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[1]A preliminary account has already appeared: R. A. B. Devine and J. S. Helman, Bull. Am. Phys. Soc. 15, 762 (1970).
[2]J. S. Helman, Phys. Kondensierten Materie 6, 297 (1967).
[3]R. A. B. Devine and R. Dupree, Phil. Mag. 21, 787 (1970); 22, 657 (1970).
[4]J. R. Asik, M. A. Ball, and C. P. Slichter, Phys. Rev. 181, 645 (1969).
[5]A system of units is used in which $\hbar = 1$.
[6]T. E. Faber and J. M. Ziman, Phil. Mag. 11, 153 (1965).
[7]For instance, see L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1955).
[8]S. Doniach and S. Engelsberg, Phys. Rev. Letters 17, 750 (1966).
[9]W. F. Brinkman and S. Engelsberg, Phys. Rev. Letters 21, 1187 (1968).
[10]T. M. Rice (private communication).
[11]L. Liu, Phys. Rev. 126, 1317 (1962).
[12]F. Herman, C. D. Kuglin, K. F. Cuff, and R. L. Kortum, Phys. Rev. Letters 11, 541 (1963).
[13]N. W. Ashcroft and D. C. Langreth, Phys. Rev. 156, 685 (1967).
[14]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

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Spin Relaxation of Conduction Electrons in Liquid Metal Alloys. II. Sodium-Potassium

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The results of conduction-electron–spin-resonance (CESR) measurements on liquid sodium-potassium alloys over the whole range of concentrations are presented. The experimental results are compared with the predictions of the theory proposed in Paper I, and with those of other theories which are valid in the low-concentration limit only. The possible errors introduced by using theoretical hard-sphere structure factors in the calculation are estimated. The relaxation time (RT) derived from the CESR linewidth exceeds the theoretical spin-lattice RT by a factor $\cong 1.85$ for all concentrations. This difference is attributed to the exchange enhancement of the conduction-electron spin lifetimes. An upper bound for the exchange-enhancement factor κ_0^2 is determined. The theory in I may also be used to calculate the contribution of vacancies to the spin relaxation of the pure metal. The results show that this effect is negligible at equilibrium vacancy concentrations.

I. INTRODUCTION

Conduction-electron spin resonance (CESR) in alloy systems has been little studied to date in either the solid or liquid phase. Most of the work reported has been involved with very dilute alloys of polyvalent impurities in monovalent hosts, the most extensive being that of Asik, Ball, and Slichter.[1,2] The work of these authors has been with lithium and sodium host metals in the solid phase and they have developed and applied two theories in an effort to explain their experimental results. As mentioned in the preceding paper[3] (henceforth I), these theories are only applicable to the dilute-alloy limit or what we may term the "initial-slope" behavior.

The results of Asik, Ball, and Slichter demonstrate the strong spin scattering produced by various heavy impurities in sodium and lithium, so large that only a fraction of one percent of impurity could be used before the resonance signal became unobservable above the detector noise in the system. To study an alloy system across the complete range of alloy concentration, one clearly requires alloys where the increased spin scattering produced by alloying is not negligible but is not sufficient to

cause loss of signal below resolution capability. CESR has been observed in so few pure metals that the choice of suitable alloying candidates is very restricted and one finds after some considerations that lithium, sodium, and potassium are perhaps the best metals to choose. However, these metals do not alloy totally in the solid state and one is forced therefore to consider liquid-phase measurements. The observation of resonance in all three of these metals in the liquid state has been reported,[4-6] although in the case of lithium, in both solid and liquid phases, the observed relaxation times have always been at least ten times shorter than the calculated intrinsic value due to the presence of impurities which could not be readily removed. As a further consideration, the alloy-phase diagram for lithium with sodium or potassium shows a temperature-dependent-solubility-limit behavior even in the liquid phases of the alloys.[7] One therefore concludes that the most viable system in which to study CESR over the whole range of concentrations is the liquid sodium-potassium system.

This paper reports the results of measurements made upon the liquid Na-K system at 383 °K over the whole range of alloy concentrations. The system has been studied before[8] but only in the dilute-potassium limit (less than 10 at. % K in Na). The results of the previous workers were fitted to a law of the form

$$\Delta H_{\mathrm{LIQ}} = AT + BTC_1 + DC_1 + E \ ,$$

where ΔH_{LIQ} is the resonance linewidth and C_1 the potassium concentration. Using values for A, B, D, and E quoted by the authors, one finds a linear increase in resonance linewidth with impurity concentration of the order of 15 G/at%.

In Secs. II-IV the experimental details and results are outlined and comparison is made between the measured alloy behavior and that calculated using the theory presented in I. It has been found that the theory may also be used to calculate the effects of vacancies upon the conduction-electron spin-relaxation rate in pure metals. The mode of calculation is outlined in the Appendix and some results for sodium at 40 and 383 °K are presented, these leading to the conclusion that vacancies have negligible effect on the spin relaxation in pure metals at any temperature.

II. EXPERIMENTAL DETAILS

The purest available sodium (99.99 at. %) and potassium (99.98 at. %) was used in all of the experiments. Two different sample preparation techniques were used, one for low concentrations of K in Na and one for high concentrations and potassium-rich alloys.

For the low concentrations of potassium in sodium the most satisfactory technique of sample preparation was found to be by vacuum alloying and injection into a sample tube under vacuum. Trials with pure sodium indicated that little or no additional impurity was introduced into the sample when using this preparation process. The method of production of a given sample was to melt the requisite amounts of sodium and potassium together in an evacuated Pyrex assembly at a temperature in excess of 150 °C. After permitting at least $\frac{1}{2}$ h for homogenization in the molten state, the liquid alloy was subjected to an over pressure of dried argon gas which forced it through a Pyrex sinter into an evacuated sample tube, producing a solid column of alloy 3–4 cm long and $\frac{1}{3}$ cm diam. After this process the space above the alloy in the sample tube was evacuated and subsequently filled with dried paraffin oil to protect the alloy surface from the corrosive effects of the atmosphere.

The second method of sample preparation, necessary for medium- and high-concentration alloys, was used to increase the effective volume of sample subjected to the microwave field, and hence the signal-observed-to-noise ratio. High-concentration alloys of the solid column type demonstrated a poor signal-to-noise ratio. The requisite amounts of sodium and potassium were alloyed under paraffin oil in a test tube at 250 °C, time being allowed for homogenization after the molten pools of Na and K had coalesced. After the homogenization period the test tubes were "corked" and shaken violently to produce a colloidal dispersion of the alloy in the paraffin oil, the colloids having diameters of the order of $\frac{1}{10}$ mm. After solidification the colloids were sucked into a hypodermic syringe and then "injected" into a sample tube containing dried paraffin oil. Some of the alloys were liquid even when cooled to room temperature; in this case the alloy was sucked into the syringe and injected into the sample tube without undergoing the vibration to produce the colloid suspension. Colloids could be produced in the sample tube itself by agitating the liquid column with a quartz rod. It should be noted that when the samples were reheated to 383 °K, well into the molten state, sufficient surface oxidation was present on the spheres to prevent them from coalescing into a molten column.

The spin-resonance measurements were made on a commercially available spectrometer operating at 9.27 GHz; this system has been described previously.[5] It should be mentioned that measurements made upon samples heated for less than $\frac{1}{2}$ h produced anomalous results due to inhomogeneity of the alloys; this period at least was necessary in order for them to reach the homogeneous liquid state.

The method of extraction of the spin-relaxation

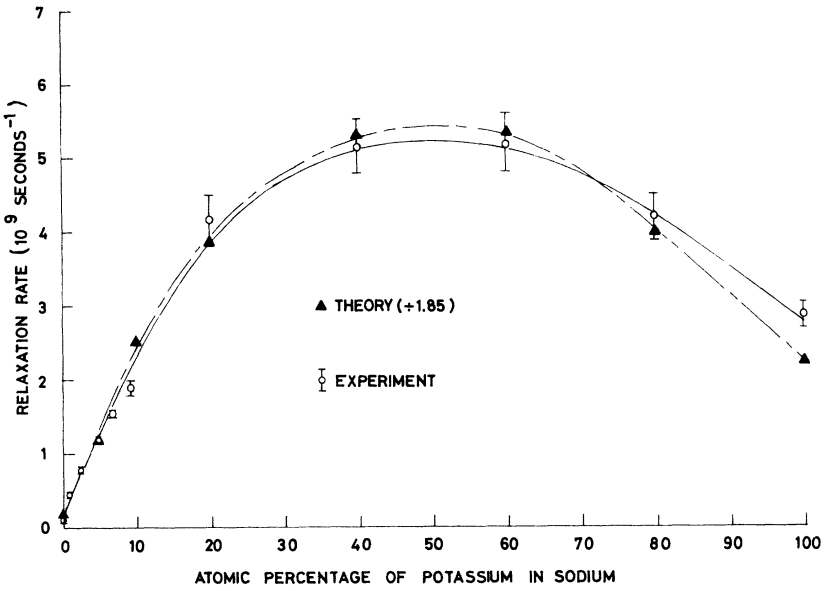

FIG. 1. Experimentally determined and calculated spin-relaxation rates in the liquid Na-K alloy system at 383 °K. (The theoretical results, appropriate to α equal to 0.85, have all been divided by 1.85).

time (T_1) from an experimentally observed resonance plot has been outlined in Ref. 5. No attempt was made to measure either the absolute values of the resonance g factor or the variation in g shift with alloy concentration since the resonance lines were too broad to permit any accurate assessments.

III. EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY

A. High-Concentration Alloys

Measurements have been made of CESR linewidths in liquid-phase alloys of sodium with potassium at 383 °K over the whole range of alloy concentrations. The relaxation rates deduced from the measured linewidths are shown in Fig. 1. It should be noted that the accuracy for the broad resonance lines (large $1/T_1$) is relatively poor due to the signal-to-noise ratio obtained and the presence of a nonlinear background resonance in the sample cavity. The errors presented, however, represent the standard deviation of five measurements at each concentration value (errors induced in conversion to relaxation rates included). The pure potassium and pure sodium results have been taken from previous publications.[5,6]

Calculations have been made of the spin-lattice relaxation rates in alloys at concentrations where experimental measurements were made, using Eq. (21) of I. The requisite binary-alloy structure factors were calculated assuming the hard-sphere model equations given by Ashcroft and Langreth.[9] Data for the structure-factor calculations were taken from Paper II of Ashcroft and Langreth,[10] i.e., packing fractions for the pure metals and ion core radii. Calculation of the radial integrals involved in Eq. (21) of I was performed using the Hartree-Fock-Slater wave functions for the filled ion core shells and the potentials as tabulated by Herman and Skillman.[11]

The calculated relaxation rates $1/T_1$, multiplied by a factor $\frac{1}{1.85}$ to obtain a fit with the experimental values, are shown in Fig. 1. According to Eq. (23) of I, the factor $\frac{1}{1.85}$ is to be interpreted as an upper bound for the exchange enhancement factor κ_0^2, although small variations of κ_0^2 are expected as a function of the composition of the alloy. A more complete discussion of the possible errors involved in the determination of the upper bound of κ_0^2 is given in Sec. IV.

The theoretical values of $1/T_1$ were obtained using a hard-sphere diameter ratio $\alpha = 0.85$.

The results of Ashcroft and Langreth[10] for the resistivity of Na-K alloys demonstrated that the best fit between theory and experiment could be obtained when the structure factors were calculated using $\alpha = 0.75$. In order to assess the importance of this parameter in the case of spin relaxation, calculations were performed using the structure factors obtained with α in the range 0.75–0.95. The ratio of the calculated to the measured relaxation rates are given as a function of α in Table I. It can be seen that the ratios do not vary systematically with the concentration; in general, however, the smallest values are found when α is taken between 0.80 and 0.85. This coincides with the value of α obtained considering the ratios of atomic volumes,[12] i.e., 0.823. In fact, the ratio of atomic volumes obtained assuming $\alpha = 0.75$ is 2.37, whereas according to Freedman and Robertson the volume ratio is 1.79. This might suggest that the results obtained by Ashcroft and Langreth for the

TABLE I. Ratio of calculated to measured relaxation rates in Na-K alloys as a function of the hard-sphere diameter ratio α.

Conc. of K (at. %)	α = 0.75	0.80	0.85	0.90	0.95
10	2.39	2.30	2.34	2.67	2.90
20	1.85	1.74	1.71	1.77	1.88
40	2.55	2.04	1.92	1.99	2.12
60	2.12	1.93	1.89	1.95	2.06
80	1.74	1.73	1.74	1.78	1.85

resistivity were a compromise between the form of the pseudopotential used and the form of the structure factors.

B. Low-Concentration Alloys of Potassium in Sodium

Results for the low-concentration limit of potassium in sodium alloys have been reported recently.[13] It is of interest to compare the results of the theory proposed in I with those of the "initial slope" theories in this region. The latter have been applied previously to the sodium-potassium system[13] with some success. One of the conclusions reached, however, was that it is important to include the effects of atomic volume differences. This of course we do in I by using partial structure factors.

There are two possible treatments we may adopt when using the theory proposed in I; one is to calculate using the full theory and the other, to calculate using a modified form of the complete theory which enables us to assess only the initial slope $[d(1/T_1)/dc]$ and not the absolute values of the relaxation rates in each alloy. In the latter case we assume that the structure factors of the alloy are all equal and given by the host-metal structure factor, i.e.,

$$S_{\mathrm{NaNa}} = S_{\mathrm{KK}} = S_{\mathrm{KNa}} = S_{\mathrm{Na}} = S \ ,$$

where S is defined in Eq. (22) of I. This amounts to assuming a substitutional model for the alloy, where an impurity of equal volume to a host ion directly replaces it in the lattice. It was stated previously that the effects of volume differences are important in calculations for sodium-potassium alloys; it is therefore of some interest to develop the initial-slope modification and to compare with the results obtained using the full theory. In this way we may obtain some indication of just how important the volume effects can be.

Assuming equality of structure factors in Eq. (21) of I and differentiating with respect to concentration we find, in the limit as concentration is taken to zero, the following expression:

$$\left.\frac{d(1/T_1)}{dc}\right|_{c=0} = \frac{4(2\pi)^3 \rho(E_F) d}{C_{k_F}^2} (\mathfrak{s}_1^{\mathrm{K}} - \mathfrak{s}_1^{\mathrm{Na}})(\mathfrak{s}_1^{\mathrm{K}} - \mathfrak{s}_1^{\mathrm{Na}} + 2S\,\mathfrak{s}_1^{\mathrm{Na}}) \ . \quad (1)$$

Using (1) we may calculate the initial slope behavior in a manner analogous to previous theories where atomic size differences were ignored. The value obtained is given in Table II together with the experimental result and the results obtained using other theories. Also included are the values one obtains using the full theory to calculate the relaxation rate at 1 at. % potassium in sodium and subtracting the calculated value for pure sodium to obtain $d(1/T_1)/dc$. The theoretical values reported in Table II are not corrected for exchange enhancement. One theory used previously enables atomic size differences to be represented as effective valence differences in a phase-shift calculation[13]; its result is contained in Table II.

Three interesting points emerge from a study of the results quoted in Table II. First, the substitutional model modification of the binary-alloy theory does not produce results which compare very favorably with experiment although it does give better agreement than the other two substitutional theories. Second, using the full theory, one obtains by far the best agreement with experiment to date, being better than the phase-shift theory which permitted volume effects to be included. Finally, an analysis of the phase shift and present results indicated that if one ignores volume effects in this alloy system, one tends to overestimate the impurity contribution per at. % by a factor of approximately 2.

IV. DISCUSSION

The results presented in Fig. 1 show that the theory proposed in I is able to reproduce both the absolute value and the concentration dependence

TABLE II. Comparison of results obtained for the "initial" slope $[d(1/T_1)dc]_{c=0}$ for potassium impurities in sodium using various theories. The theoretical values quoted are not corrected for exchange enhancement.

Experiment	Simple[a] OPW	Phase[a,b] shift I	Modified alloy theory	Phase[a,c] shift II	Full theory
$2.6 \pm 0.2 \times 10^8$	15.0×10^8	11.6×10^8	9.3×10^8	7.2×10^8	4.3×10^8

[a]See Ref. 13. [b]Atomic volume differences are ignored. [c]Atomic volume differences are included.

of the relaxation rate, using a reasonable value for the exchange enhancement factor κ_0^2. The best agreement between theory and experiment is found when the hard-sphere ratio α used in the calculation of the alloy-structure factors is close to that obtained from atomic volume data. The pure-metal relaxation rates were calculated using the hard-sphere structure factors given by Ashcroft and Lekner[14] and not the Ashcroft and Langreth forms taken to the 0 and 100% impurity concentration limit (they should, however, reduce to the Ashcroft and Lekner forms at these limits). It has been shown[15] that the use of the available empirical and theoretical structure factors for a pure metal leads to a range of calculated values for $1/T_1$. In sodium this range is 2.33–3.33 $\times 10^8$ sec^{-1} using the model of Ashcroft and Lekner and the results for Gingrich and Heaton, [16] respectively. With the same references the range for potassium is 4.17–7.14$\times 10^9$ sec^{-1}. More recent measurements in sodium[17] suggest that the empirical structure factor is more like that predicted by the theory than the previous ones.

From the uncertainties of the relaxation rates we find that the range of values for the upper bound of κ_0^2 in sodium is $\frac{1}{1.30}-\frac{1}{1.87}$ and in potassium $\frac{1}{1.42}-\frac{1}{2.43}$. As pointed out in I, the value estimated by other means of κ_0^{-2} in sodium is 1.5, which lies within those limits. Our results indicate that κ_0^{-2} in potassium could be larger than in sodium.

The results obtained for the effects of vacancies on the relaxation times in pure metals (see Appendix) are both interesting and reassuring in that one may feel confident that relaxation times measured in pure metals are in fact essentially the pure-metal values and not those "distorted" by vacancy effects. It would clearly be of interest to try to observe the effects of vacancies and confirm or disprove the results suggested by the theory. To do this, one would need to create an extremely nonequilibrium concentration of vacancies and in metals such as sodium and potassium, perhaps the most ideal to study due to their narrow linewidths, this would not be easy. Thin-foil samples of aluminum do, however, present a case where suitable treatment of the samples can produce a significant vacancy density enhancement and this metal might, indeed, be a good candidate for study. It should be further mentioned, in the case of aluminum, that one could expect interesting effects to appear. The term $(1-2S)$ of Eq. (A1) can be positive or negative depending upon the sample temperature. In the liquid phase, and down to about 260 °K, $2S$ is greater than 1 so that vacancies or zero spin-orbit scattering materials (e.g., lithium) should cause the measured relaxation rate to decrease below the pure-metal value. Below 260 °K one would anticipate the opposite effect, so that in going from 300 to 4.2 °K one would expect the impurity-doped sample to have a relaxation rate at first *less* than the pure-metal value but becoming equal and then *greater* than the pure-metal value at low temperatures.

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APPENDIX: TREATMENT OF VACANCIES

The effect of a vacancy on the spin-relaxation time in a pure metal has not been calculated previously to our knowledge. The theory for an alloy system developed in I can be used to treat this case by formulating the problem as for an alloy and then permitting the impurity scattering terms to go to zero.

If we assume that a vacancy can be created without any subsequent contraction or expansion of the surrounding lattice, then the vacancy-host "alloy" structure factors may be taken as equal in the substitutional model. Using Eq. (1), the term s_1^K, which we found for the case of potassium must go to zero for the vacancy since there is no associated spin-orbit coupling. Hence (1) becomes

$$\left.\frac{d(1/T_1)}{dc}\right|_{c=0} = \frac{4(2\pi)^3\rho(E_F)d}{C_{k_F}^2}\,(s_1^{\mathrm{Na}})^2(1-2S)\,. \qquad \text{(A1)}$$

One sees immediately that the effect of vacancies on the spin-relaxation rate is nonzero and positive if $2S<1$. At low temperatures in pure monovalent metals we find that $2S \ll 1$ so that we may approximate (A1) by

$$\left.\frac{d(1/T_1)}{dc}\right|_{c=0} = \frac{4(\pi)^3\rho(E_F)d}{C_{k_F}^2}\,(s_1^{\mathrm{Na}})^2\,. \qquad \text{(A2)}$$

Calculations have been made for sodium at 40 and 385 °K using Eq. (A2), assuming a vacancy concentration of 10^{-4} and 10^{-1} at. %, respectively. At 40 °K the spin-relaxation rate due to equilibrium concentrations of vacancies is 2×10^4 sec^{-1}, which is to be compared with the pure-metal spin-relaxation value of 1×10^7 sec^{-1}. At 385 °K the vacancy contribution is 9×10^6 sec^{-1}, while the pure-metal value is 1.9×10^8 sec^{-1}. Clearly, the effect of va-

cancies is negligible both in the solid and in the liquid state.

The calculations were made explicitly for sodium. In order to obtain a simple and accurate value for other metals at low temperatures, without the problem of detailed knowledge of the solid-phase structure factor, one can use Eq. (A2). This has been done for solid sodium at 40 °K and we find negligible error induced by using (A2) instead of (A1). Calculations for solid copper and solid silver at 40 °K using Eq. (A2) suggest a similar conclusion to that found for Na, namely, that the effect of vacancies is negligible. One may thus conclude that equilibrium concentrations of vacancies present in pure metals have no significant effect on the conduction-electron–spin-relaxation rate.

[1]J. R. Asik, M. A. Ball, and C. P. Slichter, Phys. Rev. 181, 645 (1969).
[2]M. A. Ball, J. R. Asik, and C. P. Slichter, Phys. Rev. 181, 662 (1969).
[3]J. S. Helman and R. A. B. Devine, preceding paper, Phys. Rev. B 4, 1153 (1971).
[4]J. E. Enderby, J. M. Titman, and G. D. Wignal, Phil. Mag. 10, 633 (1964).
[5]R. A. B. Devine and R. Dupree, Phil. Mag. 21, 787 (1970).
[6]R. A. B. Devine and R. Dupree, Phil. Mag. 22, 657 (1970).
[7]M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
[8]N. S. Garif'yanov, B. M. Khabibulin, E. G. Kharakhash'yan, and T. O. Alekseeva, Dokl. Akad. Nauk SSSR 180, 569 (1968) [Sov. Phys. Doklady 13, 451 (1968)].
[9]N. W. Ashcroft and D. C. Langreth, Phys. Rev. 156, 685 (1967).
[10]N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967).
[11]F. S. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).
[12]J. F. Freedman and W. D. Robertson, J. Chem. Phys. 34, 769 (1961).
[13]R. A. B. Devine and R. Dupree, Phil. Mag. (to be published).
[14]N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).
[15]R. A. B. Devine and R. Dupree, Phil. Mag. (to be published).
[16]N. S. Gingrich and Le Roy Heaton, J. Chem. Phys. 34, 873 (1961).
[17]G. Kollmannsberger, G. Fritsch, and E. Lüscher, Z. Physik 233, 308 (1970).

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Pseudopotential Approach for Dilute Alloys. I. Nontransition and Non-Noble Hosts

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The electronic structure of nontransition and non-noble-metal-based alloys including charge and node effects are discussed within a pseudopotential scheme. An equivalent scattering equation for the pseudo-wave-function is obtained in terms of a nonlocal effective impurity potential. Orthogonality requirements with respect to the alloy core states are automatically fulfilled and the effective potential is shown to contain contributions from node and charge effects, whereas the scattering equation is free-electron-like. Finally the several contributions to the charge-density variations are discussed.

I. INTRODUCTION

The impurity problem in metals involves, as is well known, two different aspects. First, one needs a precise description of the electronic structure of the host through a theoretical band calculation. Second, the self-consistent solution of the scattering problem defined by the host-metal Hamiltonian and the impurity potential must be obtained in terms of the parameters characterizing the impurity atoms. These parameters are essentially the charge difference between host and impurity atoms, and the row of the Periodic Table to which the impurity atoms belong. The latter manifests itself through the additional closed shells introduced (or removed) locally in the host by the impurity. The above-mentioned aspects are, in general, quite difficult to handle, although the main difficulty lies in the second one through the definition of the impurity potential and its self-consistent determination. Two limiting situations have been extensively discussed in the literature[1]: the free-electron-like host and the tight-binding (transition-metal) host. In the first case, accurate solutions of the scattering problem using model potentials (such as the square well) show considerable success in describing situations where the important parameter associated with the impurities is the