

Impurities in jellium

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(Received 19 June 1978)

Recently, x-ray absorption spectra of halide and rare-gas impurities in alkali metals have been measured. We study these systems by treating the alkali metal as jellium with a spherical cavity in which the halide or rare-gas impurity is placed. We use the density functional formalism with self-interaction corrections to find self-consistent solutions for the ground states and the states with a core hole. Specifically, we study F^- in Na, F^- in K, and Ne in K. We present charge densities and self-consistent potentials for these systems. We are able to find a self-consistent solution for both the ground state and the core hole state only for F^- in Na. For F^- in Na we calculate the exponent α_0 which describes the many-body enhancement of the spectrum near the edge, and find that it confirms the experimental observation that the enhancement is small. We did not calculate the exponent α_0 for Ne in K because we were unable to determine a self-consistent ground state for Ne in K. We consider one possible reason for our not finding a self-consistent ground state and discuss the possible relevance of this difficulty to understanding the large rounding seen in the x-ray edge spectra of rare-gas impurities in alkalis.

For many metals x-ray absorption and emission spectra near threshold show deviations from the expected one-electron spectra. The spectra at the edge are not step functions, but are either rounded or singular. Mahan¹ has shown that the many-electron reaction to the sudden creation of a core hole modifies the single-electron spectrum. He found that the spectrum follows a power law near threshold. Nozières and de Dominicis² have shown that the form of the power law is

$$\sigma_l(\epsilon) = A_{l+1}(\epsilon) |(\epsilon - \epsilon_{\text{Th}})/\xi|^{-\alpha_{l+1}} + A_{l-1}(\epsilon) |(\epsilon - \epsilon_{\text{Th}})/\xi|^{-\alpha_{l-1}}, \quad (1)$$

where l is the angular momentum of the core level, ϵ_{Th} is the threshold energy, dipole selection rules require transitions where l changes to $l \pm 1$, ξ is a cutoff energy, and the $A_{l \pm 1}(\epsilon)$ are the single-particle spectra. They found that the exponents have the form

$$\alpha_l = 2\eta_l(\epsilon_F)/\pi - \alpha, \quad (2)$$

$$\alpha = 2\sum_l (2l+1) [\eta_l(\epsilon_F)/\pi]^2, \quad (3)$$

where $\eta_l(\epsilon_F)$ is the phase shift for an electron at the Fermi level with angular momentum l scattered by the screened core hole potential turned on when the core hole is created.

Much work has been done to test these predictions both experimentally and theoretically. However most of the emphasis has been on pure metals. It first appeared that the many-body effect could explain both the suppression of the K edges and the enhancement of the $L_{2,3}$ edges seen in these metals.³⁻⁶ These exponents, which are often extracted from the data using the assumption that

the many-body effects make the major contribution to the structure near the edge, are sometimes inconsistent with restrictions placed on them by the Friedel sum rule⁷ and by other physical constraints.⁸ Reliable values for the exponents can be extracted from the data only after careful consideration of the effects of lifetime broadening, phonon broadening and matrix element energy dependence. When such determinations are made the exponents are in better agreement with the theoretical predictions⁹ and the restrictions imposed by the Friedel sum rule.

Because it is hard to account for the contributions of these effects, it is important that other systems, besides the simple metals, be tested to see if many-body predictions are compatible with experiments. Recently, Flynn and co-workers have made an extensive study of the x-ray absorption spectra of negative halide ion impurities¹⁰ and rare-gas impurities^{11,12} in alkali metals. Although they did not extract exponents from the absorption spectra of the halide impurities, their experimental curves show little or no enhancement in the spectra at threshold. Since the ground state of each of these systems is a singly charged negative halide ion, the excited state has one outer-shell p electron removed. Dipole selection rules require that the transition be to an s or d state. α_2 is expected to be negative since d phase shifts are much smaller than s phase shifts. Since $A_0(\epsilon)$ and $A_2(\epsilon)$ are about the same near threshold in metals, one assumes that the structure seen near threshold is an indication of the value of α_0 . A spectrum with no enhancement indicates that α_0 is nearly zero. If we use Eqs. (2) and (3) and assume that the s

and p phase shifts exhaust the Friedel sum, then α_0 is zero if

$$\eta_1 \approx 2\eta_0 \approx \pi/7$$

or

$$\eta_1 \approx -2\eta_0/13 \approx -\pi/7.$$

The first case violates the intuitive notion that s phase shifts should be as big or bigger than other phase shifts,¹² and the second case violates the idea that phase shifts for an attractive potential should be positive. Edge exponents were extracted from the data for the rare-gas impurities. A strong rounding of the edges was seen, and it was found that $\alpha_0 \approx -1.0$. Using the same assumption as for the halide impurities, this requires that

$$\eta_1 \approx -\eta_0/5 \approx -\pi/4$$

or

$$\eta_1 \approx -\eta_0 \approx \pi/4.$$

As before, these values do not conform to the expected behavior of the phase shifts. It appears that the many-body effects can not account for the observed exponents without using unrealistic phase shifts.

The phase shifts of the screened core hole potential are the differences between the phase shifts for scattering in the system with and without the core hole.¹³ In simple metals the phase shifts of the screened core hole potential are determined by taking the differences between the phase shifts for scattering due to the screened potentials of a positive ion with and without a core hole. However, for negative halide ion impurities the differences are between the phase shifts for the screened potentials of a negative ion and a neutral ion. Similarly, for the rare-gas impurities the differences are between the phase shifts for a screened neutral ion and a screened positive ion. The screened potentials of negative and neutral ions have repulsive barriers. Because these potentials differ from those of positive ions we should not assume that the phase shifts for the impurity systems are similar to these of the simple metals. For the impurity systems the phase shifts needed to explain the observed x-ray edge exponents may actually be realistic phase shifts.

To test this idea we have studied three impurity systems: F^- in Na, F^- in K, and Ne in K. Of these the only one studied by Flynn is F^- in K. His work dealt mostly with heavier rare-gas and halide impurities. We study these lighter impurities because they are similar to the pure metals we have already studied.^{9,14} Since Flynn found that the exponents of all the halide impurities were similar and that the exponents of the rare-gas impurities

were also similar, we expect his results to apply to our systems as well. The model we use is fully described in Refs. 9 and 14, hereafter referred to as I and II, respectively. Here we give only a brief description. We treat the host alkali metal as jellium with a uniform positive background, instead of a periodic lattice of metal ions, and a band of conduction electrons. The impurity ion is placed in a spherical cavity made in the positive background. Since the radius of this cavity is assumed to be the Wigner Seitz radius (R_{WS}) of the host metal, the impurity ion replaces one host ion. It is possible that the impurity ion could sit in an interstitial position rather than vacancy. Similar calculations^{15,16} have been done for H, He, and Li impurities in metals. It is found that the induced charge density is different for impurities in interstitial positions and vacancies. Unfortunately, there is no experimental evidence which determines the position of the rare-gas or halide impurities.

To study absorption we must describe states where the ion has a filled $2p$ shell (F^- or Ne) and where the ion (F or Ne^+) has a $2p$ hole. We use the density functional approach of Hohenberg and Kohn¹⁷ to obtain a single-particle equation which is corrected so that self-interaction effects are treated properly. This is solved self-consistently for both the ground-state and excited-state configurations. In each case wave functions for both the electrons bound to the impurity ion and the electrons in the conduction band are found. These are used to construct charge densities and potentials for the system. We also calculate threshold energies. These are the differences between the energies of the self-consistent ground states and final states.

We calculate the absorption cross sections using the single-electron expression for the cross section (see I or II). We calculate these cross sections using two different approximations. In the ground-state approximation we assume that the excited electron leaves the ion quickly before there is any relaxation and so can be described by a ground-state wave function. In this case the perturbation of the core hole on the excited-state wave function is ignored. Calculations of absorption cross sections done using states determined from a band-structure calculation implicitly make this assumption when using ground-state wave functions for both the core and the excited electron. In the excited-state approximation we assume that the excited electron leaves slowly and must be described by a final-state wave function. In this case the perturbation of the screened core hole on the excited-state wave function is included. We must make these approximations because, by

TABLE I. Free-ion threshold energies for photoionization of an outer p electron. The experimental values E_{exp} are from the work of Moore (Ref. 18) and Ref. 19.

Ry	F ⁻	Ne	Na ⁺	K ⁺
E	0.24	1.59	3.48	2.32
E_{exp}	0.26	1.58	3.48	2.34

using the single-electron expression for the cross section, we can not treat properly the effect of the time-dependent response of the conduction electrons to the creation core hole on the excited-electron wave function. In I we found the excited-state approximation to be better near threshold and the other approximation better far from threshold. Since neither approximation is obviously better for all energies we present the results for both.

In Table I we show some of the results of calculations we have done for free ions with filled $2p$ or $3p$ shells. More of these results are described in I and II. In all cases the calculated threshold energies are close to the experimental values. It is extremely important that we make the self-interaction correction when determining bound states (see I and II). Without this correction we can not find a self-consistent solution for the F⁻ ion because the $2p$ electron is not bound. The same result²⁰ has been found when other approximations are used for the exchange functional of the density functional method. As shown in I we also obtain good agreement with experiment for our calculation of the x-ray absorption of Ne atoms. This gives us confidence that we can describe x-ray transitions of ions with filled $2p$ shells.

We attempted to find self-consistent solutions for both the ground state and the excited state for each impurity system. Self-consistent solutions for the states with charged impurity ions and for F in Na were easily obtained. However, we could not find self-consistent solutions for the neutral impurities in K. As a consequence, our results are not complete. We can not calculate threshold energies for F⁻ in K or Ne in K, and we can calculate a cross section for F⁻ in K only in the ground-state approximation and for Ne in K only in the excited-state approximation.

When a F⁻ ion replaces a Na⁺ or K⁺ ion two extra charges are introduced into the system. To preserve charge neutrality the conduction band must lose two electrons and there should be little conduction charge near the negative ion. Similarly, the neutral ion introduces one extra charge and the conduction band must lose one charge.

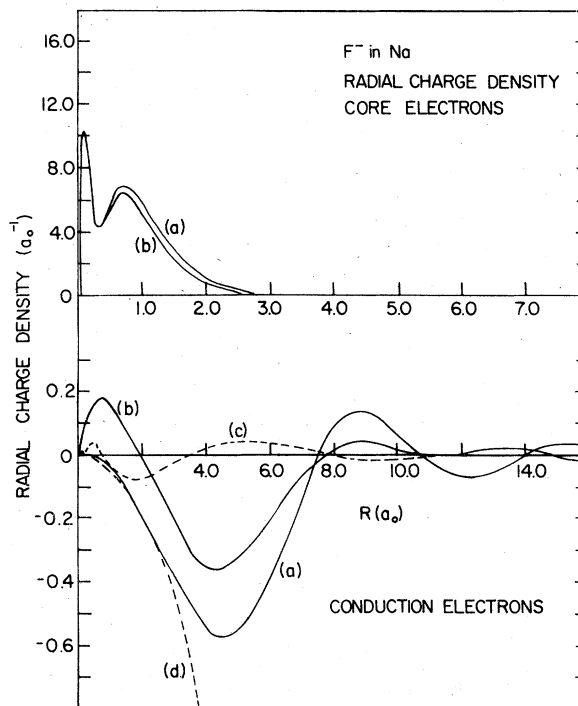


FIG. 1. Radial charge density of the core electrons and the excess conduction electrons for impurities in Na: (a) F⁻ in Na and (b) F in Na. The dashed lines are (c) the excess conduction charge around a Na⁺ ion and (d) the excess charge density if there were no conduction electrons in the Wigner Seitz sphere. R_{WS} is $3.94 a_0$.

For Ne⁺ in K no extra charge is added so there should be little perturbation of the band. These expectations are borne out in Figs. 1 and 2, where the radial charge densities of bound and conduction electrons (with the density of the unperturbed band subtracted out) are shown. When an F⁻ ion is placed in the metal the conduction charge is pushed almost completely out of the cavity. The charge begins to build up only near the edge of the cavity. Note that large perturbations of the conduction charge extend to about two R_{WS} . In pure metals the screening is almost complete after R_{WS} since only one charge must be screened. When an F⁻ impurity is present two charges must be removed so the perturbation is much bigger. The perturbation is larger for F⁻ in Na than for F⁻ in K because the electron gas of Na has a higher density. When an F ion is placed in Na the conduction charge density in the cavity increases near the center. This increase is due to the charge that wants to refill the $2p$ hole. Further from the center there is a deficit of charge to insure that one electron is taken from the conduction band. Finally, for Ne⁺ in K there is little perturbation of the conduction charge density. It looks like the perturbation when the K⁺ ion is placed in the vacancy.

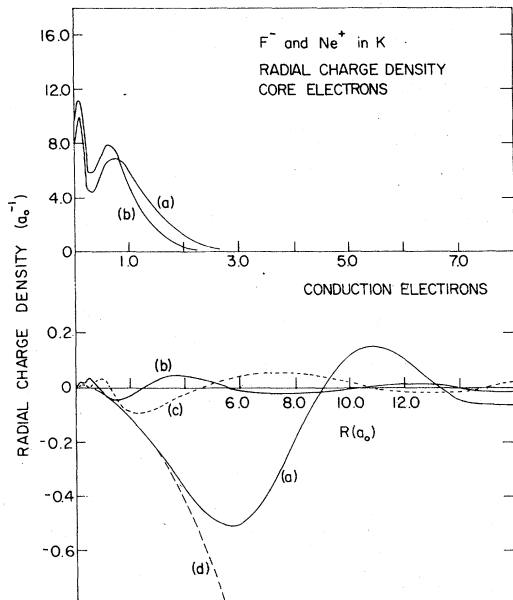


FIG. 2. Radial charge density of the core electrons and the excess conduction electrons for impurities in K: (a) F^- in K and (b) Ne^+ in K. The dashed lines are: (c) the excess conduction charge around a K^+ ion and (d) the excess charge density if there were no conduction electrons in the Wigner Seitz sphere. R_{WS} is $4.86 a_0$.

Only the phase of the Friedel oscillations is changed.

Since we have self-consistent solutions for the ground state and the final state of only F^- in Na, it is the only system for which a threshold energy was determined. We found that the threshold for ionization of a $2p$ electron was 0.113 Ry. This is much less than the value of 0.56 Ry found by Flynn for F^- in K. It is not clear why we should have a large discrepancy since our threshold calculations for pure metals in I and II are much more accurate. Because our threshold is less than that for free F^- ions we would expect the difference to be due to relaxation of the electron gas around the core hole. However, we must also include the work to get the excited electron away from the F^- ion. The conduction charge plus the background can be crudely treated as a shell of positive charge surrounding the F^- ion to neutralize the extra charge originally there. It takes work to move an electron from the center of that shell out to infinity. As a simple calculation of the electrostatic energy shows,²¹ it takes more energy to move the electron to infinity than is gained from the relaxation of the conduction charge around the core hole. For that reason the threshold of F^- in an alkali is actually higher than the threshold for free F^- .

To calculate the x-ray edge exponents we need

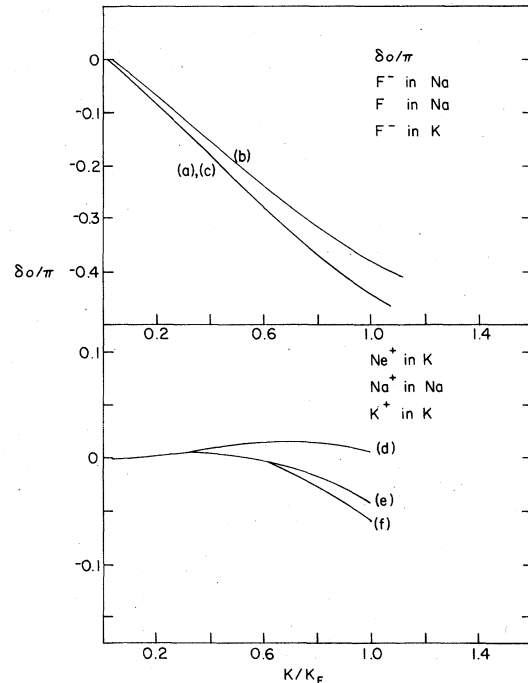


FIG. 3. S phase shifts as a function of wave vector for: (a) F^- in Na, (b) F in Na, (c) F^- in K, (d) Ne^+ in K, (e) Na^+ in Na, and (f) K^+ in K.

the phase shifts for scattering from the screened core hole. As mentioned before, these phase shifts are the differences between phase shifts for scattering in the systems with and without the core hole. In Table II and Figs. 3 and 4 we show the phase shifts for the different impurities. A comment should be made about the normalization of the phase shifts. In the table the number of factors of π indicates the number of extra nodes in the wave function relative to an unperturbed wave function. In the figures the phase shifts are normalized to zero at zero momentum. S waves have two extra nodes around a F^- , F , Ne^+ , or Na^+ ion. They have this $3s$ character since these ions have filled $2s$ shells and empty $3s$ shells. Since there are no filled d shells the d wave functions have no extra nodes. The interesting behavior occurs for the p electrons. In the pure metals they have the expected number of extra nodes. However, for the F^- impurities there are no extra nodes although you would expect one when the $2p$ shell is filled. Similarly for F in Na there are no extra nodes in the p waves. Because we make the self-interaction correction for bound states, the potentials used in the single-particle equation to find bound states differ from the potential used to find conduction states. For that reason the conduction levels need not have nodal structure different from that of the bound levels. Because the potentials

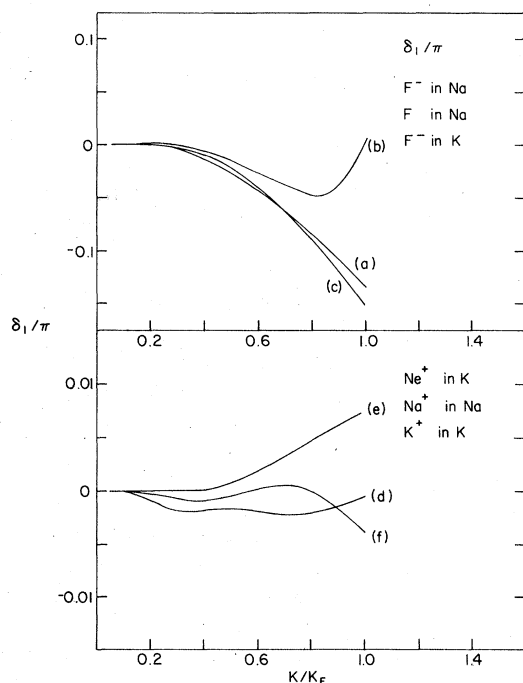


FIG. 4. P phase shifts as a function of wave vector for: (a) F^- in Na, (b) F in Na, (c) F^- in K, (d) Ne^+ in K, (e) Na^+ in Na, and (f) K^+ in K.

used to find the conduction states (see Fig. 5) have repulsive barriers in the region where the centrifugal barrier is no longer dominant, the potentials can not induce the extra node. For Ne^+ in K the potential has no barrier and the p waves have the extra node.

There are several things to be noted about the variation of the phase shifts with momentum. First, the phase shifts for F^- impurities in Na and K are very similar. This supports our earlier assumptions that Flynn's results for F^- in K would be similar to our results for F^- in Na and that the scattering would depend mainly on the impurity

and not the host metal. Second, δ_0 for the F^- and F impurities and δ_1 for the F^- impurities are large and negative. This happens because at large distances the F^- and F impurities have repulsive barriers and because the Friedel sum rule

$$Q = (2/\pi)\sum_l(2l+1)[\delta_l(\epsilon_F) - \delta_l(0)]$$

must be satisfied with Q equal to -2.0 for F^- impurities and equal to -1.0 for F impurities. (A measure of the self-consistency of our calculations is that the Friedel sum rule is satisfied to five decimal places by the calculated phase shifts.) Third, the phase shifts for Ne^+ in K are very small because there is no extra electron added to the system when a Ne^+ ion is substituted for a K^+ ion.

As mentioned before, the p phase shifts for F^- impurities are large and negative because they must help exhaust a Friedel sum of -2.0 and because the potential has a repulsive barrier. Unlike the p phase shifts of F^- in Na, the p phase shifts for F in Na decrease only until $0.8k_F$. At that momentum the kinetic energy is equal to the barrier height and the p phase shift begins to increase with momentum. Until $0.8k_F$ the difference between the phase shifts for F in Na and the phase shifts for F^- in Na is greater for s waves than for p waves. However, once the p phase shift of F in Na starts increasing, the difference in p phase shifts becomes larger. This is crucial since it explains the small observed value of α_0 . Using the phase shifts, we determine α_0 to be almost zero in agreement with experiment and we find that $[\eta_1$ is the difference between $\delta_l(\epsilon_F)$ for excited and ground states]

$$\eta_1 \approx 2\eta_0 \approx \pi/7.$$

For simple metals these phase shifts would be unrealistic; however, for systems with anomalous features such as potential barriers these phase shifts are reasonable. The potential barrier es-

TABLE II. Phase shifts and Friedel sums for various states and x-ray exponents for F^- in Na. δ_l is the phase shift at zero wave vector. $\Delta\delta_l$ is the change between phase shifts at the Fermi level and zero wave vector. FS is the Friedel sum.

	δ_0	$\Delta\delta_0$	δ_1	$\Delta\delta_1$	δ_2	$\Delta\delta_2$	FS
F^- in Na	2π	-1.389	0.0	-0.424	0.0	-0.091	-2.000 01
F in Na	2π	-1.200	0.0	0.008	0.0	-0.078	-1.000 00
Na ground state	2π	-0.130	π	0.023	0.0	0.013	0.000 00
F^- in K	2π	-1.409	0.0	-0.466	0.0	-0.077	-2.000 00
Ne^+ in K	2π	0.017	π	-0.002	0.0	-0.002	0.000 00
K ground state	3π	-0.181	2π	-0.013	0.0	0.044	0.000 00
x-ray edge exponents	α	α_0	α_1	α_2			
F^- in Na	0.122	-0.001	0.153	-0.113			

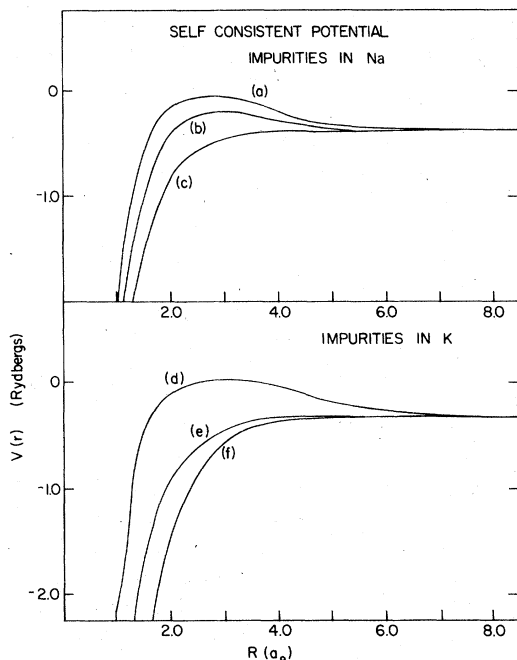


FIG. 5. Self-consistent screened potentials for: (a) F^- in Na, (b) F in Na, (c) Na^+ in Na, (d) F^- in K, (e) Ne^+ in K, and (f) K^+ in K.

essentially determines the s phase shift because the s phase shifts change very little when the core hole is created. However, p electrons are excluded from the region near the core by the centrifugal barrier and should be less sensitive to the presence of the potential barrier. In fact, inspection of Fig. 5 shows that the range of the screened core hole potential for F^- in Na [the difference between curves (b) and (a)] extends beyond the potential barrier. Thus the large response of the p phase shifts to the creation of the core hole is possible. One can adequately test the theory of Mahan, Nozières, and de Dominicis (MND) only if these impurity systems are treated accurately and if the anomalous features are taken into account.

We can not calculate the exponents for Ne in K because we do not find a self-consistent solution for the ground state. If we assumed that the phase shifts for Ne in K were similar to those for F in Na, we would still be left with a problem. The p phase shifts for the final state would have an extra factor of π . It is not clear from the original derivation² of the forms for α and α_l , what the normalization for the η_l should be. If we used the prescription of Combescot and Nozières,²² then the absorption spectra would be rounded when there is a bound state in the l channel of the outgoing electron. Even if we considered this extra factor of π to be indicative of a bound state, it would not be in the channel of the outgoing elec-

tron (which must be the s or d channels) since the bound state would occur in the p channel. However, a bound state has negligible overlap with a conduction electron, in the limit of large volume, since the conduction-electron wave functions must be normalized as $V^{-1/2}$, where V is the volume of the system. If there were a bound state in the p channel then there would be little overlap of this bound state with the ground-state conduction electrons. This could explain the larger suppression seen in the cross section. If this extra factor of π did not indicate a bound state but were just a signature of the number of nodes in the wave functions for conduction electrons, then it would still be true that the overlap between p electrons in the excited state and p electrons in the ground state should be less than if there were no extra node in the final state. In either case the threshold spectrum would be suppressed.

The ambiguity in the normalization of the p phase shifts for systems with neutral impurities is related to the difficulties we have in obtaining self-consistent solutions for these systems. In the standard iteration procedure used to get self-consistency an initial potential is used to calculate wave functions and generate a new potential. An average of these two potentials is then used as the next starting potential. This procedure is repeated until the two potentials of a given step agree. For F in K and Ne in K this iteration procedure breaks down. Our calculation converge toward unstable solutions rather than stable ones. The iteration procedure generates two types of potentials. Either the potentials are deep and generate p wave functions which have an extra node, or they are shallower and generate a strong resonance in the p conduction band. The resonance occurs when the potential becomes so shallow that the $2p$ level would not be bound if we did not make the self-interaction correction. The low-energy p conduction states then do not have an extra node. However, the potential is sufficiently attractive so that the high-energy p states, which can penetrate the repulsive barrier, do have the extra node. Thus we get a resonance in the p band. This does not occur for the F^- impurities or for F in Na because the high-energy p states do not have the extra node either. If the first type of potential is used as an initial potential, then the iteration procedure converges toward the second type of potential. This shallower potential does not produce a stable solution because the virtual bound p state in the conduction band must be filled with too many electrons. The filling of this resonant level greatly modifies the potential so we can not obtain self-consistency. We can not start the iteration procedure with the second type of potential

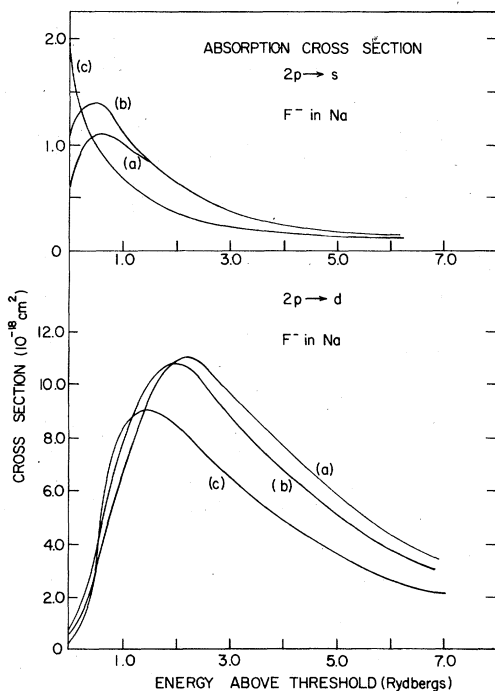


FIG. 6. Absorption cross sections for F^- in Na: (a) ground-state approximation, (b) excited-state approximation, and (c) absorption for free F^- ions using the excited-state approximation.

just because it is unstable. Although we can not find a self-consistent solution for Ne in K and thus can not calculate α_0 , our difficulty in getting a self-consistent solution suggests that this ground state is more complicated than originally assumed. The MND theory needs to be extended to include this possibility of a resonant p level in the conduction band before a comparison with the experimental results is made.

The calculated absorption cross sections are shown in Figs. 6 and 7. Since we did not obtain reasonable threshold energies, we have used the experimental value of 0.56 Ry for F^- in K. For F^- in Na we have used a slightly lower value of 0.54 Ry as suggested in Ref. 21. For Ne in K we assume that the threshold is 1.00 Ry after seeing how the threshold energies of Kr and Xe decrease when they are placed in K.¹¹ Near threshold the cross sections are uncertain by less than 15% due to the uncertainty in the threshold energy. At higher energies the uncertainty in the threshold energy is much less important. As mentioned before, the cross section for F^- in K is calculated only in the ground-state approximation and for Ne in K only in the excited-state approximation, since the other approximations correspond to the states for which we did not find self-consistent solutions.

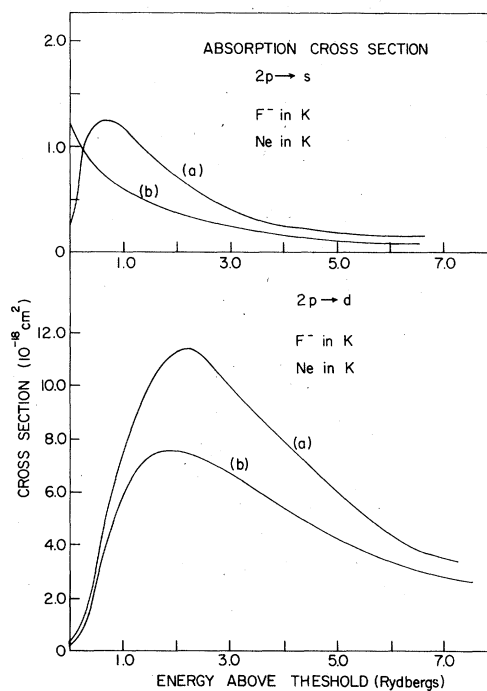


FIG. 7. Absorption cross sections for impurities in K: (a) F^- in K and (b) Ne in K.

In Fig. 6 we compare the results for free F^- ions and for F^- in Na. Near threshold the $2p$ to s cross section for free F^- ions increases with decreasing energy. When F^- is placed in Na the cross section is suppressed near threshold. The self-consistent potentials for F^- and F in Na have repulsive barriers. This prevents low-energy s electrons from overlapping the core electrons and suppresses the $2p$ to s transition. For F in Na this barrier is not due to the potential of F (because it is neutral), but rather it is caused by the conduction electrons which are not completely excluded from the central cavity. For free F^- ions there is no suppression in the excited-state cross section since there is no barrier in the final-state potential. Likewise, there is no suppression of the excited state s cross section for Ne in K. The other trends seen in the results are typical of the results seen in I for pure metals.

The cross sections for F^- and Ne impurities in K are of comparable size, whereas Flynn observes that the rare-gas impurities have much smaller cross sections than the halide impurities have. Since we use a single-particle matrix element and the golden rule to calculate the cross sections, we ignore the overlap of the other electrons. It is possible that the small overlap due to the possible bound or virtual states discussed earlier explains why the rare-gas impurity cross sections are so much smaller. However, our cal-

culated F^- in Na and F^- in K cross sections are much smaller than the measured ones. Since the values are supposed to be absolute cross sections it is not clear where this enhancement comes from. It is hard to believe that the experimental values are that much larger than values calculated for free F^- ions and F^- in K.

In this paper we have discussed the properties of halide and rare-gas impurities in alkali metals. The behavior seen by Flynn for the x-ray edge exponents was thought to throw doubt on the MND theory. However, one can not rely too much on the experience gained from considering the pure metals when trying to understand the exponents for these impurity systems. The negative and neutral ion impurities are different because their self-consistent potentials have large repulsive barriers. The phase shifts calculated for the halide impurities may not be considered reasonable when compared to the phase shifts of the pure metals, but they do explain the small enhancement

in the edge spectra of these impurities. We can not make a definitive conclusion about the α_0 for the rare-gas impurities because we did not find the necessary self-consistent ground states. However, our difficulty in finding these solutions suggests that these ground states may be more complicated than originally assumed, having a resonant p level in the conduction band. The MND theory should be extended to include these effects before it is tested by the results for the rare-gas impurities.

ACKNOWLEDGMENTS

The author is grateful to Dr. Mahan for suggesting this problem. The author would like to thank Dr. S. Lundqvist and the Institute of Theoretical Physics for their hospitality during his stay at Chalmers University of Technology. This research has been supported by the NSF under Grant No. NSF-DMR77-11305.

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