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OPTICAL ABSORPTION OF DILUTE SOLUTIONS OF METALS
IN MOLTEN SALTS *

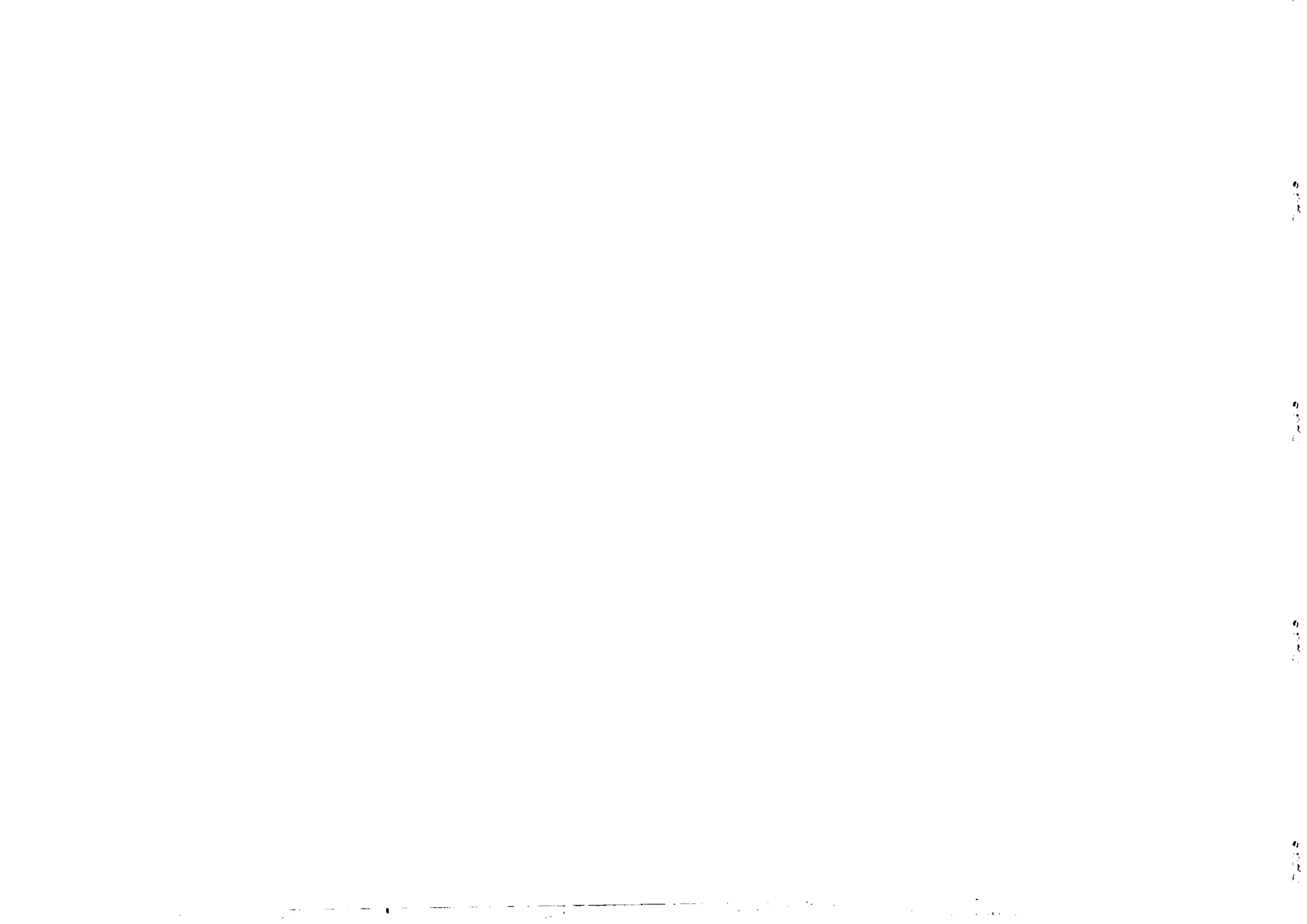
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ABSTRACT

The F-centre model for the bound state and the first optical transition of an electron in a metal-molten salt solution is examined in the high dilution limit appropriate for comparison with optical absorption data. It is first argued that the model is consistent with recent neutron diffraction and computer simulation data on the structure of pure molten salts, and not incompatible with an Anderson localization model for the electronic conductivity of the solution at higher concentration of metal. A detailed evaluation of the model is presented for the case of a molten salt of equi-sized ions simulating molten KCl. The treatment of the electronic states is patterned after semicontinuum approximations previously applied to the F-centre in ionic crystals, but the equilibrium radius of the electronic cavity and its fluctuations are determined self-consistently from the free energy of the solution. The detailed analysis of this case and the agreement of the results with experiment allow the construction of a simple parametrization scheme, which is then applied to explore the trends of the optical absorption spectrum and of the volume of mixing through the whole family of M-MX solutions, where M is an alkali and X a halogen. Similarities and differences of the electronic bound state in the crystal and in the liquid are underlined.

1. Introduction

The alkali metals dissolve in molten alkali halides to give true solutions, with partial miscibility at lower temperatures and a critical point above which the two liquids become miscible in any proportion (for general reviews see Bredig 1964, Corbett 1964). The electrical conductivity of the solutions, which has been measured in several instances near the salt-rich and metal-rich ends of the concentration range and over the entire range for the K-KBr system (Bronstein and Bredig 1958 and 1961; Bronstein, Dworkin and Bredig 1962), changes from that of an ionic liquid to that of a liquid metal. The simultaneous presence of a critical point and of a metal-non-metal transition is an evident reason for interest in these systems.

At low metal concentrations the most interesting question concerns the nature of the states of the valence electrons of the alkali atoms added to the molten salt. An electronic contribution to the conductivity in the concentration range 0.01 + 0.1 moles of metal has been approximately extracted from the experimental data, and is found to be appreciable at these high temperatures and to increase with temperature. Various models for this electronic transport and for electronic traps have been discussed in the past (for a review see Nachtrieb 1975). More recently, Katz and Rice (1972) have pointed out that the observed features of the conductivity are qualitatively consistent with a phenomena of Anderson localization. Durham and Greenwood (1976) have given an account of the data by assuming that current is carried by a small fraction of the added electrons in extended states, in numbers which may depend on temperature and composition and undergoing scatterings against optic modes and disorder.

At still lower concentrations (0.01 moles of metal or less) broad bands of optical absorption have been reported for

a number of metal-molten salt solutions (Mollwo 1935, Young 1963, Rounsaville and Lagowski 1968 and other references given therein). The spectroscopic evidence seems incompatible with a model in which the electron responsible for the optical absorption is bound in an alkali atom or in an alkali diatomic molecule in the solution (Rounsaville and Lagowski 1968). It instead suggests a bound state akin to the F-centre in the crystal, in which the electron would be bound in a bubble inside the liquid structure where it replaces a halogen ion (Pitzer 1962). In particular, the absorption peak frequency in the liquid joins smoothly with the F-band peak in the crystal when plotted against the two-thirds power of the density, in spite of the discontinuous change in density at melting (Gruen, Krumpelt and Johnson 1969). This is the well-known Mollwo-Ivey law for the F-centre peak in the crystal (see e.g. Fowler 1968), which thus holds across the melting transition. A similarly smooth connection exists for the width of the absorption band in the crystal and in the liquid when plotted against the heat content of the system, which for the liquid includes the latent heat of melting (Nachtrieb 1975).

It should be stressed that an F-centre-like model for the electronic bound state in the dilute solution is fully consistent with the recent evidence on the structure of pure molten salts provided both by neutron diffraction experiments (Edwards, Enderby, Rowe and Page 1975, Derrien and Dupuy 1975, Mitchell, Poncet and Stewart 1976) and by computer simulation (Woodcock and Singer 1971, Sangster and Dixon 1976). These data show a high degree of short-range order in the molten salt, where each halogen ion is surrounded by a rather well defined shell of between five and six alkali ions on average. This first-neighbour shell can be expected to provide the attractive well binding the electron when it replaces a negative ion. On the other hand, there is no obvious contradiction between an F-centre model for the optical absorption

at low metal concentration and an Anderson localization model for electronic conductivity at higher concentrations. Indeed, the F-centre bound states may well be the lowermost electronic states in an Anderson tail below the conduction band of the solution, and these, of course, are the only occupied states at high metal dilution.

In this paper we explore the numerical consequences of adopting an F-centre-like model for the electronic bound state in metal-molten salt solutions in the limit of infinite dilution. Such a calculation clearly presents some aspects of complexity when compared with the corresponding problem for the ionic crystal or for a neutral fluid. First of all, liquid-state disorder will allow a sizeable relaxation of the local structure around the electron bubble as contrasted with the case of the crystal. In the estimation of the mean radius of the bubble, on the other hand, one cannot resort to a simple argument which invokes the electronic kinetic pressure and the surface tension of the liquid, since the neighbours of the bubble will prevalently be positive ions whereas the equilibrium surface of the ionic liquid is electrically neutral. Furthermore, liquid-state fluctuations imply a distribution of sizes for the electronic bubble, whose importance is stressed by the broadness of the observed absorption spectrum. In summary, one needs to know the structure of the ionic liquid around the electronic bubble and the corresponding free energy of the system as functions of the radius of the bubble. Once these are known, the electronic states in the ensuing potential well can be determined by standard techniques.

We treat the problems that we have just underlined by the simplest possible approximation (Senatore, Parrinello and Tosi 1978), that is we schematize the solution as a mixture of charged hard spheres and estimate its structure and free energy by the

analytic expressions yielded by the so-called mean spherical approximation (MSA) for a charged-hard-sphere fluid (Waisman and Lebowitz 1972, Blum and Høje 1977). In short, this approximation combines hard-sphere boundary conditions with a Debye-Hückel treatment of the long-range effects due to the Coulomb interaction, and is known (Abramo, Caccamo, Pizzimenti, Parrinello and Tosi 1978) to yield a reasonably accurate account of the observed diffraction patterns of pure molten salts, at least when the sizes of cations and anions are not too different. The MSA presents some difficulties in the equation of state, that we shall later point out and try to remedy by a judicious choice of the size parameters for the pure solvent. Of course, the charged hard sphere which schematizes the effect of the electronic bubble on the solvent has an a priori arbitrary size, to be determined eventually by minimizing the free energy. It contributes to the free energy also through the ground state energy of the electron in the bubble and through polarization of the electronic shells of the ions. We shall tackle the electronic problem in detail for the case of a solvent of equi-sized ions adapted to represent molten KCl, and then examine a parametrization of the results for extension to other systems.

The layout of the paper is briefly as follows. Section 2 presents the essential formulae for the calculation of the electronic states, the thermodynamic and structural properties of the dilute solution in the MSA, and the optical absorption spectrum. The choice of the parameters for the solvent is discussed in Section 3. Sections 4 and 5 present the results obtained for the system K-KCl through a detailed evaluation of the electronic states and for the family of M-MX systems through a parametrization scheme, respectively. Section 6 offers a few concluding remarks.

2. Description of the model

We consider the replacement of a halogen ion in a molten alkali halide by an electron. Since the Madelung energy in the liquid is only marginally reduced relative to the crystal (see e.g. Adams and McDonald 1974, 1975), we expect that the surrounding liquid structure will confine most of the electronic wave function within a spherical cavity kept open by the electronic kinetic pressure, and only the tails of the wave function will extend beyond the first shell of neighbours. We denote by σ an effective hard-core diameter of the cavity through which we shall describe the distortion induced in the surrounding liquid; that is $R = \frac{1}{2}(\sigma + \sigma_+)$ is the distance of closest approach of an alkali ion with diameter σ_+ to the centre of the cavity with diameter σ . Fluctuations will lead to a distribution of values for σ around the value σ_0 that minimizes the free energy of the system. We neglect fluctuations leading to non-spherically-symmetric configurations.

2.1 The electronic ground state

The potential felt by the electron associated with a cavity of given diameter is flat within the sphere of radius R and determined by the detailed liquid structure and electronic polarization outside. We estimate this potential by a semicontinuum Hartree-Fock method, in analogy with previous work on the F-centre in the crystal (Gourary and Adrian 1960). We first introduce the probability $p_0(r)$ of finding the electron within a sphere of radius r ,

$$p_0(r) = \int d\Omega \int_0^r s^2 |\psi_0(\mathbf{z})|^2 ds, \quad (2.1)$$

and proceed on the assumptions that $p_0(R)$ is not far from unity and that the ions and the core electrons do not follow the detailed motion of the trapped electron, but only its average. The potential for $r < R$ consists of a Coulomb contribution and a core-polarization term,

$$V_{in} = V_{in}^C + V_{pol} \quad (2.2)$$

The Coulomb contribution can be expressed through the pair correlation functions $g_{\alpha\alpha'}(r)$, which describe the probability of finding an ion of species α at a distance r from the centre of the cavity as

$$V_{in}^C = -e^2 \int_R^\infty 4\pi r \sum_{\alpha} \rho_{\alpha} Z_{\alpha} g_{\alpha e}(r) dr \quad (2.3)$$

Here, ρ_{α} and Z_{α} are the density and the valence of the α -th ionic species, and we should note that $g_{\alpha e}(r)$ depends on the probability $p_0(r)$ of finding the electron within the shell of first neighbours. The core polarization term in eq. (2.2) vanishes if $p_0(R) = 1$ and is taken to have the Hartree-Fock expression

$$V_{pol} = \left(1 - \frac{1}{\epsilon_{\infty}}\right) e^2 \int_R^\infty \frac{1 - p_0(r)}{r^2} dr, \quad (2.4)$$

where ϵ_{∞} is the high-frequency dielectric constant of the solvent. Finally, the potential for $r > R$ is taken in the form of a screened Coulomb potential,

$$V_{out} = -\frac{e^2}{\epsilon_0} \int d_3 \sum_{\alpha} \rho_{\alpha} Z_{\alpha} g_{\alpha e}(1 - \beta|z|) / |z - \beta| \quad (2.5)$$

The "lattice polarization" terms usually included in calculations

on the F-centre in the crystal (Gourary and Adrian 1960, Iadonisi and Preziosi 1967) are already accounted for in our treatment through the use of the ion-cavity correlation functions in eqs. (2.3) and (2.5).

We shall restrict the detailed evaluation of the electronic states to the case of a solvent of equi-sized ions, adopted to simulate molten KCl. The diameter of these ions is taken as $\bar{\sigma} = \frac{1}{2}(\sigma_+ + \sigma_-)$, the average of the diameters of the K^+ and Cl^- ions. The MSA yields an analytic expression for the quantity given in eq. (2.3), which in the present case reads

$$V_{in}^C = -\frac{2e^2\Gamma}{1 + \Gamma\bar{\sigma}} p_0(R), \quad (2.6)$$

where Γ is a parameter of the solvent determined by eq. (2.11) below. It also yields in the same case an analytic expression for the charge-cavity correlation function $\sum_{\alpha} \rho_{\alpha} Z_{\alpha} g_{\alpha e}(r)$ entering eq. (2.5) (Henderson and Smith 1978). The potential calculated for $p_0(R) = 1$ is reported in Fig. 1. It is evident that the potential outside R is reasonably well represented by the simple expression

$$V_{out}(r) = -\frac{e^2}{\epsilon_{\infty} r} \quad (2.7)$$

that we shall use in the following.

It is now a simple matter to solve the Schrödinger equation for each value of σ with the above prescriptions for the potential, determining the function $p_0(r)$ self-consistently. We have done so by the method originally used by Krumhansl and Schwartz (1953) (see also Gourary and Adrian 1960). We only note here that $p_0(R)$ turns out indeed to be close to unity in the ground state ($p_0(R) = 0.82$ for $\sigma = \sigma_0$ in molten KCl) and defer a discussion of the other

results to Section 4. We now turn instead to a discussion of the free energy of the dilute solution.

2.2 The free energy

The MSA for an n -component mixture of charged hard spheres yields also an analytic expression for its Helmholtz free energy, consisting of a hard-sphere contribution and a Coulomb contribution:

$$F(V,T) = F_{hs} + F_c \quad (2.8)$$

We take for F_{hs} the expression obtained by integration of the virial pressure for a neutral-hard-sphere fluid,

$$F_{hs} = F_{vd} + \frac{6}{\pi} V k_B T \left[\frac{3\bar{\xi}_1 \bar{\xi}_2}{\Delta} + \frac{3\bar{\xi}_2^3}{\bar{\xi}_3 \Delta} + \frac{3\bar{\xi}_2^3}{\bar{\xi}_3^2} \ln \Delta - \bar{\xi}_0 \ln \Delta \right], \quad (2.9)$$

with $\bar{\xi}_m = \frac{\pi}{6} \sum_{\alpha} \rho_{\alpha} \sigma_{\alpha}^m$ and $\Delta = 1 - \bar{\xi}_3$, and adopt for F_c the expression obtained by integration of the excess internal energy (Blum and Høje 1977),

$$F_c = V k_B T \frac{\Gamma^3}{3\pi} - V e^2 \left(\Gamma \sum_{\alpha} \frac{\rho_{\alpha} Z_{\alpha}^2}{1 + \Gamma \sigma_{\alpha}} + \frac{\pi}{2\Delta} \Omega P_n^2 \right). \quad (2.10)$$

Here, the charges, partial densities, and diameters of the component species are $Z_{\alpha}|e|$, ρ_{α} , and σ_{α} , respectively; Γ is to be determined by solving the algebraic equation

$$\Gamma = \left(\frac{\pi e^2}{k_B T} \right)^{1/2} \left[\sum_{\alpha} \rho_{\alpha} \left(\frac{Z_{\alpha} - \frac{\pi}{2\Delta} P_n \sigma_{\alpha}^2}{1 + \Gamma \sigma_{\alpha}} \right)^2 \right]^{1/2}, \quad (2.11)$$

and the quantities Ω and P_n have simple expressions in terms of the quantities that we have just defined. In the present case, components 1 and 2 of the fluid represent the alkali and halogen

ions, and component 3 represents electronic bubbles with diameter $\sigma_3 = \sigma$ and valence $Z_3 = -p_0(R)$.

The relevant σ -dependent term in the free energy, to first order in ρ_3 , is the chemical potential $\mu_e(\sigma)$ of the electronic bubble, which can be written

$$\mu_e = \mu_e^{hs} + \mu_e^c + \mu_e^{pol} + E_e. \quad (2.12)$$

We aim to account for core polarization effects through the term μ_e^{pol} and for the internal degrees of freedom of the electronic bubble through $E_e(\sigma)$, the energy of the electronic ground state relative to the bottom of the potential well binding the electron, determined by the solution of the Schrödinger equation in the preceding section. Differentiation of eqs. (2.9) and (2.10) in the limit $\rho_3 \rightarrow 0$ yields at once

$$\begin{aligned} \mu_e^{hs} = & \mu_{vd} - k_B T \ln \Delta + 3 k_B T \frac{\bar{\xi}_2}{\Delta} \sigma + k_B T \left(\frac{3\bar{\xi}_1}{\Delta} + \frac{9\bar{\xi}_2^2}{\bar{\xi}_3 \Delta} + \frac{9\bar{\xi}_2^2}{\bar{\xi}_3^2} \ln \Delta \right) \sigma^2 \\ & + k_B T \left(\frac{\bar{\xi}_0}{\Delta} + \frac{3\bar{\xi}_1 \bar{\xi}_2}{\Delta^2} + \frac{3\bar{\xi}_2^3}{\bar{\xi}_3 \Delta^2} - \frac{6\bar{\xi}_2^3}{\bar{\xi}_3^2 \Delta} - \frac{6\bar{\xi}_2^3}{\bar{\xi}_3^2} \ln \Delta \right) \sigma^3 \end{aligned} \quad (2.13)$$

and

$$\mu_e^c = - \frac{e^2}{1 + \Gamma \sigma} \left[\Gamma P_n^2(R) - \frac{2}{3} \left(\frac{\pi}{2\Delta} P_n \right)^2 \sigma^3 - \frac{\pi}{\Delta} P_n \sigma P_n(R) + \frac{1}{3} \left(\frac{\pi}{2\Delta} P_n \right)^2 \Gamma \sigma^3 \right], \quad (2.14)$$

where the quantities Γ , $\bar{\xi}_m$ and P_n now refer to the pure solvent. In particular, P_n vanishes in the case of a solvent of equi-sized ions.

The core polarization term μ_e^{pol} can be estimated by considering the polarization work involved in replacing a halogen

ion by the electronic bubble in an adiabatic process, as is appropriate for the calculation of a thermodynamic quantity. The change in free energy of the system upon addition of an alkali ion and an electronic bubble is

$$\Delta F = \mu_e + \mu_+ = (\mu_e - \mu_-) + (\mu_+ + \mu_-). \quad (2.15)$$

Core polarization effects are negligible in the quantity $(\mu_+ + \mu_-)$, which corresponds to the addition of an alkali-halogen ion pair to the liquid (see also Section 3 below). In the evaluation of $(\mu_e - \mu_-)$, on the other hand, we must adiabatically extract a halogen ion, creating a core polarization field in the system, and replace it adiabatically by the electron, which would completely cancel the core polarization field only if $p_0(R) = 1$ and $\sigma = \sigma_-^v$, the diameter of an "anion vacancy". A continuous-dielectric calculation yields

$$(\mu_e - \mu_-)_{\text{rel}} = \left(1 - \frac{1}{\epsilon_\infty}\right) e^2 \int_R^\infty \left[1 - \frac{1}{2} p_0(r)\right] p_0(r) \frac{dr}{r^2} - \left(1 - \frac{1}{\epsilon_\infty}\right) \frac{e^2}{\sigma_+ + \sigma_-^v}, \quad (2.16)$$

where the first term is the polarization work involved in bringing $p_0(r)$ adiabatically from zero to its actual value in the polarization potential of the medium, and the second term is the same quantity calculated with $p_0(R) = 1$ and $\sigma = \sigma_-^v$. Of course, this second term is irrelevant since we need only the dependence of μ_e on σ . We can cancel the rigid-ion contribution to μ_- in $(\mu_e - \mu_-)$ against μ_- in $(\mu_+ + \mu_-)$, and must then use the rigid-ion value for μ_+ in ΔF .

The equilibrium value of σ , denoted by σ_0 , will be determined by minimizing the expression (2.12) for $\mu_e(\sigma)$. Of course, a knowledge of the free energy allows one to evaluate other thermodynamic properties of the dilute solution. We shall be interested in particular in the isothermal compressibility

of the pure solvent,

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \rho_3=0}, \quad (2.17)$$

and in the volume change upon addition of a metal atom to the molten salt,

$$v = \left(\frac{\partial V}{\partial N} \right)_{T, P, \rho_3=0} = K_T \left(\frac{\partial P}{\partial \rho_3} \right)_{T, V, \rho_3=0}, \quad (2.18)$$

with $N = \rho_3 V$. For the evaluation of v we shall need also the chemical potential μ_+ of the alkali ion, that we shall take, for reasons just indicated above, to have the rigid-ion value given by expressions analogous to eqs. (2.13) and (2.14).

2.3 The optical absorption spectrum

For a given diameter σ of the electronic bubble in the electronic ground state, the energy of a Franck-Condon transition is the difference

$$\hbar \omega(\sigma) = E_1(\sigma) - E_0(\sigma) \quad (2.19)$$

between the energies of the first p-type excited state and of the ground state. In the evaluation of $E_1(\sigma)$ we have used again the expressions (2.2) and (2.7) for the potential well, but have allowed for a readjustment of core polarization by replacing $p_0(r)$ in eq. (2.4) by $p_1(r)$, the corresponding self-consistent probability for the excited state. We must then account in (2.19) for the relative shift of the bottom of the wells for the two states, as well as for a (small) term representing the polarization work involved in the change of core polarization.

On account of fluctuations, which occur with probability

$$P(\sigma) \propto \exp \left\{ - [H_e(\sigma) - H_e(\sigma_0)] / k_B T \right\}, \quad (2.20)$$

the absorption line at $\omega(\sigma_0)$ will be broadened into a band, with a peak frequency ω_m , which may be different from $\omega(\sigma_0)$. Additional broadenings and shifts can arise from non-spherically-symmetric fluctuations and from relaxation of the liquid structure in the electronic transition. The probability of a transition at frequency ω by electrons in bubbles with diameter between σ and $\sigma + d\sigma$ is

$$dW_\sigma(\omega) \propto P(\sigma) M(\sigma) \delta(\omega(\sigma) - \omega) d\sigma, \quad (2.21)$$

where $M(\sigma)$ is the square modulus of the transition matrix element. Inversion of eq. (2.19) to get a function $\sigma(\omega)$ and integration of eq. (2.21) over σ yield the absorption intensity

$$I(\omega) \propto P(\sigma(\omega)) M(\sigma(\omega)) \left| \frac{d\sigma(\omega)}{d\omega} \right|. \quad (2.22)$$

The peak frequency ω_m of this spectrum and its full width $\Delta\omega$ at half maximum will be compared later with the available data on optical absorption.

3. Parameters of the solvent

In the present discussion of the dilute solutions of metals in molten salts the solvent, taken near the freezing point and at the measured density at atmospheric pressure, is described by three parameters, i.e. the diameters σ_+ and σ_- of alkali and halogen ions and the electronic dielectric constant ϵ_{∞} . For the latter we adopt values appropriate to the crystal (Tessman, Kahn and Shockley 1953). The choice of diameters is quite critical, especially in the calculation of the equilibrium diameter σ_0 of the bubble and of the volume change v of the solution through the solvent compressibility, and we have reconsidered their determination from properties of the pure solvent.

The recent determination of these parameters for molten salts by Abramo *et al.* (1978) was based on a fit of the compressibility by the MSA expression yielded by the Ornstein-Zernike relation. Our expression for the compressibility, derived from the MSA free energy reported in Section 2.2, does not coincide with the Ornstein-Zernike expression. This "thermodynamic inconsistency" in the equation of state is indeed the main difficulty of the MSA in the evaluation of thermodynamic properties, and we try to remedy it for our purposes by refitting the solvent diameters to the measured compressibility so that the equation of state of our model is consistent with its free energy. We find again that each ion in the family of salts can be assigned a characteristic diameter at a given temperature, but the diameters are increased by $0.05 + 0.1 \text{ \AA}$ and are somewhat less sensitive to temperature. As shown in Fig. 2, where the calculated partial structure factors for a salt of nearly equi-sized ions (molten RbCl) are compared with the neutron diffraction data of Mitchell *et al.* (1976), the MSA with the new diameters still yields a good description of the structure of the pure solvent.

The values of the new diameters at the freezing point of each salt, and of the parameter Γ determined from eq. (2.11) for the pure solvent, are collected in Table I. The table reports also the MSA values of the Madelung energy E_M of the solvent, which is clearly related to the value of V_{in}^C in eq. (2.2). Comparison with the experimental values of the cohesive energy U at freezing, reported in the table whenever available (Adams and McDonald 1974), shows that the MSA estimate of E_M is quite reasonable, since the discrepancy of 10 + 15 % between E_M and U can be largely attributed to the Born-Mayer repulsive energy.

It should be noted that the above calculations on the pure solvent were carried out without account of core polarization. Introduction of dielectric screening through a k -independent dielectric function ϵ_∞ would greatly reduce the heights of the main peaks in the partial structure factors reported in Fig. 2 and sizeably decrease $|E_M|$, which is mainly determined by the liquid structure in this region of k -space. This observation supports our claim that the chemical potential $(\mu_+ + \mu_-)$ discussed in Section 2.2 should not include polarization effects, and that the latter are arising in the problem at hand from differences between the electronic bubble and the halogen ion that it replaces.

4. Results for a model of K-KCl

The solution of the Schrödinger equation for the two electronic states in a model molten salt of equi-sized ions simulating KCl yields the self-consistent distributions of radial probability

$$R_n(r) = r^2 \int d\Omega |\psi_n(r, \Omega)|^2, \quad (4.1)$$

which are reported in Fig. 3 for the value of σ , which minimizes the free energy. The corresponding values of $p_0(R)$ and $p_1(R)$ are 0.82 and 0.49, respectively, indicating a strong localization of the ground state and an appreciable spread of the excited state.

The other results of the calculation are collected in Table II and compared with the available data on optical absorption. The following points are worth noting:

(i) the relaxation of the ionic liquid around the electronic bubble is not a large one ($(\sigma - \sigma_-)/\sigma_- \approx 0.14$) but is appreciably larger than one expects for the F-centre in the crystal;

(ii) liquid-state fluctuations induce a large broadening of the spectrum, in substantial accord with the observed width although the theory does not take account of all mechanisms for broadening;

(iii) the calculated spectrum has a somewhat asymmetric Gaussian-like shape with a high-frequency tail, in accord with the observed spectra, and the asymmetry leads to a downward shift of the peak frequency, bringing it into reasonable agreement with the measured value;

(iv) the volume change ν of the solution upon addition of a metal atom is comparable to the volume ν_m of the atom

in the alkali metal, namely the excess volume of mixing is small. Galka, Suski and Moscinski (1973) have been unable to observe an excess volume of mixing for this system over the concentration range between 0.02 and 0.15 molar fractions of metal. An error of 4 % in our value of σ_0 would be sufficient to reduce $v-v_m$ to zero, so that our calculated value for $(v-v_m)/v_m$ may be within the likely uncertainties of the theory. It should be stressed, on the other hand, that one is not justified in comparing results at very high dilution with results at finite dilution. Indeed, the optical properties change drastically around concentrations of 0.01 moles of metal (Young 1963), indicating that the nature of the electronic states is rapidly changing with concentration. This behaviour is well known in metal-ammonia solutions (see e.g. Mott 1974).

The present calculation for the K-KCl system thus agrees with experiment in the conclusion that the electronic bound state in very dilute metal-molten salt solutions is of the F-centre type. The similarity of behaviours in the solid and in the liquid is ultimately related to the affinity of their structures, while the differences arise in essence from the greater compressibility and from fluctuations in the liquid. In the next section we shall use the results obtained for the K-KCl system to build a simpler model for the other metal-molten salt solutions. We shall be particularly concerned, for the reasons just given above, with the behaviour of the optical absorption spectrum through the family of systems at very high dilution, but shall also comment on the qualitative behaviour of their thermodynamic properties.

5. Results for the family of metal-molten salt solutions

Our aim is to build a simple parametrization scheme for the detailed quantum-mechanical results obtained above for the K-KCl system, that we shall then extend to the other systems. The first consideration is that the electronic ground state is so well localized that the ground state energy ought to be reasonably well represented in its dependence on σ by the spherical-well formula,

$$E_0(\sigma) = \frac{A}{(\sigma + \sigma_0)^2} \quad (5.1)$$

This simple expression does indeed reproduce with good accuracy the calculated behaviour of $E_0(\sigma)$ near the equilibrium diameter σ_0 , and the parameter A is determined by fitting the calculated value of $dE_0(\sigma)/d\sigma$ at $\sigma = \sigma_0$. On the other hand, the core-polarization correction (2.16) to the electronic chemical potential can be approximately accounted for by screening the Coulomb term (2.14) through a factor $1/\epsilon_\infty$, as far as its dependence on σ is concerned. This can be seen by noticing that $p_0(\sigma) \approx 1$ in eq (2.16) and that Γ_σ is appreciably larger than unity. If we further take for the K-KCl system the value $p_0(R) = 0.82$, independent of σ , we can redetermine the equilibrium diameter in this scheme and find $\sigma_0 = 3.46\text{\AA}$ instead of the value $\sigma_0 = 3.49\text{\AA}$ found in Section 4. Finally, the empirical validity of the Mollwo-Ivey law suggests that the optical transition energy defined in eq. (2.19) can be written approximately

$$h\nu(\sigma) = \frac{B}{(\sigma + \sigma_0)^2} \quad (5.2)$$

The parameters A and B are not expected to bear a simple relation

to each other, because of the appreciable spread of the excited state that we have seen in the preceding section. The value of B is fitted to the observed peak frequency ω_m in the K-KCl system, with account of fluctuations in the theory.

The evaluation of the equilibrium diameter of the bubble and of the absorption spectrum can now be carried out for all the systems if we assume that the three parameters A, B and $p_0(R)$ are constants independent of the system. This already yields a reasonable account of the optical data available for various solutions, and in particular reproduces qualitatively the observed trend of ω_m to increase through the family of chlorides from Cs-CsCl to Li-LiCl. A better account of this trend can be obtained by allowing for a dependence of the parameter A on the cation, in the form of a proportionality to the cation diameter σ_+ . This factor seems to account qualitatively for the effect of a greater depth of the potential well in freezing the kinetic pressure of the electron, and yields a regular variation of the bubble diameter σ_b through the family of systems.

Obviously, by this rough type of approximate scheme we can only hope to assess the qualitative trends of the properties of the dilute solutions. The results for the bubble diameters and for the optical spectrum are collected in Table III. The experimental evidence on the trend of ω_m with varying anion for a given cation is conflicting, in that the results of Mollwo (1935) for both the sodium and potassium halides depend only on the cation while those of Rounsaville and Lagowski (1968) for the potassium halides show a decrease of ω_m from the chloride to the iodide. A trend of the latter type in ω_m seems implicit in the theory, although its magnitude could be altered by further hypotheses on the parameters. It should be noted that this dependence of ω_m on the anion is anyway weaker than for the F-centre in the crystal, owing again

to the larger compressibility of the liquid.

The calculated values of the excess volume of mixing of the dilute solutions are also reported in Table III. The only available experimental study of this quantity is that of Galka *et al.* (1973), who have also examined the system K-KI at concentrations from 0.02 to 0.2 molar fractions of metal, finding again no evidence for a sizeable effect. Our approximations could imply an error of a factor of two in $(V-V_m)/V_m$ for this system at very high dilution. Our results, on the other hand, definitely suggest that large volumes of mixing should be present, and possibly observable, in the systems with lighter cations at higher dilutions than those explored by Galka *et al.* (1973).

Experimental values for the activity of the salt in the dilute solution have been reported by Pitzer (1962) on the basis of an analysis of the phase diagram. The evaluation of this thermodynamic quantity requires a knowledge of the free energy to second order in the concentration of metal, and can be carried out in the present scheme through a strict application of the MSA expression (2.8) + (2.10), thus effectively neglecting the quantum-mechanical nature of the electronic centres as well as core polarization. The results are very rough but qualitatively agree with the trends revealed by the data.

6. Concluding remarks

It may be useful to conclude by commenting briefly on the similarities and differences of the electronic bound state in the crystal and in the liquid. Our treatment of the problem in the K-KCl system is similar to treatments previously given for the F-centre in the crystal (see e.g. Iadonisi and Preziosi 1967), except that we have allowed the system to relax to its free energy minimum and have allowed for fluctuations around this minimum. We have also been able to test in Fig. 1 the closeness of the outer potential to a simple Coulomb tail. The overall agreement of the results with optical data is of comparable quality.

As we have previously pointed out, the bound state in the liquid originates from the good short-range order of the spacial distribution of ionic charges around a halogen ion, which yields as in the crystal a strong Madelung potential. The degree of order can be gauged directly from the height and narrowness of the main peaks in the partial structure factors illustrated in Fig. 2. The strong negative trough in the cross-correlation function $S_{+-}(\mathbf{k})$ at the same wavenumber is a precise mark of ordering in the charge distribution (see e.g. Parrinello and Tosi 1979).

On the other hand, the looseness of the liquid structure revealed by its greater compressibility and its transport properties implies quantitative modifications of the bound state and of the optical transition to the first excited state. Relaxation around the electronic bubble as well as fluctuations lower the absorption peak frequency, reduce its dependence on the solvent ion species, and greatly broaden the spectrum.

On the experimental side, more systematic studies of the absorption spectrum in the family of metal-molten salt solutions would seem useful at this stage. It may also prove possible, by a suitable choice of system, to extend the studies

of the volume of mixing to the relevant range of metal concentration.

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TABLE I

Properties of pure molten salts near freezing

	σ_+ (Å)	σ_- (Å)	Γ (Å ⁻¹)	$-E_M$ (eV/molecule)	$-U$ (eV/molecule) ^a
LiF	1.58	2.24	1.60	11.55	10.0
LiCl	1.62	3.12	1.18	9.44	8.25
LiBr	1.63	3.38	1.26	9.40	-
LiI	1.64	3.75	1.20	8.97	-
NaF	2.18	2.18	1.27	9.71	-
NaCl	2.24	3.04	1.06	8.14	7.38
NaBr	2.25	3.30	1.01	7.81	-
NaI	2.28	3.68	0.956	7.38	-
KF	2.76	2.24	1.13	8.56	7.69
KCl	2.79	3.05	0.939	7.24	6.68
KBr	2.80	3.31	0.899	6.94	6.38
KI	2.82	3.68	0.846	6.56	-
RbF	3.01	2.27	1.08	8.17	-
RbCl	3.03	3.07	0.912	6.94	6.51
RbBr	3.04	3.33	0.873	6.66	6.26
RbI	3.06	3.68	0.819	6.30	-
CsF	3.29	2.30	1.04	7.80	7.19
CsCl	3.32	3.10	0.882	6.63	-
CsBr	3.32	3.35	0.841	6.36	-
CsI	3.33	3.70	0.783	6.02	-

(a) From Adams and McDonald 1974.

TABLE II

Properties of the K-KCl system at infinite dilution

	σ_0 (Å)	$\omega(\sigma_0)$ (eV)	ω_m (eV)	$\Delta\omega$ (eV)	ν (cm ³ mol ⁻¹)	$(\nu-\nu_m)/\nu_m$
Theory	3.49	1.55	1.49	0.38	65.0	0.10
Experiment	-	-	1.27 ^a , 1.33 ^b	0.79 ^b	-	-

(a) From Mollwo, 1935

(b) From Rounsaville and Lagowski, 1968

TABLE III

Properties of dilute metal-molten salt solutions *

	$\sigma_0(\text{\AA})$	$\omega(\sigma_0)(\text{eV})$	$\omega_m(\text{eV})$	$\Delta\omega(\text{eV})$	$(\bar{v}-\bar{v}_m)/\bar{v}_m$
LiF	2.50	3.34	3.14	1.15	0.29
LiCl	3.24	2.35	2.22(2.26 ^a)	0.78	1.14
LiBr	3.48	2.13	2.01	0.70	1.63
LiI	3.75	1.91	1.81	0.62	2.34
NaF	2.61	2.42	2.25	0.90	0.00
NaCl	3.31	1.80	1.69(1.57 ^b , 1.61 ^c)	0.65(1.41 ^c)	0.62
NaBr	3.53	1.66	1.56(1.57 ^b)	0.59	0.86
NaI	3.83	1.49	1.40(1.57 ^d)	0.52(0.63 ^d)	1.26
KF	2.77	1.82	1.70	0.66	-0.29
KCl	3.46	1.42	1.33(1.27 ^b , 1.33 ^d)	0.51(0.79 ^d)	0.11
KBr	3.66	1.33	1.25(1.27 ^b , 1.19 ^d)	0.48(0.90 ^d)	0.24
KI	3.96	1.21	1.13(1.27 ^b , 1.13 ^d)	0.43(0.79 ^d)	0.48
RbF	2.93	1.58	1.48	0.56	-0.30
RbCl	3.51	1.30	1.22	0.46	-0.03
RbBr	3.71	1.22	1.14	0.43	0.08
RbI	4.02	1.11	1.04	0.39	0.29
CsF	3.07	1.37	1.29	0.47	-0.32
CsCl	3.70	1.13	1.06(1.07 ^d)	0.38(0.63 ^d)	-0.07
CsBr	3.50	1.09	1.03	0.38	-0.01
CsI	4.12	1.00	0.94	0.35	0.19

* The parameters used in the calculation are $A = 72.1 \sigma_0/\sigma_{K^+} \text{ eV \AA}^2$, $B = 55.5 \text{ eV \AA}^2$, and $p_0(R) = 0.82$. Experimental values are reported in parentheses from: (a) Young 1963, (b) Mollwo 1935, (c) Gruen et al. 1969, (d) Rounsaville and Lagowski 1968.

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FIGURE CAPTIONS

- Fig.1 Potential well for an electron in the K-KCl system, for $p_0(R) = 1$ and $\sigma = 3.49\text{\AA}$. The broken curve gives the Coulomb tail of eq (2.7).
- Fig.2 Partial structure factors in molten RbCl at 1023 K. Full lines, MSA results; circles, neutron diffraction data of Mitchell *et al.* (1976).
- Fig.3 Radial probability distributions for the ground state and for the first p-like excited state of the electron in the K-KCl system, for $\sigma = 3.49\text{\AA}$.

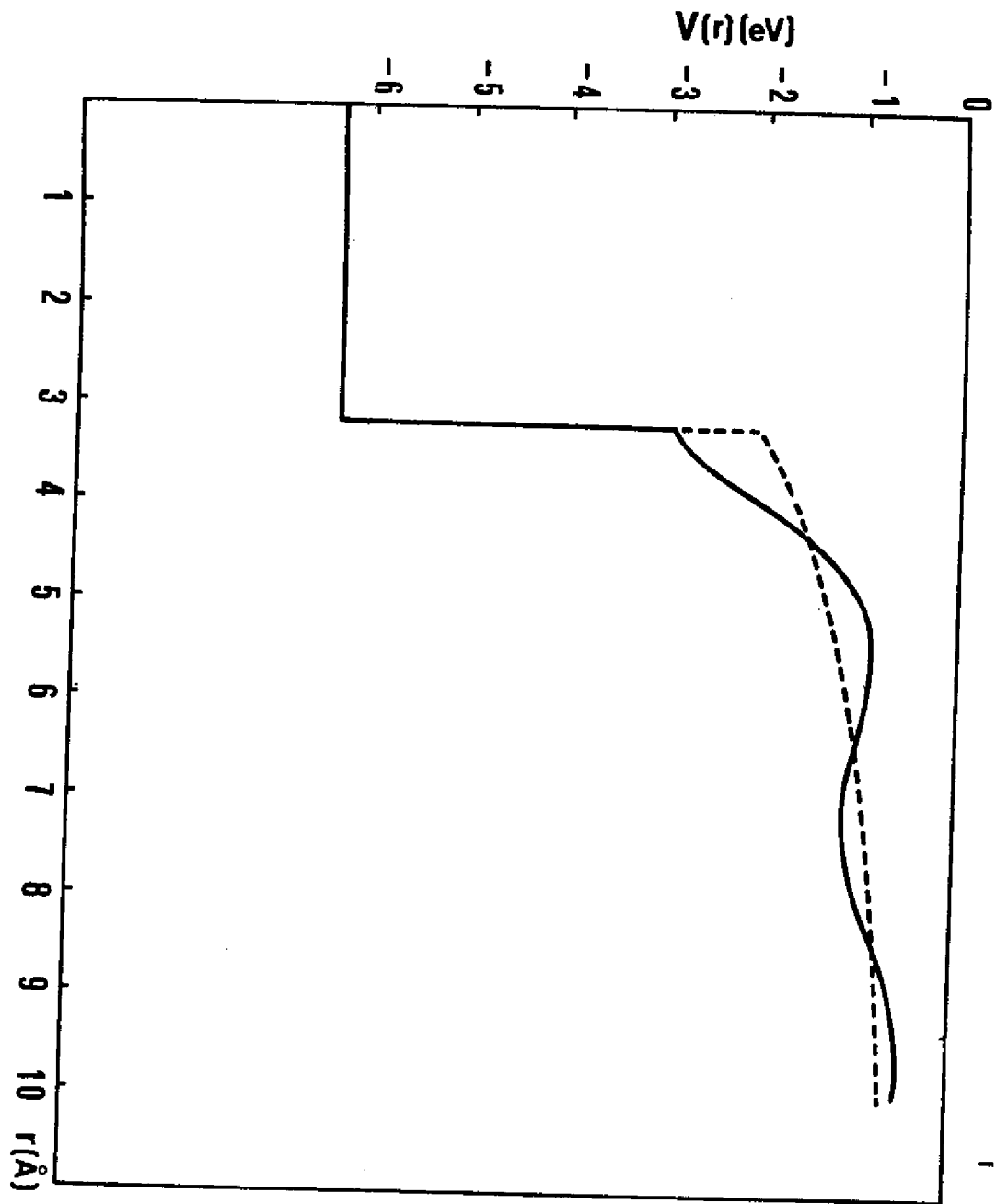


Fig. 1

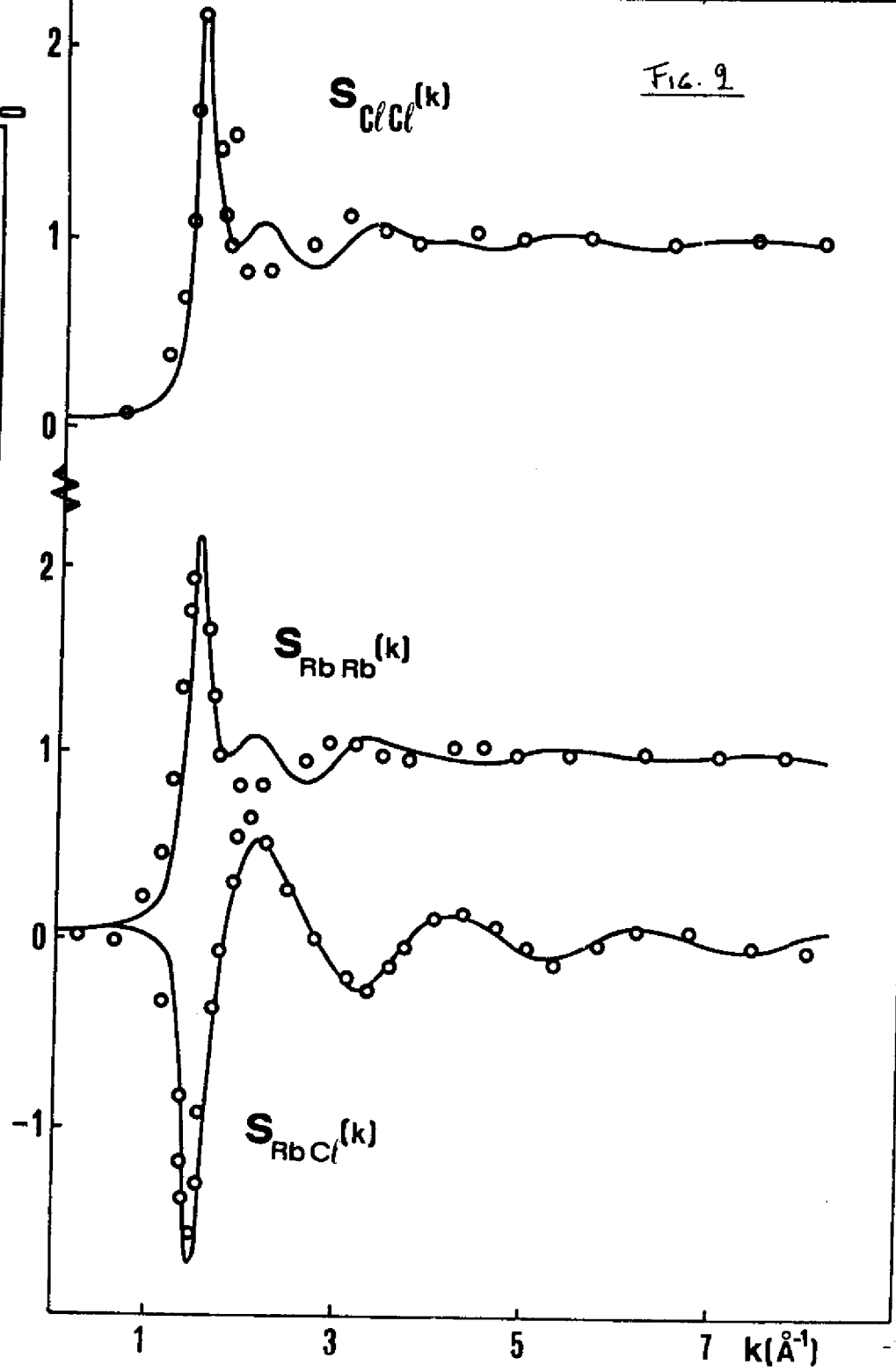
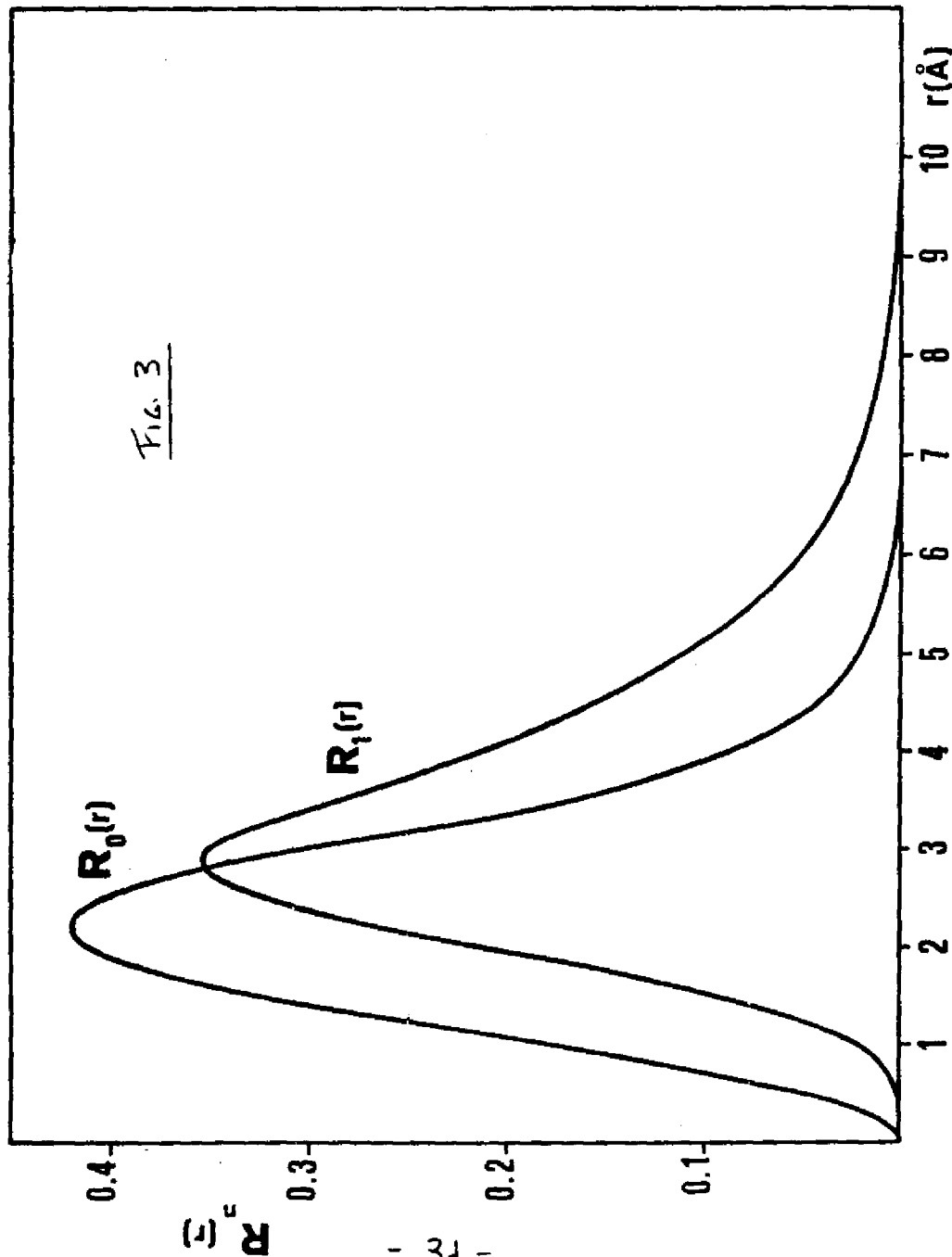


Fig. 9



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