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Soft-X-Ray Absorption Threshold in Metals, Semiconductors, and Alloys*

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We report calculations of the K edges in Li and Be and the L_{23} edges in Na, Mg, Al, and Si. The calculations use self-consistent core and valence-electron densities for both the ground and excited configurations; corrections for the host ionic fields are incorporated, using pseudopotential methods. It is found that the calculated edge energies are in close agreement with experiment when Schneider's values of the bulk chemical potential are used for the excited electron. In further studies of inhomogeneous systems, we show that the core threshold is highly insensitive to atomic environment, so that amorphous materials can be discussed. The case of dilute alloys is treated and core recombination in AlMg alloys is analyzed in detail. The effects studied here indicate that the surface barriers caused by the dipole moments of surface atoms are small, most probably $\lesssim 0.1$ Ry, in all the materials treated here.

I. INTRODUCTION

Considerable theoretical and experimental interest has recently been focused on the nature of core holes in solids.[1-3] The use of the synchrotron radiation continuum as a soft-x-ray source has allowed access to the excitation spectra of deep levels and provided data that complement and augment spectra obtained by the traditional approach of soft-x-ray emission. Deep levels in metals, salts, semiconductors, and, in several cases, alloys have now been accurately probed and the results are available for theoretical analysis. It turns out that photons provide results that are in some respects less complicated than those obtained by methods of electron spectroscopy for chemical analysis (ESCA).[4]

The theory of core holes in solids has been developed in two directions concerned, respectively, with the threshold energy and with the structure of additional excitations. When an electron is excited from a core level to the band continuum there ensue in general many-body effects that originate in the recoil of the solid under the influence of the freshly created electron–hole pair. The sluggish lattice motion is of no consequence in optical transitions and it is the electronic recoil to which we refer here. These processes are sensitive to the electronic structure of the host lattice and to the nature of the excited orbital. Of course, whatever the nature of the crystal may be, there exists a threshold for optical absorption that corresponds in energy to the difference between the electronically relaxed ground and excited configurations. This energy is simultaneously the minimum absorption energy from the relaxed ground state and the maximum emission energy from the electronically relaxed excited state. It is on this threshold energy in metals, semiconductors, and alloys that the theoretical discussion in the present paper is principally centered.

It has been shown by Friedel[5] and by Hopfield,[6] following Mahan,[7] that the threshold in metals has a characteristic absorption-edge singularity that depends on details of the ground- and excited-state orbitals. At threshold, the oscillator strength for transitions to any specific excited configuration is vanishingly small but the large multiplicity of low-lying excited states causes the edge to become singular with an absorption coefficient

$$I(\omega) \sim |\omega - \omega_0|^{-\alpha} .$$

Here $\hbar\omega$ is the photon energy and $\hbar\omega_0$ the threshold; α depends in sign and magnitude on the excited configuration through the phase shifts that describe screening. Combescot and Nozières[8] have analyzed a model system that clearly reveals the salient features. The edge characteristics show qualitative differences when the hole attraction becomes strong enough to bind the excited electron and when the conduction electron density becomes so small that the bound relaxed excited state becomes typical of insulating crystals.

These interesting general features of the core-excitation problem are, however, mainly peripheral to our present discussion of the threshold energy in metals, semiconductors, and alloys. In these cases the excited orbital is certainly not bound (metals) or else is so weakly bound as to introduce negligible effects. The only property of the spectrum that may influence the measured $\hbar\omega_0$ appreciably is a broadening originating in the limited lifetime of the excited state. Direct recombination can hardly cause the observed short lifetimes, $\sim 10^{-15}$ sec. It appears likely, then, that the broadening arises from the large multiplicity of Auger processes in which the recombination transition leaves other electrons excited. Despite the edge broadening, the attainable resolution, ~ 0.1 eV for L_{23} transitions with $\hbar\omega \sim 100$ eV,[2,3] allows the spin-orbit splitting of the core hole to be resolved with great clarity. The threshold energy can therefore be determined with an accuracy much better than 1%, whatever interpretation be placed on the edge structure. For this reason, the edge energies in the soft-x-ray region provide accurate structural information with the energy resolution $\lesssim 1$ eV of typical interest in the band structure and surface barrier properties of metals and semiconductors. The excessive broadening of deeper levels makes them less useful in this respect. It was with the aim of clarifying the relationship between the soft-x-ray edge energies and the core and valence-band properties of the host lattice that the present work was undertaken.

Two previous detailed theoretical analyses of soft-x-ray edge energies have been published. One, due to Kunz,[9] treats the rather different problems encountered in salts and does not concern the types of band structure of interest here. The second, by Hedin and co-workers,[10] which deals with the edge energy in metallic crystals, relates most closely to the present work. A calculation of the edge energy $\hbar\omega_0$ necessarily involves a comparison of the crystal energy in the ground state and in the relaxed excited state in which the core hole is screened by the electron gas containing one extra electron. In Hedin's work the ionization energy E^{Z+} to the core with charge $Z|e|$ is taken from experiments on free ions. The core-hole energy in the solid is obtained by means of a correction $V_H^c = 3Z/r_s$ (rydbergs), with r_s in atomic units, for the Hartree field of a *uniform* electron gas at the cell center. A second correction Σ^c for exchange and polarization in the electron gas is a composite of contributions associated with electron-gas screening and core-to-valence exchange, the latter contribution being small. For the energy associated with the extra conduction state, Hedin takes the chemical potential obtained from band-structure calculations and corrects this, using the Hartree potential $2.417Z/r_s$ of a *uniform* electron gas and the self-energy term Σ^g for exchange and correlation in the electron gas. Σ^g and Σ^c are almost equal and of opposing sign. The summed contribution for the Li $1s$ core hole, the Na and Al $2s$ core holes, and the K $3s$ core hole are reproduced in Table I as values of $\hbar\omega_{0H}$. They lead to agreement with experiment that is generally well within 0.1 Ry.

There are, however, several features of this calculation that give cause for concern. They are as follows. (a) The effect of electron-gas inhomogeneity on $\hbar\omega_0$ is neglected. We show in Sec. III that this effect can amount to 0.5 Ry. (b) The electron-gas polarization by the core hole is treated in a simplified fashion. (c) The effect of conduction states on the core functions is taken into account only to first order, although the energy involved is several rydbergs. (d) The bulk chemical potential employed in the calculation disagrees, for higher valence materials, with the results of a careful

TABLE I. Contributions to the theoretical excitation threshold $\hbar\omega_{0H}$, calculated by Hedin, compared with the observed energy $\hbar\omega_0$. The μ_s are alternative values of the bulk chemical potential calculated by Schneider. All numerical values are given in rydbergs.

1	2	3	4	5	6	7	8	9[a]
Solid	Edge	E^{Z+}	V_H^c	Σ_H^c	μ	μ_s	$\hbar\omega_{0H}$	$\hbar\omega_0$
Li	K	5.560	−0.924	−0.448	−0.157	−0.152	4.03	4.03
Na	L_1	5.887	−0.763	−0.396	−0.148	−0.169	4.58	4.67
Al	L_1	12.089	−3.010	−0.661	0.049	−0.120	8.47	8.48
K	M_1	3.529	−0.617	−0.304	−0.153	−0.149	2.46	2.51

[a] These results are tabulated in Ref. 1.

study by Schneider,[11] also shown as values of μ_S in Table I. It therefore appeared appropriate to undertake a systematic investigation of core-excitation energies, including the effects of electron-gas inhomogeneity and core-orbital distortions, in these and other similar materials.

Point (d) above bears on a second area of interest in the present work. This is the difficult and still troublesome question of the bulk chemical potential μ in crystals. The work function W measures the difference between μ and the surface dipole potential change $\Delta\phi$ associated with the detailed structure of the electron wave functions at the crystal surface. When the dipole moments of surface atoms cause the electrostatic potential ϕ to increase by $\Delta\phi$ in passing outwards through the surface, the observed

$$W = -\Delta\phi |e| - \mu \tag{1}$$

does not serve to specify μ and $\Delta\phi$ separately, and quoted values of these important quantities may vary from one source to the next by several eV in higher-valence crystals. This uncertainty is of profound concern in this and previous calculations of $\hbar\omega_0$, as errors in the values of μ employed introduce similar errors into the predicted $\hbar\omega_0$. The importance of this point is illustrated by the difference between the values of μ for Al employed by Hedin and calculated by Schneider, both given in Table I.

There have recently appeared attractive model calculations by Lang and Kohn[12,13] in which both the surface energies and the work functions of many simple metals (including polyvalent crystals) are rather accurately reproduced. As a starting point, these studies employ a model in which the ionic charge is smoothed into a uniform background charge. A large surface dipole potential appears in the self-consistent charge distribution of this model because the Hartree potential is otherwise zero and electrons near E_F are not bound. Electrons therefore spill out of the solid surface and the resulting dipole layer stabilizes all band states. The model is then improved[12,13] by a first-order calculation of the change in W caused by the true ionic field as simulated by Ashcroft pseudopotentials.[14] The first-order correction proves to be $\lesssim 0.5$ eV in most cases and is weakly dependent on surface orientation. The calculated values of W are in very good accord with the experimental evidence in most cases.

When corrected for dissimilar definitions of $\Delta\phi$, the calculations of Lang and Kohn, and of Schneider give a consistent account of the way the potential change at the crystal surface is divided between surface terms and bulk terms. In this respect, the later calculations therefore support Schneider's contention that the surface barrier is small. It has, of course, long been realized that electrons bound into solids by strong Hartree fields do give rise only to small surface barriers, typically $\lesssim 1$ eV.[15] However, there remain added complications. The early work of Smoluchowski[16] established that the normal atomic surface irregularity of crystal faces creates a dipole layer that opposes the part caused by the tendency of electrons to penetrate the surface field, thereby reducing $\Delta\phi$ further. Model calculations by Bennett and Duke[17] have revealed added effects of the periodic potential. Each of these theoretical contributions therefore adds weight to the view that surface atoms have only a small average dipole moment, although the detailed numerical results may contain residual uncertainties. This in turn suggests that the simplified procedures by which μ was obtained in earlier calculations of core-excitation energies may, as remarked above, be much less accurate than is apparent from the final computed values of $\hbar\omega$.

The present calculations provide a more systematic evaluation of $\hbar\omega$, including band effects, and also cast light on these important questions concerning μ and $\Delta\phi$ in real materials. The method outlined in Sec. II and detailed in Sec. III proceeds by an examination of the energy changes that ensue when a core electron is annihilated. Since the core hole experiences the interior field, the energy is sensitive to $\Delta\phi$. The neutral excited solid is obtained by adding an electron in the lowest available level. We can obtain the energy change in this step either by using Schneider's value of μ, in which case $\Delta\phi$ is eliminated, or by assuming that $\Delta\phi$ is small and subtracting the work function from the total energy. It turns out that results obtained by these two methods have a comparable degree of agreement with the observed $\hbar\omega_0$. Our results, therefore, support Schneider's contention that the surface barrier caused by surface atom dipole moments is small.

II. GENERAL APPROACH

We shall calculate the transition energy in an approximation substantially better than Hartree–Fock theory for the cores and for the electron gas separately. To do so, we first write the Hamiltonian of the electrons of the solid in the form

$$\mathcal{H} = \mathcal{H}_c + \mathcal{H}_g + \mathcal{H}_{cg} \ , \tag{2}$$

in which

$$\mathcal{H}_c = \sum_{\alpha} \frac{\hbar^2}{2m} \nabla_\alpha^2 - \sum_{\alpha A} \frac{Ze^2}{r_{\alpha A}} + \frac{1}{2} \sum_{\alpha\beta}{}' \frac{e^2}{r_{\alpha\beta}} \ , \tag{3}$$

$$\mathcal{H}_g = \sum_{i} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{iA} \frac{Ze^2}{r_{iA}} + \frac{1}{2} \sum_{ij}{}' \frac{e^2}{r_{ij}} \ , \tag{4}$$

and

$$\mathcal{H}_{cg} = \sum_{\alpha i} \frac{e^2}{r_{\alpha i}} \quad . \tag{5}$$

Here, Greek subscripts denote core electrons, italic lower-case subscripts denote valence electrons, and italic upper-case subscripts denote nuclei of charge Z. The core-band wave functions we denote by Φ and the valence-band wave functions by Ψ, so that the total wave function is

$$\chi = \Phi\Psi \tag{6}$$

and the total energy is obtained from Eqs. (2) and (7) as

$$E_t = \langle \Phi | \mathcal{H}_c | \Phi \rangle + \langle \Psi | \mathcal{H}_g | \Psi \rangle + \langle \chi | \mathcal{H}_{cg} | \chi \rangle \quad . \tag{7}$$

By writing the wave function in terms of specific core electrons and valence electrons in this way, we acknowledge that exchange between core and valence states will be ignored, although it will become apparent later that intracore and intravalence effects are to be included fully. The neglect of core-to-valence exchanges is justified for deep-core levels by the small overlap of core orbitals with valence levels that are, in any event, largely excluded from the core volume.

We shall represent by primed symbols Φ', Ψ', χ', $\mathcal{H}'$, etc., properties of the lowest excited state of the entire system in which one core electron is removed to a stationary state of zero energy at infinity. The excitation energy $\hbar\omega_0$ is thus obtained as

$$\hbar\omega_0 = E_t' - E_t + \mu_0 = \delta E_c + \delta E_g + \delta E_{cg} + \mu_0 \quad , \tag{8}$$

in which

$$\delta E_c = E_c' - E_c = \langle \Phi' | \mathcal{H}_c' | \Phi' \rangle - \langle \Phi | \mathcal{H}_c | \Phi \rangle \quad , \tag{9}$$

$$\delta E_g = E_g' - E_g = \langle \Psi' | \mathcal{H}_g' | \Psi' \rangle - \langle \Psi | \mathcal{H}_g | \Psi \rangle \quad , \tag{10}$$

$$\delta E_{cg} = E_{cg}' - E_{cg} = \langle \chi' | \mathcal{H}_{cg}' | \chi' \rangle - \langle \chi | \mathcal{H}_{cg} | \chi \rangle \quad , \tag{11}$$

and with μ_0 the energy increase when the removed electron is returned to the lowest orbital available for occupation in the conduction band. In these expression E_c' and E_c are core energies of the excited and ground state configurations, respectively, in the presence of the electron gas. The energies include all interactions between core electrons but exclude, except in the determination of Φ and Φ', the Coulombic interaction between valence and core electrons. The latter contribution appears in δE_{cg}, which gives the change in core-to-valence coupling energy associated with the transition. Finally, δE_g represents the difference in energy of the electron gas, including interactions among valence electrons, between the excited- and ground-state configurations. In summary then, δE_c and δE_g are, respectively, the changes in self-energy of the self-consistent core and electron-gas distributions, and δE_{cg} is the change in core-to-valence coupling energy.

It is convenient to keep δE_c in the form given by Eq. (9), since this contains the major part of $\hbar\omega_0$ in a tractable form, and to rewrite the two remaining terms δE_g and δE_{cg} of $\hbar\omega_0$ in a form that has had notable success in problems related to the band structure of solids. We shall regard both the excited-state and the ground-state electron-gas configurations as derived from the uniform background charge model by the replacement of the uniform background by the correct ionic fields. Suppose that the initial model electron gas has an energy E_0. Keeping the electron gas rigid, we now replace the uniform background by the true ionic potential with an accompanying energy change E_s, which resembles a Madelung energy. The electron gas is next released and there results an energy change E_r by relaxation. Similarly, for the excited state one obtains energies E_s' and E_r' for the electrostatic and relaxation contributions. Clearly,

$$E_0 + E_r + E_s = E_g + E_{cg} \tag{12}$$

and

$$E_0' + E_r' + E_s' = E_g' + E_{cg}' \quad , \tag{13}$$

provided only that the core distributions used in the calculations of the E_s and E_r are precisely the self-consistent functions that describe the core-electron motion *in the presence of the relaxed electron gas.* With

$$\delta E_s = E_s' - E_s \tag{14}$$

and

$$\delta E_r = E_r' - E_r \; , \tag{15}$$

we now obtain, from Eqs. (8), (12), and (13), the result

$$\hbar\omega_0 = \delta E_c + \delta E_r + \delta E_s + \mu_0 \quad . \tag{16}$$

The energy E_0 of the uniform background charge model is not relevant to the excitation energy and has disappeared from Eq. (16).

In summary, then, the evaluation of $\hbar\omega_0$ may usefully be partitioned into the following steps: (a) An evaluation of the self-energies of the cores as distorted by the presence of the final self-consistent electron-gas distributions; (b) a determination of the electrostatic self-energies of a uniform electron gas together with the rigid (deformed) cores; (c) a calculation of the electron-gas relaxation energy when it is exposed to the field of the full core band and the excited core band; and (d) an evaluation of the energy change μ_0 when the annihilated core electron is returned to the lowest unoccupied valence orbital of the solid.

These steps are treated separately in the detailed discussion that follows in Sec. III.

III. DETAILED EVALUATION OF CORE-EXCITATION ENERGIES

We now present a detailed description of the evaluation of the several terms contained in Eq. (16) for the core-excitation energy $\hbar\omega_0$.

A. Core Self-Energy

Complex and precise methods are now available that allow the accurate calculation of the total energy of atomic systems. These methods can account accurately for correlation effects in valence orbitals[18] and for correlation and relativistic effects in core states.[19] However, even nonrelativistic Hartree–Fock calculations in the absence of external fields remain time consuming for heavy atoms and are much too demanding for use in surveys having the breadth of the present work.

It is therefore fortunate that the complexity of these procedures is entirely unnecessary in calculations of the quantities of interest here. The point is that the core self-energy enters as a difference between the core ground state and the ionized core. Relativistic effects important for deep states enter only as a negligible difference into the calculations of $\hbar\omega_0$. It has also been known for some time that correlation corrections to the one-electron Hartree–Fock scheme take a simple and reproducible form for core orbitals. To the desired accuracy of ~ 0.01 Ry, the correlation energy turns out to be an additive property of the particular orbital occupied that is highly insensitive to the charge state of the ion (provided that the core shell remains full) and to the particular atom in which the core orbital is embedded.[19,20] These points are demonstrated again in the Appendix for several cases involving the free ions of light elements. For these reasons correlation corrections to the Hartree–Fock scheme can be added with high accuracy and a minimum of effort even for core orbitals distorted by the crystal field of valence states and other ions. This does not, of course, lessen interest in the precise calculation of the corrections themselves; it merely indicates that, for the purpose of our present study of core excitations, questions of core correlation can be dealt with to all necessary precision.

There is a final simplification that is of greatest importance to the present investigation. It is not widely recognized that full Hartree–Fock procedures dures are unnecessary for accurate calculations of the ionization potentials of outer core electrons. We show in the Appendix that Hartree–Fock procedures using the Slater[21] exchange approximation reproduce to ~ 0.02 Ry the Hartree–Fock transition energies of free ions. It should be emphasized that Koopman's theorem is of no utility whatever in these studies. The self-consistent wave functions of the ground state and ionized cores must be calculated completely and independently. When these wave functions are then employed with the Fock Hamiltonian to calculate the energy, the excitation energy $\hbar\omega_0$ agrees with the full Hartree–Fock value to high accuracy. Presumably this occurs because the energy is stationary for the true Hartree–Fock wave functions. For this reason, the correlation correction we apply to the ionization energy calculated using the Slater exchange approximation has the status of a true correlation energy rather than merely representing a systematic error in the calculations procedure. Since relativistic effects in $\hbar\omega_0$ are negligible, our method provides core contributions to the excitation energy that are reliable to ~ 0.02 Ry.

The procedure we have employed to calculate δE_0 is therefore as follows. Different cores in the solid are assumed to be independent and are coupled only through $\mathcal{H}_{cg}$. We calculate, using a modified Hermann–Skillman[22] routine, the core wave function of an ion in the presence of an assumed field from the electron gas. The field is then recalculated for the deduced distribution of core charge, using methods discussed in Sec. III C, and the core structure redetermined for this new valence field. The process is found to converge after some 25 iterations to final values of the core wave functions and the associated electron-gas potential. Using these Hartree–Fock Slater wave functions, we then calculate the core self-energy using the full Hartree–Fock expression for the core energy[21] to obtain the core energy $E_{c0} = E_c - \delta_c$, with δ_c the correlation energy of the ground-state core. Similar procedures yield $E'_{c0} = E'_c - \delta'_c$, the energy, less correlation, of the ionized core in the presence of its self-consistent electron-gas field. The core contribution to the excitation energy follows as

$$\delta E_c = E'_c - E_c = \delta E_c^0 + \delta'_c - \delta_c, \tag{17}$$

with $\delta E_c^0 = E'_{c0} - E_{c0}$. The correlation contribution $\delta'_0 - \delta_c$ to δE_c is obtained from subsidiary calculations for free ions, as explained in the Appendix.

Values of δE_c^0 computed in this way for the $1s$ ionization potential of Li^+ and Be^{2+} and the $2p$ ionization potentials of Na^+, Mg^{2+}, Al^{3+}, and Si^{4+}, all in the solid state, are given in column 1 of Table II. Also shown in Table II are values of the correlation correction $\delta'_c - \delta_c$. The resulting values of δE_c are believed to be accurate to ~ 0.02 Ry. They also differ only to this extent from the corresponding ionic excitation energies, but the influence of the dissimilar orbitals for the ground-state and excited cores have more significant effects on the electron-gas contributions, as described below.

B. Electrostatic Energy

We now turn to a calculation of the electrostatic energies E_s, E'_s, and δE_s defined in Sec. II.

TABLE II. Contributions to the core excitation energy $\hbar\omega_0$ in various solids. All numerical results are given in rydbergs.

		1	2	3	4	5	6	7	8	9	10
Solid	Edge	δE_c^0	$\delta_c' - \delta_c$	δE_s^0	δE_{ps}	δE_h	μ_s	$\hbar\omega_{0s}$	W	$\hbar\omega_0$	$\hbar\omega_0$
Li	K	5.407	0.15	−0.824	−0.080	−0.382	−0.152	4.12	0.194	4.08	4.02[a]
Be	K	11.152	0.16	−2.326	0.107	−0.560	...	...	0.242	8.29	8.24[a]
Na	L_{23}	3.344	0.12	−0.682	0.014	−0.330	−0.198	2.27	0.169	2.29	2.26[a]
Mg	L_{23}	5.771	0.12	−1.644	0.080	−0.434	−0.208	3.68	0.229	3.66	3.65[a]
Al	L_{23}	8.711	0.12	−2.800	0.098	−0.518	−0.120	5.49	0.262	5.35	5.36[a]
Si	L_{23}	12.148	0.12	−3.593	−0.595	−0.529	...	...	0.330	7.22	7.29[b]

[a] See Ref. 2.

[b] See Ref. 3.

If the ions were simply point charges of magnitude $Z|e|$, then the energy required to establish the ions in place of the uniform background charge in the uniform electron gas would simply be the negative of the Ewald energy E_E of the lattice. This follows from the fact that the electrostatic energy of the uniform charge model is zero, neglecting surface effects, while that of the point-ion lattice is the Ewald energy by definition. It should be remarked that the surface energy of the solid is negligibly changed by the annihilation of a core electron and we can neglect all surface contributions to $\hbar\omega_0$, other than the part that arises from the uniform potential in the bulk material from the surface dipole layer.

In practice the ionic potential deviates strongly from the point-ion form inside the atomic cell, so the Ewald energy requires correction. However, the core functions terminate inside the atomic cell so the correction arises only from the interaction of the uniform electron gas with the deviation of the core potential from the point-ion form *inside* the cell. If the ionic potential is $V(r)$ and the point-ion is $Z|e|/r$, then the electrostatic energy of the solid containing N ions may be written

$$E_s = E_E + N\int n[V(\vec{r}) - Z|e|/r]\, d^3r \;, \tag{18}$$

in which n is the density of the uniform electron gas. The integrand is nonzero only within the cell, as remarked above.

For the excited state we may similarly write the electrostatic energy

$$\begin{aligned} E_s' = E_E &+ |e|[V_e(0) - \Delta\phi] \\ &+ \int n[V'(\vec{r}) - (Z+1)|e|/r]\, d^3r \\ &+ (N-1)\int n[V(\vec{r}) - Z|e|/r]\, d^3r \;. \end{aligned} \tag{19}$$

This is the Ewald energy E_E of the point-ion lattice, together with the work $|e|V_e(c)$ required to place an additional charge on the ion to be excited, with $V_e(0)$ the potential at the point-ion from the electron gas and the surrounding ions, and $-|e|\Delta\phi$ the work against the surface potential $\Delta\phi$. The remaining terms in Eq. (19) correct the point-ion expression for the interaction of the uniform electron density n with the differences $[V'(\vec{r}) - (Z+1)|e|/r]$ and $[V(\vec{r}) - Z|e|/r]$ between the true potentials and the point-ion potential of the excited core and the $N-1$ unexcited cores, as in Eq. (18). We thus find

$$\begin{aligned} \delta E_s &= E_s' - E_s \\ &= |e|V_e(0) + |e|\Delta\phi \\ &\quad + \int n[V'(\vec{r}) - V(\vec{r})|e|/r]\, d^3r \;. \end{aligned} \tag{20}$$

We defer a discussion of the surface term $|e|\Delta\phi$ until Sec. III D and here focus attention on the electrostatic energy

$$\delta E_s^0 = \delta E_s - |e|\Delta\phi \tag{21}$$

given by the remainder of Eq. (20). The core-electron density vanishes outside the excited cell and therefore so also does the integrand of Eq. (20). For spherical core fields we can transform this to a radial integral with any desired upper limit that lies outside the cores, and as this limit we choose the Wigner–Seitz cell radius r_s. Then

$$\delta E_s^0 = |e|\, V_e(0) + 4\pi\int_0^{r_s} n[V'(r) - V(r) - |e|/r^2]dr. \tag{22}$$

Now to the accuracy of the Wigner–Seitz approximation,[23] the potential from the entire lattice at the point-ion core is just the potential of the sphere of electronic charge in the cell, so that

$$V_e(0) = -4\pi\int_0^{r_s}[n|e|/r]r^2\, dr \;. \tag{23}$$

To this approximation we therefore find from Eqs. (22) and (23)

$$\delta E_s^0 = 4\pi n\int_0^{r_s}[V'(r) - V(r)]\, r^2\, dr \;. \tag{24}$$

It may be noted that the sphere approximation is accurate to 0.5% in simple lattices.[24]

The electrostatic energy has been expressed in the convenient form of Eq. (24) to bring out an important feature of the present work. All details of the crystal structure are erased from Eq. (24); it contains only the electron density and the atomic cell radius. We shall find that the relaxation effects discussed below in Sec. III C introduce the lattice into the energy only through the pseudoatom charge density in the atomic cell, which again is only weakly dependent on the host lattice. These are the first signs of a central point that emerges from this work: the core-excitation energy is very insensitive to the environment of the excited atom.

We have evaluated the energies δE_s^0 given in column 3 of Table II for the host lattices listed there. In each case the potentials $V'(r)$ and $V(r)$ were obtained from the self-consistent core-electron densities evaluated in Sec. III A above. Note that the nuclear potential is eliminated from Eq. (24) and that for the main part the integrand represents the smooth potential of a single (isotropic) core hole. The values given in Table II vary up to several rydbergs and should have the accuracy of the Wigner–Seitz sphere approximation for the uniform electron gas.[24] Corrections to these results arising from the inhomogeneous electron-gas distribution are treated in Sec. III C.

C. Relaxation Energy

In this section we examine the inhomogeneity of the electron gas caused by the interaction between core and valence electrons. The precise configuration of the electron gas influences the core-excitation energy in three distinct ways. First, the inhomogeneous electron gas creates a potential at the core that differs from $V_0(0)$ and the excited ion is left in a different potential which therefore modifies $\hbar\omega_0$. Second, the excited ion has an extra positive charge that perturbs the electron gas. The screening response of the host lattice causes a large energy reduction that again has a major effect on $\hbar\omega_0$. Last, the electric fields arising from the inhomogeneous electron gas in the ground and excited configurations distort the core functions in a way that must be accurately incorporated into the calculations of Sec. III A to obtain accurate core self-energies. For these reasons it is of importance in calculations of $\hbar\omega_0$ that the mutually self-consistent forms of the core- and valence-electron distributions be accurately incorporated into the total energy calculations.

Many recent studies have focused on questions related to the way in which the atomic cores influence the valence-electron distribution. Diverse properties such as band structure, transport phenomena, and cohesion-related areas concerned with total energy, elastic constants, defect formation energies and electronic surface properties have in turn come under close scrutiny. While it cannot be asserted that complex phenomena concerned with cohesion have thereby become well understood for multivalent solids, it is nevertheless true that those investigations employing pseudopotential or model potential methods have on average played by far the most important part in the recent elucidation of crystal properties. This applies not only to the semiquantitative tracing of related properties in particular crystals but also to the accurate and relatively simple evaluation of specific model predictions for a wide variety of solid types. The field of model potential calculations up to 1970 is reviewed by Heine and coworkers.[25] It is on the foundation of these earlier studies that we shall treat the relaxation energy using pseudopotential methods.

An application of pseudopotential methods to the present problem cannot go completely unquestioned. While other investigators have found that the structural dependence of the energy in metals and semiconductors (not the total energy) can be estimated by these means to ~0.01 Ry,[24] the present problem provides a more severe test of this elegant method. The point is that the core-hole potential appears in the sensitive region in which the true core potential is judiciously parameterized by the pseudopotential structure. There is at present no clear answer to the questions posed by the possible nonadditivity of the pseudopotential and any additional fields arising from core holes. A second difficulty stands quite apart from the merits of the pseudopotential representation itself; it concerns rather the almost mandatory use of linear-response theory in conjunction with model potentials to deduce the self-consistent valence-electron distribution. For Al with $Z=3$ the electron gas screening the hole suffers a fractional density disturbance $\delta n/n \sim \frac{1}{3}$, but for Na the electron density increases by a factor ~2 in the cell containing the excited core. Now the dielectric (linear response) approximation can only be expected to apply satisfactorily for small fractional changes in n so the very basis of the procedure comes into question for monovalent metals. Fortunately, it is for precisely these cases that the relaxation energy contributes least to $\hbar\omega_0$ and fractional errors assume a lesser significance in the final result. In addition, the surface fields are best understood for the monovalent metals, so that the accuracy of the procedures employed becomes subject to clear inspection. In what follows we therefore study from a pseudopotential approach the relaxation energy contribution to the core-hole excitation energy.

Consider then the energy change as the uniform electron gas relaxes in response to the fields $V(r)$ of the rigid-ion cores. There are two contributions: a decrease in the core-to-valence coupling energy is partly offset by an increase in the self-energy of the valence electrons. It is well known that in a linear dielectric the latter term is just half the magnitude of the former term. The total energy change, typical of all linear dielectrics, is then

$$E_r = -\frac{1}{8\pi}\sum_{\vec{g}} g^2 |V(\vec{g})|^2 \left[1-\frac{1}{\epsilon(\vec{g})}\right] . \tag{25}$$

Here, $V(\vec{k})$ is a Fourier component

$$V(\vec{k}) = \int \sum_i V_i(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} d^3r \tag{26}$$

of the potential (summed over all ions i) experienced by the valence electrons for their proximity to the cores, and the summation extends over all non-zero reciprocal lattice vectors $\vec{g}$. The quantity $\epsilon(\vec{g})$ is the dielectric constant of the electron gas for that value of $\vec{g}$.

Similar expressions hold for the excited configuration. Suppose that the core hole exposes the conduction electron gas to an additional potential

$$\delta V(\vec{r}) = V'(\vec{r}) - V(\vec{r}) , \tag{27}$$

with Fourier components $\delta V(\vec{k})$ that extend throughout the entire reciprocal space. Then, for the excited configuration we find in place of Eq (25),

$$E_r' = -\frac{1}{8\pi}\sum_{\vec{g}} g^2\{|V(\vec{g})|^2 + [V(\vec{g})\,\delta V(\vec{g}) + \text{c. c.}]\} \times\left[1-\frac{1}{\epsilon(\vec{g})}\right] - \frac{1}{8\pi}\sum_{\vec{k}} k^2 |\delta V(\vec{k})|^2 \left[1-\frac{1}{\epsilon(\vec{k})}\right] . \tag{28}$$

The difference between the ground- and excited-state relaxation energies may therefore be written

$$\delta E_r = E_r' - E_r = \delta E_{\text{ps}} + \delta E_h , \tag{29}$$

in which

$$\delta E_{\text{ps}} = -\frac{1}{8\pi}\sum_{\vec{g}} g^2 [V(\vec{g})\,\delta V(\vec{g}) + \text{c. c.}] \left[1-\frac{1}{\epsilon(\vec{g})}\right] \tag{30}$$

and

$$\delta E_h = -\frac{1}{8\pi}\sum_{\vec{k}} k^2 |\delta V(\vec{k})|^2 \left[1-\frac{1}{\epsilon(\vec{k})}\right] . \tag{31}$$

We emphasize that δE_{ps} and δE_h each have a transparent significance. δE_h is just the relaxation energy of a *uniform* electron gas screening the core hole in the excited configuration. The structure of δE_{ps} is made obvious by noting first that

$$V_g(\vec{k}) = -V(\vec{k})\,[1 - 1/\epsilon(\vec{k})] \tag{32}$$

is the potential due to the final self-consistent electron-gas distribution of the ground state and, second, that from Poisson's equation

$$\delta\rho(\vec{g}) = (g^2/4\pi)\,\delta V(\vec{g}) \tag{33}$$

is the change in core charge density caused by the excitation. Therefore,

$$\delta E_{\text{ps}} = \sum_{\vec{g}} V_g(\vec{g})\,\delta\rho(\vec{g}) \tag{34}$$

simply gives the interaction of inhomogeneities in the electron-gas distribution with the change in core charge distribution.

This latter contribution to δE_r may be brought into the most convenient form by observing that the total potential V_{ps} in the crystal is the sum of the core and valence potentials:

$$V_{\text{ps}}(\vec{g}) = V(\vec{g}) + V_g(\vec{g}) = V(\vec{g})/\epsilon(\vec{g}) . \tag{35}$$

From Eq. (31) we thus obtain

$$\delta E_{\text{ps}} = -\frac{1}{8\pi}\sum_{g} g^2[\epsilon(\vec{g}) - 1][V_{\text{ps}}(\vec{g})\,\delta V(\vec{g}) + \text{c. c.}] . \tag{36}$$

We have calculated values of δE_{ps} from the empirical pseudopotentials $V_{\text{ps}}(\vec{g})$ tabulated by Cohn and Heine[26] and obtained principally from de Haas–van Alphen-effect measurements. These results are presented in column 4 of Table II. Various correlation corrections to the random-phase approximation for $\epsilon(\vec{k})$ [24] were employed in preliminary calculations. It transpires that the transition energy $\hbar\omega_0$ is extremely insensitive to correlation in the electron gas and, while the various contributions to $\hbar\omega_0$ varied somewhat more, different approximations for $\epsilon(\vec{k})$ caused $\hbar\omega_0$ itself to change only by ~0.01 Ry. The values quoted in Table II were obtained using the Sham[27] correlation correction.

Two exceptions to the procedure outlined above must be noted. First, in the case of Si, the dielectric function was modified to an isotropic form which tended to the Si static dielectric constant at $\vec{k}\to 0$, following the model of Srinivasan,[28] which rests on earlier work of Penn[29] and Nara.[30] Second, in the case of Li, the sign of the pseudopotential is not well determined. Cohen and Heine[25] express the opinion that $V_{\text{ps}}(1, 1, 0)$ is positive but our calculations are highly sensitive to the pseudopotential in this case and strongly indicate that $V_{\text{ps}}(1, 1, 0)$ is in fact negative. An incorrect sign here would throw $\hbar\omega_0$ off by several eV.

Values of the remaining relaxation contribution δE_h have been calculated from Eq. (31) using the dielectric function specified above; these results are presented in column 5 of Table II. As mentioned earlier, minor changes in dielectric function cause small compensating effects on δE_{ps}, δE_h, and δE_c that have no significant influence on the resulting $\hbar\omega_0$.

The preceding analysis yields also the electron-gas fields experienced by the ground and excited-core configurations. In the ground state the core experiences a field obtained from Eqs. (32) and (35) as

$$V_g(\vec{r})=\sum_{\vec{g}} V_{ps}(\vec{g})[1-\epsilon(\vec{g})]\,e^{i\vec{g}\cdot\vec{r}} \quad . \tag{37}$$

Similarly, in the excited configuration the field from the electron gas is

$$V'_g(\vec{r})=-\sum_{\vec{g}}[\epsilon(\vec{k})\,V_{ps}(\vec{k})\,\delta(\vec{k}-\vec{g})+\delta V(\vec{k})]\times[1-1/\epsilon(\vec{k})]e^{i\vec{k}\cdot\vec{r}} \quad . \tag{38}$$

These fields were included as static perturbations in the iterative procedures employed in the calculation of δE_c by methods explained in Sec. III A.

Two interesting features of these results bear explicit comment. First, the structure of the solid has very little influence on the value of δE_{ps}. It is, after all, only the local electron density in the cell that perturbs the core transition, as demonstrated by Eq. (34), and the electron gas is well known to reproduce approximately from one solid to the next in the form of a sensibly invariant pseudoatom charge distribution.[31] Therefore the excitation energy $\hbar\omega_0$ should exhibit a marked insensitivity to the atomic environment. Second, the form of the relaxation energy tends to alleviate serious doubts as to the applicability of pseudopotential methods. The pseudopotential term is, after all, just the energy change expected if the electron gas were held rigid during the excitation, and the effect on the transition energy is in any event $\lesssim 0.1$ Ry. The screening contribution δE_h is much more important as it rises to ~ 0.5 Ry. For attractive potentials, linear-response theory may underestimate the relaxation energy, but this should not be too serious for Al with $\delta n/n \sim 1/3$. Although a precise estimate of the likely error in the calculated δE_h is very difficult to establish, we think that the quoted values should be accurate to ~ 0.1 Ry. It should further be borne in mind that the clear separation of δE_r into δE_{ps} and δE_h occurs only in linear-response theory.

D. Excited Electron

The various terms in the energy considered so far sum (apart from the contribution $|e|\Delta\phi$) to give the work required for the annihilation of a core electron. To obtain values of the core-hole-excitation threshold $\hbar\omega_0$, we must include the energy μ of the excited electron when introduced into the lowest available valence orbital. As indicated in the Introduction, this energy remains imperfectly understood. We may certainly write the energy

$$\mu_0=\mu+\Delta\phi\,|e| \quad , \tag{39}$$

with μ the bulk contribution and $\Delta\phi\,|e|$ the barrier due to surface dipoles. We thus obtain, from Eqs. (16), (17), (21), (29), and (39),

$$\hbar\omega_0=\delta E_c^0+(\delta'_c-\delta_c)+\delta E_s^0+\delta E_{ps}+\delta E_h+\mu \quad . \tag{40}$$

Values of μ_s of μ calculated by Schneider[11] are reproduced in column 6 of Table II. It should be remarked that the μ_s are not fully consistent with the present calculations as Schneider calculates μ to second order in the crystal potential, whereas our present results include first-order terms only. However, the second-order effect is at most ~ 0.05 Ry and is often ~ 0.01 Ry, so no attempt has been made to modify this inconsistency.

A second approach takes us by way of Eq. (1). If we assume that the surface barrier due to the dipole moments of surface atoms is negligible, then $\mu=-W$ and we have

$$\hbar\omega_0=\delta E_c^0+(\delta'_c-\delta_c)+\delta E_s^0+\delta E_{ps}+\delta E_h-W \quad . \tag{41}$$

The present calculations therefore allow us to examine the assumption $\Delta\phi=0$ in many cases of interest. These results are discussed in Sec. III E, in terms of the observed values of W presented in column 8 of Table II.

E. Discussion of Results for Simple Solids

Column 7 of Table II gives the values $\hbar\omega_{0S}$ of the theoretical core-excitation energy obtained from Eq. (40) using Schneider's values of the bulk chemical potential μ. These results presumably represent the most complete theoretical predictions for comparison with the observed edge energies given in column 10 of Table II. The agreement is rather satisfactory, with the observed transition energy falling ~ 0.1 Ry below the calculated values for the Li K edge and the Al L_{23} edge, and being essentially indistinguishable from the theoretical predictions for the L_{23} edges of Na and Mg. It appears therefore that the analysis presented here is capable of providing good accuracy in calculations of core excitation energies in a variety of solids.

Some comparison of the present results with previous calculations by Hedin[10] of the Li K edge and the Al L_{23} edge energies is possible. In the case of Li, $\delta E_s^0+\delta'_c-\delta_c$ agrees very closely with free-ion excitation energy and $\delta E_s^0+\delta E_{ps}=-0.904$ Ry agrees, fortuitously, with the value $3Z/r_s=-0.924$ Ry used by Hedin. The hole relaxation energy of $\delta E_h=-0.382$ Ry is also in fair accord with $\Sigma_c=-0.448$ Ry obtained by Hedin. For Al, however, larger differences arise, although a precise comparison is not possible because our present results pertain to the L_{23} edge, whereas Hedin studied the L_1 edge. In our case δE_s^0 again closely approximates the free-ion excitation energy, which Hedin uses. However, the Hartree contribution, $3Z/r_s=3.010$ Ry, is in very poor accord with $\delta E_s^0+\delta E_{ps}=-2.702$ Ry obtained here, and the value $\mu=0.049$ Ry employed by Hedin differs markedly from Schneider's result $\mu_S=-0.120$ Ry. We feel that the correct value of μ may be still more negative, for reasons discussed below. Thus, for polyvalent materials, there appear discrepancies which amount to several tenths of a rydberg. It may be noted that the approximation $3Z/r_s$ is inaccurate both because the core functions contract on ionization, thus changing δE_s^0, and because the electron-gas inhomogeneity introduces an added term δE_{ps}. For monovalent metals these discrepancies are much reduced and the alternative calculations are in generally better agreement.

The results described above pertain to calculations in which each step is undertaken from first principles, except for the underlying empiricism of pseudopotentials which have only a limited influence on the value of $\hbar\omega_0$. There remains the question of how well the bulk chemical potentials of crystals, particularly those formed from multivalent atoms, can at present be specified. As mentioned above, there exists at present no experimental procedure by which μ can be determined, and theoretical estimates vary. To investigate this aspect of the problem we have adopted the hypothesis that the surface barrier $\Delta\phi$ is negligibly small and employed value of $-W$ in Eq. (42) to obtain additional estimates $\hbar\omega_{0w}$ of $\hbar\omega_0$. For this purpose the observed work functions tabulated by Lang and Kohn[12] were employed except in the case of Si, for which a carefully established electron affinity is available.[32] The resulting $\hbar\omega_{0w}$, given in column 9 of Table II, are in startling agreement with the observed $\hbar\omega_0$ listed in column 10.

There are, of course, two alternative conclusions that could be drawn from these results. It may be that the surface barrier in a wide variety of solids are indeed small. Certainly, the high accuracy obtained by calculating $\hbar\omega_0$ from the best theoretical values of μ makes it appear unlikely that the several contributions calculated here have a summed error $\lesssim 0.1$ Ry. The alternative possibility, that the theoretical contributions contain errors that precisely cancel the surface-atom dipole potential $\Delta\phi$ from the observed W, undoubtedly merits consideration, but appears rather remote in view of the wide diversity of materials studied in this work. On the whole, we are inclined toward the view that the surface barrier caused by the dipole moments of surface atoms must in general be quite small, say $\lesssim 0.1$ Ry, as indicated also by the trend of estimates leading to the most recent results of Schneider. Further brief remarks concerning this interesting question will be found in the following discussion of alloys and amorphous materials.

IV. ALLOYS AND AMORPHOUS MATERIALS

A. General Features of Inhomogeneous Systems

We now turn to a brief discussion of inhomogeneous materials, for which the experimental evidence is at present less perfectly assembled. The materials of current experimental interest include amorphous solids (vacuum deposited as thin films) and alloys in which two atomic species are intermixed. Our principal interest lies in the striking insensitivity of the core excitation and absorption threshold to the crystalline environment of the excited atom.

As emphasized above, the contributions δE_c, δE_s^0, δE_h, and δE_{ps} contain little or no reference to the crystal structure. Only δE_{ps} contains reciprocal-lattice parameters, and this relatively small term depends on the host lattice only to the extent that the pseudoatom concept is invalid. The present analysis therefore provides a direct explanation from first principles of the observed minor effect of host environment on the core excitation energy. The degree to which this characteristic reproduces in nature is made evident by recent comparative studies of soft-x-ray absorption in amorphous and crystalline Si films.[33] It is found that the edge structure changes on annealing but that the threshold energy remains invariant to ~0.01 Ry. Since we may reasonably suppose that neither the electron affinity nor the surface barrier are changed significantly by disorder in which the short-range bonding remains largely intact, this result is reproduced to high precision by Eq. (41).

Certain data are now available for alloys containing two atomic species. These concern the soft-x-ray recombination spectra of CuNi, CuAg, AgAu, CuAu, and AlMg alloys.[34-36] For the main part, these spectra also exhibit the insensitivity to alloy composition discussed above. In the classic case of CuNi, for example, the recombination spectra of Cu and Ni core holes can be synthesized quite adequately from an appropriate superposition of the recombination spectra of the two pure metals, even though the spectra overlap in the alloys.[34] Some merging of the recombination spectra of the *d* bands is observed in the remaining noble-metal alloys, but the threshold remains almost unperturbed throughout the range of composition.

Despite the factual simplicity of the experimental results, there exist underlying complexities in the theory for inhomogeneous systems. In what follows, we investigate the theory of the recombination edge for the case of AlMg alloys. Neither the Al nor the Mg recombination edges exhibit large shifts in passing from the pure metals to alloys of compositon Al_3Mg_2 and $Al_{12}Mg_{17}$. The separate recombination spectra of the two cores do show distortion of conduction-band width and shape which point to band-structure changes in the alloys, but the thresholds are not strongly affected. Since Mg and Al can be represented quite well by available pseudopotentials, we might expect that the edge characteristics can be reproduced with reasonable accuracy by an extension of our previous analysis. It is to a discussion of this case that we now turn.

B. Recombination Threshold in Alloys

The theory takes its simplest form when foreign atoms are present at infinite dilution in the host lattice because interactions among solutes then becomes negligible. We shall therefore consider the two cases of (a) recombination at Mg impurities at infinite dilution in an Al host and (b) the opposite limit of Al solutes isolated in the Mg lattice. Neither limit has been studied experimentally, presumably because intensity problems limit the available sensitivity, but the smooth trends of existing data over two-thirds of the phase diagram suggest that abrupt shifts of $\hbar\omega_0$ in the dilute region are unlikely.

Of the two major changes in the theory introduced by questions of the threshold for solutes in a foreign host material, one may be treated accurately and conveniently inside the framework of Sec. III, while the other requires additional model assumptions. First, the impurity in its ground state presents a substantial perturbation on the host electron gas and the valence redistribution in the ground state must be incorporated into the calculation of the recombination edge energy of the solute. However, this can be accomplished by methods directly analogous to those employed for the excited state of the pure metal in Sec. III. The second aspect of this problem is less simple but has a clear physical importance. Impurities disturb the geometry of the surrounding host lattice in a way that modifies $\hbar\omega_0$ and must be included in an accurate calculation of the edge energy. The point is that large solutes occupy a large volume in the host lattice, and the volume is linked to the screening charge distribution by the requirement for local electrical neutrality.

The charge shift caused by misfit can, in principle, be calculated from the positions of the solvent atoms. Suppose that the solvent atom occupies the site $\vec{r}_n$. The change in lattice potential at $\vec{r}$ due to a displacement $\delta\vec{r}_n$ is, in the absence of electronic redistribution, just

$$\delta V_n(\vec{r}) = -\vec{\nabla} V(\vec{r}-\vec{r}_n)\cdot\delta\vec{r}_n \quad . \tag{42}$$

By summing over all solvent atoms we therefore find that the total change in potential due to the deformation is

$$V_d(\vec{r}) = \sum_{n'} \delta V_n(\vec{r}) = -\sum_{k}\sum_{n} i\vec{k}\cdot\vec{\delta}r_n\, V(\vec{k})\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}_n)} \quad , \tag{43}$$

in which $V(\vec{k})$ is the Fourier coefficient $\vec{k}$ of $V(\vec{r})$. The deformation therefore introduces a local potential near the central atoms with Fourier coefficients

$$V_d(\vec{k}) = -\sum_{n'} i\vec{k}\cdot\vec{\delta}r_n\, V(\vec{k})\, e^{i\vec{k}\cdot\vec{r}_n} \quad . \tag{44}$$

To evaluate this field in particular cases we require displacement $\delta\vec{r}_n$ of the host atoms that are not readily accessible either to theory or experiment. We must therefore rely on model assumptions concerning the form of $\delta\vec{r}_n$ as a function or $\vec{r}_n$. Since $\hbar\omega_0$ is unlikely to be sensitive to the exact details of the atomic displacements we shall take for these displacements the values

$$\delta\vec{r}_n = A\vec{r}_n/|\vec{r}_n|^3 \tag{45}$$

that follow from the continuum limit of the lattice-deformation problem.[37] Here, A is a constant that determines the amplitude of the deformation field. It can be obtained in practical cases from the change in lattice parameter caused by alloying, using methods indicated below.

With this choice of $\delta\vec{r}_n$ we obtain the following Fourier components of the deformation potential:

$$\begin{aligned} V_d(\vec{k}) &= -iAV(\vec{k})\sum_n \frac{\vec{k}\cdot\vec{r}_n}{|\vec{r}_n|^3}\, e^{-i\vec{k}\cdot\vec{r}_n} \\ &= -AV(\vec{k})\,k^3\sum_m \frac{N_m}{x_m^2}\, j_1(x_m) \quad , \end{aligned} \tag{46}$$

with N_m the number of atoms in coordination shell m and $x_m = kr_m$. It is assumed here that the atoms in each shell have an isotropic distribution so that the angular average can be completed analytically. This corresponds to neglecting the anisotropy of $V_d(\vec{r})$, which in any event should not interact with the spherical core. As a further useful approximation, we can truncate the summation at some suitable radius r_0 and presume that atoms appear continuously thereafter. The summation then becomes an integral which can be evaluated to obtain finally

$$\begin{aligned} V_d(k) = -A\,\epsilon(\vec{k})\,V_{\mathrm{ps}}(k) \\ \times\left(k^3 \sum_{r_m<r_0} \frac{N_m}{(kr_m)^2}\, j_1(kr_m) + \frac{4\pi}{\Omega}\, j_0(kr_m)\right) , \end{aligned} \tag{47}$$

with Ω the atomic volume of the solvent lattice and with $V_{\mathrm{ps}}(k)$ replacing $V(k)$ in after the manner of Eq. (35).

With the lattice-deformation problem firmly in hand we can now proceed to treat the core-excitation energy of impurities. The problem falls into steps entirely analogous to those outlined in Sec. II and III for the perfect lattice. The first step is to calculate the core self-energy difference δE_c in both the ground and excited configurations just as in Sec. III A. The only change arises from the electron-gas field, which contains contributions that originate in the difference between the host and impurity ionic potentials. These are treated later as part of the relaxation problem. The second step, in which the impurity core is inserted into the host lattice containing the uniform solvent electron gas, also proceeds as in Sec. III C. Equations (21) and (24) still apply for the impurity ionic potentials $V_i(r)$ and $V_i'(r)$ in the ground and excited configurations, respectively.

The major difference between the alloy problem and the theory presented above for pure materials occurs in the relaxation energy. In the ground state the electron gas is exposed to a lattice potential with Fourier components having coefficients

$$V_t(\vec{k}) = V(\vec{g})\,\delta(\vec{k}-\vec{g}) + \Delta V(\vec{k}) + V_d(\vec{k}) \ . \tag{48}$$

Here, the first term is the perfect-lattice potential as in Eq. (25). The second term incorporates the difference between the potential $V_i(k)$ of the impurity actually occupying the excited site and the host atom potential presumed here in $V(g)$. Thus

$$\Delta V(\vec{k}) = V_i(\vec{k}) - V(\vec{k})\,\delta(\vec{k}-\vec{g}) \ . \tag{49}$$

Finally, $V_d(\vec{k})$ is the potential caused by the lattice dilation around the unexcited impurity, and is given by Eq. (47). Following the route leading to Eq. (25), we now find the relaxation energy

$$E_r = \frac{1}{8\pi}\sum_{\vec{k}} k^2 \left| V(\vec{g})\,\delta(\vec{k}-\vec{g}) + \Delta V(\vec{k}) + V_d(\vec{k})\right|^2 \times[1 - 1/\epsilon(\vec{k})] \ . \tag{50}$$

In the same way we obtain for the relaxation energy of the excited impurity configuration

$$E_r' = -\frac{1}{8\pi}\sum_{\vec{k}} k^2 \left| V(\vec{g})\,\delta(\vec{k}-\vec{g}) + \Delta V'(\vec{k}) + V_d(\vec{k})\right|^2 \times[1 - 1/\epsilon(\vec{k})] \ , \tag{51}$$

in which

$$\Delta V'(\vec{k}) = V_i'(\vec{k}) - V(\vec{k})\,\delta(\vec{k}-\vec{g}) \tag{52}$$

is the difference between the potentials of the excited impurity and the ground-state host cores.

We thus obtain for the relaxation contribution to $\hbar\omega_0$,

$$\delta E_r = E_r' - E_r = \delta E_h' - \delta E_h + \delta E_{ps} + \delta E_d \ , \tag{53}$$

in which

$$\delta E_h' = -\frac{1}{8\pi}\sum_{\vec{k}} k^2 |\Delta V'(\vec{k})|^2 \left(1 - \frac{1}{\epsilon(\vec{k})}\right) \ , \tag{54}$$

$$\delta E_h = -\frac{1}{8\pi}\sum_{\vec{k}} k^2 |\Delta V(\vec{k})|^2 \left(1 - \frac{1}{\epsilon(\vec{k})}\right) \ , \tag{55}$$

$$\delta E_{ps} = -\frac{1}{8\pi}\sum_{\vec{g}} g^2 [\epsilon(\vec{g}) - 1][V_{ps}(\vec{g})\,\delta V_i(\vec{g}) + \text{c.c.}] \ , \tag{56}$$

and

$$\delta E_d = -\frac{1}{8\pi}\sum_{\vec{k}} k^2 [V_d(\vec{k})\,\delta V_i(\vec{k}) + \text{c.c.}]\left(1 - \frac{1}{\epsilon(\vec{k})}\right) , \tag{57}$$

with

$$\delta V_i(\vec{k}) = V_i'(\vec{k}) - V_i(\vec{k}) \ , \tag{58}$$

the difference between the excited- and ground-state impurity potentials. As in Sec. III C, these contributions each have a simple significance. $\delta E_h'$ and δE_h give the relaxation energy of a uniform electron gas perturbed by the differences between the excited core and the host core, and between the ground-state impurity core and the host core, respectively. δE_{ps} corrects the difference between $\delta E_s'$ and δE_s for the inhomogeneity of the electron gas caused by the host lattice, and δE_d corrects in a similar way for the potential caused by the lattice deformation.

The final contribution to the energy is, as in Sec. III C, the energy of the excited electron. We may employ either Schneider's results for the host lattice, or alternatively we may presume that $\Delta\phi = 0$ and use $-W$ for the host lattice. In the first case we find for the impurity excitation threshold $\hbar\omega_{0i}$,

$$\hbar\omega_{0i} = \delta E_c^0 + (\delta_c' - \delta_c) + \delta E_s^0 + \delta E_h' - \delta E_h + \delta E_{ps} + \delta E_d + \mu_s \tag{59}$$

and in the second case we find

$$\hbar\omega_{0i} = \delta E_c^0 + (\delta_c' - \delta_c) + \delta E_s^0 + \delta E_h' - \delta E_h + \delta E_{ps} + \delta E_d - W \ . \tag{60}$$

These are the final expressions by means of which we shall compare the theory with experiment.

C. Application for AlMg Alloys

The numerical results for alloys follow closely along the lines established in Sec. III E for pure materials. The potential of the nonuniform electron gas was employed in iterating the core and band functions to self-consistency, and the potentials of these cores were then employed in an accurate calculation of E_s^0. In the same way, E_h', E_h, and E_{ps} follow in a straightforward manner from the core functions and from the pseudopotentials employed in Sec. III. Only the contribution δE_d requires further discussion. It is well known that in elasticity theory the lattice surrounding a spherical defect is dilated according to Eq. (46) by a fraction $\xi = (1+\sigma)/3(1-\sigma) \simeq$ two-thirds of the added volume of the defect. Here σ is Poisson's ratio. The outer surface of the lattice expands by the entire excess defect volume, but the extra part corresponds to a uniform dilation and is of no consequence here. Now when a concentration c of Mg is added to Al the lattice parameter is observed to increase by a fraction $0.35c$; using the factor ξ given above, we find that $A_{\text{Al}} = 0.019\Omega_{\text{Al}}$ with Ω_{Al} the Al atomic volume.[38] Just the reverse happens when Al is

TABLE III. Contributions to the impurity core-excitation energies (in rydbergs) for the L_{23} edges of Mg in Al and Al in Mg.

Core	δE_c^0	$\delta_c' - \delta_c$	δE_s^0	δE_{ps}	δ_h'	δE_h	δE_d	μ_s	$\hbar\omega_{0s}$	W	$\hbar\omega_{0W}$	$\hbar\omega_{0i}$[a]
Mg in Al	5.778	0.12	−2.730	0.094	−0.002	−0.473	0.360	−0.120	3.97	0.262	3.83	(3.65)
Al in Mg	8.698	0.12	−1.683	0.081	−1.763	−0.422	−0.221	−0.208	5.45	0.229	5.43	(5.36)

[a] See Ref. 36.

added to the Mg lattice,[38] so $A_{\mathrm{Mg}} = -0.019\Omega_{\mathrm{Mg}}$. These values have been employed in Eq. (47) to obtain the deformation potential $V_d(k)$ and the results incorporated into a calculation of δE_d by means of Eq. (57). In each case we have employed the Ashcroft "empty core" pseudopotential[14] in evaluating δE_d. In initial studies the necessary computations were carried out for Mg in Al using values of r_0 in Eq. (47) corresponding to summations over various shells of neighbors up to the fourth. The results proved highly insensitive to r_0 and so, for the more complex geometry of Al in Mg, only the first neighbors were included in the discrete summation.

A comparison of Tables II and III shows that the core self-energy contributions for Mg and Al as impurities are little different from the values in the pure metals. The pseudopotential terms are also sensibly unchanged. However, the electrostatic energies of cores in the uniform *host* electron gas are modified by ~ 1 Ry. These large contributions to $\hbar\omega_{0i}$ are largely canceled by the screening terms δE_h and $\delta E_h'$ which contain contributions to $\hbar\omega_{0i}$ of similar size but opposite sign to the change in the electrostatic contribution. The way in which screening stabilizes the recombination edge energy thus emerges clearly from our results.

A further important shift arises from the dilation terms which contribute ~ 0.3 Ry to $\hbar\omega_{0i}$ in these alloys. The final predicted $\hbar\omega_{0i}$ containing these results are compared in Table III with experimental results for the *pure* metals using both Schneider's values of μ and the hypothesis $\mu = -W$ (i.e., $\Delta\phi = 0$). As for the case of pure materials, reported above, results obtained with $\mu = -W$ lead to a somewhat better account of the data. The belief that the surface dipole moment is small thereby gains further independent support. For Al in Mg the predicted edge energy of 5.43 Ry falls within 0.07 Ry of the observed recombination energy for pure Al. For Mg in Al the predicted energy of 3.83 Ry lies 0.18 Ry above the edge at 3.65 Ry of pure Mg, but the experimental results for concentrated alloys also appear to contain a mild trend to higher energies with decreasing Mg content.[36] While these studies require more detailed experimental information before a full assessment becomes possible, it seems clear that existing data confirm the theoretical conclusions within a small fraction of the important dilation term, which has been treated here in a rather rudimentary fashion. The incorporation of a more refined lattice model, where required, would appear to allow calculations for the impurity problem to attain a precision comparable to that obtained in Sec. III for pure host lattices.

V. SUMMARY

We have presented a compact and flexible theory of core excitation energies in metals and semiconductors. The theory neglects core-to-valence exchange but otherwise provides a mutually consistent description of core orbitals within the Hartree–Fock approximation and of valence orbitals within the random-phase approximation. It is cast in a form which exposes the insensitivity of the core edge energy to core environment in these materials.

In applications to diverse cases, including metals having various valences, semiconductors, and alloys, the theory reproduces observed edge energies to ~ 1% or ~ 1 eV. Its accuracy over the spectrum of parameters studied indicates that the theory is comfortably within the range of its validity. There emerges a strong indication from the excitation energies that the surface dipole moment is small ($|e\Delta\phi| \lesssim 0.1$ Ry) in all the solids studied here. In its present form the theory provides a clear and quantitative insight into the roles of valence screening and atomic size in stabilizing the core-excitation energies. It is our opinion that any substantial improvement in accuracy to reproduce structure reliably on a much finer scale (say, 0.1 eV) will require a radical reformulation of the theory.

APPENDIX: CALCULATION OF CORE EXCITATION ENERGIES

It is well known that many-body calculations for atoms and crystals can only be carried through approximately, and even then remain difficult and tedious. Exchange is correctly incorporated into the one-electron approximation by Hartree–Fock methods, but the nonlocality of the exchange potential makes calculations exceedingly complicated, particularly when the problem includes a crystal potential. Many local potentials that approximate the nonlocal exchange potential have been suggested

TABLE IV. Comparison between experimental transition energies (in rydbergs) for several free ions and values calculated using wave functions derived from the local exchange approximation of Kohn and Sham. It is believed that the differences Δ arise mainly from correlation in the full $2p$ core of the ground state.

Atom		$1s^22s^22p^6$ $\rightarrow 1s^22s^22p^5$	Δ_0	$1s^22s^22p^63s^1$ $\rightarrow 1s^22s^22p^53s^1$	Δ_s	$1s^22s^22p^63p^1$ $\rightarrow 1s^22s^22p^53p^1$	Δ_p
Na	Expt.	3.483	0.140	2.805	0.118	2.946	0.114
	Calc.	3.343		2.687		2.832	
Mg	Expt.	5.900	0.132	5.004	0.116	5.121	0.107
	Calc.	5.768		4.888		5.014	
Al	Expt.	8.834	0.132	7.739	0.116	7.835	0.112
	Calc.	8.702		7.623		7.723	
Si	Expt.	12.282	0.135	11.002	0.126	...	
	Calc.	12.147		10.876		10.966	...

since Slater first introduced the idea.[39,40] Recent studies show that the local potential proposed by Kohn and Sham[41] yields energies that are in good agreement with the results of true Hartree–Fock calculations.[42] This scheme has therefore been employed in the present work as a tractable method of obtaining the ground- and excited-state core wave functions required in the calculation of the absorption edges of interest here. It is particularly gratifying that the comparison of energies is found to become still more favorable when excitation energies, rather than total energies, are compared.

The ground- and excited-state energies were therefore obtained in the one-electron approximation as follows. The one-electron energies and wave functions were first calculated, using the Kohn and Sham local exchange potential, by means of a modified Hermann–Skillman program.[22] The total energy E_t of the ion was then calculated from the resulting wave functions using the full Hartree–Fock expression for the one-electron energy, namely,[43]

$$E_T=\sum_i \langle i|-\nabla^2-\frac{Z}{r}|i\rangle+\frac{1}{2}\sum_i\sum_j\langle ij|\frac{1}{r}|ij\rangle -\frac{1}{2}\sum_i\sum_j\langle ij|\frac{1}{r}|ji\rangle\ .$$

A one-electron approximation to the excitation energy was then obtained as the difference between values of E_T for the excited- and ground-state configurations.

The results of calculations for $2p$ core-ionization energies of free ions of Na, Mg, Al, and Si are presented in Table IV in rows labeled "Calc." In order, the three columns of data refer to $1s^22s^22p^6 \rightarrow 1s^22s^22p^5$, $1s^22s^22p^63s^1\rightarrow 1s^22s^22p^53s_1$, and $1s^22s^22p^63p^1\rightarrow 1s^22s^22p^53p^1$ transitions. Ionic asymmetry is, of course, ignored in these calculations and the results are calculated for spherically averaged wave functions, as is customary in the Hermann–Skillman method. Relativistic corrections are neglected (and are probably negligibly small for outer-shell excitations); spin-orbit coupling in the unfilled shells is also ignored. For this latter reason the experimental transition energies presented in the rows labeled "Expt." in Table IV are weighted averages over the appropriate multiplets of experimentally observed transition energies.[44] For the Si $1s^22s^22p^63p^1\rightarrow 1s^22s^22p^53p^1$ transitions are required information is, apparently, not yet available.

The calculated one-electron energies compare very satisfactorily with the experimental results. This is best seen from the columns marked (in an obvious notation) Δ_0, Δ_s, Δ_p, for the three series of transitions, which give the differences between the experimental and theoretical transition energies. For any transition the Δ for the few elements are seen to lie within a range of ± 0.005 Ry, and the entire series of results are spanned by the assignment $\Delta = 0.124 \pm 0.017$ Ry. This excellent reproducibility of the calculation takes on an added valuable significance when it is realized that the values of Δ obtained here have precisely the magnitude expected from correlation in the full $2p$ shell, namely, 0.126 ± 0.008 Ry.[19] The correlation, which is neglected in the Hartree–Fock scheme and cannot possibly be rectified by the local exchange approximation, serves to lower the energy of the full $2p$ shell and so raises the observed transition energy. But it has been observed that the correlation energy is closely represented by a sum over pairs of electrons occupying common orbitals.[19] Our calculations conform to this expectation by yielding values of Δ that are affected very little by the presence of an extra valence electron outside the core shell. The small differences among Δ_0, Δ_s, and Δ_p may well be in part caused by residual correlation effects *between* shells and a small lowering of the excited-state energy associated with these effect.

To whatever cause the residual scatter in Δ may be ascribed, it is evident that the predicted transition energies obtained from wave functions calculated using the local exchange approximation are very close to true Hartree-Fock transition energies. Furthermore, the reproducibility of the differences Δ, which we believe to be associated almost wholly with correlations neglected in the one-electron scheme, allows us to predict with an accuracy of ~ 0.02 Ry the *exact* change in core self-energy that accompanies a core excitation. One simply adds to the calculated one-electron transition energy the correlation error of 0.12 Ry.

For the crystal calculations described in Sec. III A the wave functions were calculated using precisely analogous procedures, apart from an added self-consistent valence field derived by methods described in Sec. III C. The self-energy changes are little different from the free-ion self-energy differences and, in view of the insensitivity of the Δ in Table IV to ionic charge, it seems very unlikely that the core correlation energy could differ markedly from the values for free ions. The correlation energy

$$\delta_c' - \delta_c = 0.12 \text{ Ry}$$

is therefore employed for Na, Mg, Al, and Si in Tables II and III in the belief that the self-energy differences calculated in this way are accurate to within a few hundredths of a rydberg. This lies satisfactorily within the limits of accuracy we have set for the calculation of the core edge energy in this paper. The slightly different correlation energies for the 1*s* shell of Li and Be were obtained by similar methods.

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