 ^a 0.83 ^b 1.2 ^c	2.90	5.99
3.15	Slightly expanded lattice	3.517	0.56 ^a 0.80 ^b 1.17 ^c	2.96	6.28

TABLE III. Small polaron (V_K -center) stability as a function of lattice constant (pressure).

^aFrom a self-consistent Hartree-Fock calculation with correlation correction [A. B. Kunz (private communication), generalized from Ref. 21]; these values give half the full width of the valence band. Widths vary roughly as a^{-1}

^bAs with footnote a above, from a self-consistent Hartree-Fock calculation with correlation correction, except that these values give the separation of the top of the band from its centroid. Widths vary roughly as a^{-4} . From Ref. 18 using their value of $E_{\nu}(a_0)$ and their proposed a^{-2} dependence of E_{ν} . The value tabulated here is thus $1.2(a_0/a)^2$ eV.

^dThe stabilization energy, $E_D + A/a - \frac{1}{2}E_v$, using $\frac{1}{2}E_v$ of the values labeled by footnote b above.

"The stabilization factor $F = (E_D + A/a)/\frac{1}{2}E_v$ is greater than unity for a stable polaron [cf. Eq. (1)].

MX	a ₀ (Å)	$\frac{\Delta E_{\pi}(^{2}\Pi_{g}-X^{2}\Sigma_{u}^{+})^{a}}{(eV)}$	$\frac{\Delta E_g(^2\Pi_u - X^2\Sigma_u^+)}{(eV)}$	$\frac{\Delta E_{\sigma}(^{2}\Sigma_{g}^{+}-X^{2}\Sigma_{u}^{+})}{(eV)}$
LiCl	2.539	2.10	3.18	4.04
NaCl	2.789	2.19	3.32	4.22
KCl	2.95	2.43	3.70	4.69
KCl	3.00	2.29	3.49	4.42
KCl	3.05	2.28	3.47	4.40
KCl	3.10	2.28	3.47	4.40
KCl	3.116	2.28	3.47	4.40
KCl	3.15	2.29	3.48	4.41
RbCl	3.259	2.32	3.54	4.48
KBr	3.262	2.27	3.46	4.39
KI	3.489	2.26	3.44	4.37

TABLE IV. Summary of calculated electronic excitation energies for $\text{KCl}:\text{Cl}_2^-$ systems as functions of lattice constant a_0 . (Energy results in eV. Energy values are vertical energy differences between the $X^2\Sigma_{\mu}^+$ state and the pertinent excited state at the minimum.)

^aThe theoretical results employ $R_c(V_K)$ as calculated from the present study with the calculated ΔE_i obtained from the fits to the theory of Tasker *et al.* (Ref. 10) given in the Appendix.

of possible high-pressure investigations for the V_K center. Jacobs²³ studied the *F*-center optical spectrum up to 8000 atm and was followed by Maisch and Drickamer²⁴ $(p \le 50\,000$ atm), and Eppler and Drickamer²⁵ $(p \le 166\,000$ atm). In these experimental studies, the *F* band was followed as a function of pressure and Maisch and Drickamer²⁴ are able to follow the *F* band right through the discontinuity associated with the *B*1-*B*2 phase transition for KCl and other alkali halides. The high-pressure optical spectra for other defects in the alkali halides have been recently published by Drotning and Drickamer²⁶ in a series of papers defining their experimental capabilities. Wolbarst and Zwicker²⁷ have report-



FIG. 3. Predicted optical spectrum for $\operatorname{Cl}_2^- V_K$ centers. $E_i(eV)$, as a function of lattice constant a_0 . \triangle , normal $MCl:\operatorname{Cl}_2^- V_K$ centers (Ref. 1); \bullet , KCl:Cl₂⁻ (δa_0) V_K centers; \bigcirc , hybrid KX:Cl₂⁻ V_K centers (Ref. 12).

ed electron-nuclear double resonance (ENDOR) experiments on the F center in KCl under external pressure, and Zwicker²⁸ has presented a theoretical treatment of this pressure behavior. While these F-center (and other) studies do not relate to the V_K center discussed here, they probably represent accurately the scope of possible highpressure studies on V_K centers. The V_K -center spin resonance would be of particular interest, since the hyperfine constants define the ionic s and p character within the "molecule in a crystal" model, with the g factor providing additional information on the one excited state energy not monitored optically. Spin resonance should also identify any significant spread of the hole wave function beyond the Cl_2^- ion.

IV. CONCLUSIONS

The dependence of the ion relaxation, the defect energy, and the optical spectra of the $KCl:Cl_2 V_K$ center with lattice constant has been presented using the conventional models and procedures embodied in the HADES program. This relaxation procedure appears to provide a useful means to explore the effects of external pressure on the properties of defects in ionic crystals, complementing other studies of the perfect-crystal systems. We note, in particular, a relative independence on pressure for the optical spectrum of the V_K center until a threshold value is reached, after which rather large spectral shifts are predicted. The pressure dependence may also provide a useful further dimension in defining the scope and limitations of our assumed potentials and of the procedures as defined in HADES, as well as a test of the "molecule in a crystal" picture of the self-trapped holes in alkali halides.

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APPENDIX

The transition energies are derived from the calculated results of Tasker, Balint-Kurti, and R. N. Dixon¹⁰ and the related derivative analysis of Tasker and Stoneham.²² As described in the text, the HADES calculations give values of $R_c(V_K)$ for the relaxed internuclear separation of the

 V_K center. This value is then used to calculate the corresponding excitation energies from theoretical results for the *free* Cl₂⁻ molecular anion. The excitation energies were derived from the fitted expressions given below (ΔE in eV and R in angstroms)

$$\Delta E_{\pi} = 47.5455 R^{1/2} e^{-1.3510 R} ,$$

$$\Delta E_{g} = 83.7873 R^{1/2} e^{-1.4075 R} ,$$

$$\Delta E_{\sigma} = 97.9002 R^{1/2} e^{-1.3757 R} .$$

These analytic forms reproduce with good accuracy the calculated $\Delta E_i(R)$ curves of Tasker, Balint-Kurti, and Dixon.¹⁰

- *Permanent address: Department of Chemistry, University of Massachusetts, Amherst, MA 01003.
- ¹P. E. Cade, A. M. Stoneham, and P. W. Tasker, Atomic Energy Research Establishment Report No. TP1021 (1983); Phys. Rev. B 30, 4621 (1984).
- ²M. J. Norgett, Atomic Energy Research Establishment Report No. AERE-R7650 (1974); Atomic Energy Research Establishment Report No. AERE-R7015 (1972). The present calculations were performed on HADES-2.
- ³A. B. Lidiard and M. J. Norgett, in *Computational Solid State Physics*, edited by F. Herman, N. W. Dalton, and T. R. Kohler (Plenum, New York, 1972), pp. 385-412.
- ⁴Computer Simulation of Solids, edited by C. R. A. Catlow and W. C. Mackrodt (Springer-Verlag, Berlin, 1982).
- ⁵C. R. A. Catlow, K. M. Diller, and M. J. Norgett, J. Phys. C 10, 1395 (1977). Also, Atomic Energy Research Establishment Report No. AERE-TP672 (1976).
- ⁶C. R. A. Catlow, K. M. Diller, M. J. Norgett, J. Corish, B. M. C. Parker, and P. W. M. Jacobs, Phys. Rev. B 18, 2739 (1978).
- ⁷C. R. A. Catlow, M. Dixon, and W. C. Mackrodt, in *Computer Simulation of Solids*, edited by C. R. A. Catlow and W. C. Mackrodt (Springer-Verlag, Berlin, 1982), Chap. 10, pp. 130–161.
- ⁸R. Eggenhoffner, F. G. Fumi, and C. S. N. Murthy, J. Phys. Chem. Solids 43, 583 (1982).
- ⁹A. M. Stoneham, Atomic Energy Research Establishment Report No. AERE-R9598 (corrected 1981).
- ¹⁰P. W. Tasker, G. G. Balint-Kurti, and R. N. Dixon, Mol. Phys. **32**, 1651 (1976).

- ¹¹M. J. Gillan, J. Phys. C 17, 1473 (1984).
- ¹²P. E. Cade, A. M. Stoneham, and P. W. Tasker (unpublished).
- ¹³J. H. Harding and A. M. Stoneham, J. Phys. C 17, 1179 (1984).
- ¹⁴K. Mansikka and F. Bystrand, J. Phys. Chem. Solids 27, 1073 (1966).
- ¹⁵R. H. Bartram, A. M. Stoneham, and P. W. Gash, Phys. Rev. 176, 1014 (1968).
- ¹⁶M. J. Norgett and A. M. Stoneham, J. Phys. C 6, 229 (1973).
- ¹⁷R. Monnier, K. S. Song, and A. M. Stoneham, J. Phys. C 10, 4441 (1977).
- ¹⁸S. T. Pantelides and W. A. Harrison, Phys. Rev. B 11, 3006 (1975).
- ¹⁹W. Pong and J. A. Smith, Phys. Rev. B 9, 2674 (1974).
- ²⁰R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Lecky, Phys. Rev. B 11, 5194 (1975).
- ²¹A. B. Kunz, Phys. Rev. B 26, 2056 (1982).
- ²²P. W. Tasker and A. M. Stoneham, J. Phys. Chem. Solids 38, 1185 (1977).
- ²³I. S. Jacobs, Phys. Rev. **93**, 993 (1954).
- ²⁴W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).
- ²⁵R. A. Eppler and H. G. Drickamer, J. Chem. Phys. 32, 1734 (1960).
- ²⁶W. D. Drotning and H. G. Drickamer, Phys. Rev. B 13, 4568 (1976); 13, 4586 (1976); 13, 4592 (1976).
- ²⁷A. B. Wolbarst and R. D. Zwicker, Phys. Rev. Lett. 37, 1487 (1976).
- ²⁸R. D. Zwicker, J. Phys. Chem. Solids 39, 445 (1978).