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SYMMETRY AND HIGHER SUPERCONDUCTIVITY IN THE LOWER ELEMENTS

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Abstract: At one atmosphere 29 elements are classified as superconductors; at high pressures there are to date an additional 23, many of these being drawn from the lighter elements. The number of superconductors for the elements in combination appears to be illimitable. Observed symmetries in these systems generally include orderings in both nuclear and electronic degrees of freedom. The fluctuations impelling order in the electron sub-system include those originating with the nuclear degrees of freedom but also with the electrons themselves, both itinerant and localized. For the elements in combination coherent multipole fluctuations in localized states may arise, and the relative contributions of such excitations to electron-pairing is then of some especial interest. When the elements are placed in combination the effects of external pressure may be replicated in part by an equivalent internal pressure, this resulting from a form of chemical pre-compression.

1. INTRODUCTION

Perhaps the most striking early claim of high temperature superconductivity came in 1946 [1] for the light elements H , N and a lower alkali metal M , all in combination. In experiments involving the metal ammines $M(NH_3)_x$ which remain controversial [2-5], R.A. Ogg [1] invoked the elegant Kamerlingh-Onnes ring geometry for his samples and when these

were quenched cooled in an external magnetic field a number of them displayed persistent currents even at temperatures as high as 180K. Ogg's quite prescient comment was that "the probable explanation is to be found in trapped electron pairs, recently demonstrated to be stable in fairly dilute [i.e non-metallic] metal ammonia solutions". Under ordinary conditions these are in states of wholly continuous symmetry. This appears to be the first recognition of the importance of electron pairing and its deeper relation (via Bose-Einstein condensation, as Ogg had it) to the extraordinary phenomenon of superconductivity.

Though Ogg's viewpoint has evidently never gained wide acceptance (the matter has been discussed in depth by Edwards [6]), there are certain aspects of his motivating systems (the metal ammines) which possess exceedingly interesting properties. One only has to observe the appearance of a high density of hydrogen implying the presence in a non-diffusive environment of lattice dynamical modes with very significant energies. Further, for H in combination with N , there is an electronic charge distribution with a scale of linear dimension that implies the possibility of a substantial dipole polarizability. This manifestation of localized charge, and its internal fluctuations, can lead (especially in a crystalline environment) to coherent wave-like excitations to which, as with their phonon counterparts, valence electrons can couple.

From the standpoint of symmetry, and its breaking, the issues raised by these light element systems, and many like them, are several. It will be convenient to introduce and discuss them starting with a pure single-component system, but keeping firmly in mind that for contributions to electron pairing arising from fluctuations in localized electronic charge, it is the groupings of the elements in combination that may well be best placed to achieve this.

2. STARTING HAMILTONIANS AND THEIR SYMMETRY

Beginning therefore with an element (atomic number Z_α), and with one- and two-particle densities $\hat{\rho}_\alpha^{(1)}(\mathbf{r})$ and $\hat{\rho}_\alpha^{(2)}(\mathbf{r}, \mathbf{r}')$ as appropriate observables for macroscopic systems, the Hamiltonian for a neutral ensemble of nuclei ($\alpha = n$) and electrons ($\alpha = e$) established in a volume V is, in three-dimensions,

$$\hat{H} = \hat{T}_n + \hat{T}_e + (1/2) \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ Z_a^2 \hat{\rho}_n^{(2)}(\mathbf{r}, \mathbf{r}') - 2Z_a \hat{\rho}_n^{(1)}(\mathbf{r}) \hat{\rho}_e^{(1)}(\mathbf{r}) + \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') \} \quad (1)$$

where, $v_c(\mathbf{r} - \mathbf{r}') = e^2 / |\mathbf{r} - \mathbf{r}'|$ is the fundamental Coulomb interaction. Here \hat{T}_n and \hat{T}_e are respectively, the kinetic energy operators for N nuclei of mass m_n and $Z_a N$ electrons of mass m_e , i.e in terms of the linear momentum operators \hat{p}_{ai} , $\hat{T}_a = \sum \hat{p}_{ai}^2 / 2m_a$. Since the system fundamentally involves long-range interactions, an alternative way of writing (1) is

$$\hat{H} = \hat{T}_n + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ Z_a^2 \hat{\rho}_n^{(2)}(\mathbf{r}, \mathbf{r}') - 2Z_a \hat{\rho}_n^{(1)}(\mathbf{r}) \bar{\rho} + \bar{\rho}^2 \} \quad (2a)$$

$$+ \hat{T}_e + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') - 2\hat{\rho}_e^{(1)}(\mathbf{r}) \bar{\rho} + \bar{\rho}^2 \} \quad (2b)$$

$$- \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ Z_a \hat{\rho}_n^{(1)}(\mathbf{r}) - \bar{\rho} \} \{ \hat{\rho}_e^{(1)}(\mathbf{r}') - \bar{\rho} \} \quad (2c)$$

where, apart from endowed statistics, (2a) and (2b) represent formally equivalent quantum mechanical problems each well defined in the thermodynamic limit and differing only according to length scale. In (2) the quantity $\bar{\rho} = NZ_a / V$ (in the limit $NZ_a \rightarrow \infty, V \rightarrow \infty$, and $NZ_a / V \rightarrow \bar{\rho}$). The form of the coupling in (2c) arises when the two sub-systems are taken to occupy a common volume (the backgrounds then cancelling). Starting with (1) (or (2)) the fundamental problems of the physics of condensed matter are to determine ground and excited states and non-equilibrium properties in this limit and, importantly for what follows, the states of order or broken symmetry. It is clear that according to context the orderings may be brought about by changes in average density (i.e in V at fixed N , say) or by changes when the system is in contact with a supplied heat bath (i.e in temperature for a canonical arrangement), or both.

It is immediately evident that in this same limit (1) and (2) possess both continuous translational and rotational symmetry. Yet it is a matter of common experimental experience that at sufficiently low temperature (with

the exception of the helium at normal pressures), this symmetry in the nuclear degrees of freedom is broken in the states taken up by (1) or (2), specifically in the profusion among the elements of crystalline phases. There is also no specific reference to the spin of the electrons (or of the nuclei). In the presence of a magnetic field, with associated vector potential $\mathbf{A}(\mathbf{r})$ the modifications to (1) or (2) follow from the minimal substitutions $\hat{p}_{\alpha i} \rightarrow \hat{p}_{\alpha i} - (e_{\alpha}/c)\mathbf{A}$, and the ensuing Hamiltonian continues to preserve some of the original symmetry of H . But once again this symmetry can be broken and (1) admits of phases with spontaneous magnetic order (e.g. for $Z = 24$, under ordinary conditions). This order resides in the electronic spin degrees of freedom, and in a comparative sense this elementary observation now raises the central questions to be addressed here, namely whether further order in the spatial degrees of freedom may arise and then whether order involving both may occur. Independent of the symmetry of the developing phases the form of (1) suggests the emergence of scaling laws for the thermodynamic and correlation functions (and these have been verified explicitly for $Z_a = 1$ [7]).

Before proceeding, it may be noted that for $Z_a = 1$, (1) (or (2)) represents the Hamiltonian for hydrogen, where m_n/m_e takes its lowest value, namely 1836, and where quantum effects of the nuclei are most prominent. The case $Z_a = 3$ corresponds to the first metal in the periodic table under normal conditions, and it will be discussed further below. For $Z_a = 1$ the scale of the associated collective modes is crucial to the possibility of superconducting states of hydrogen when it enters a metallic phase. For values of Z_a larger than unity, and especially for elements taking up metallic states at one atmosphere, (1) leads to a class of electronic states (the 'core states' possessing their own internal fluctuational physics) significantly localized around nuclei, but not especially different in terms of local electronic density from their strictly atomic counterparts. In fact, from the tight binding perspective these states are not expected to change appreciably with currently attainable pressures which presently impel reductions in linear dimensions of a factor of two or more. However (and a key point for what follows), these changes can nevertheless lead to significant outer core-state overlaps, and the consequence of this when coupled with the requirement that the valence electrons states remain orthogonal to the core-states, is of considerable physical importance.

Obviously the electrons most affected in the process of formation of the condensed state are the valence electrons and in the lighter elements the primary physical effects of the remaining (core) electrons is often included through the concept of a pseudo potential, generally non-local. With this understanding Hamiltonian (1) is then modified to reproduce simply the valence electron spectrum. To within density dependent constants (1) is therefore replaced by

$$\hat{H} = \hat{T}_n + \hat{T}_v + \frac{1}{2} \int_v d\mathbf{r} \int_v d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ Z_v^2 g(\mathbf{r}, \mathbf{r}') \hat{\rho}_n^{(2)}(\mathbf{r}, \mathbf{r}') - 2Z_v f(\mathbf{r}, \mathbf{r}') \hat{\rho}_n^{(1)}(\mathbf{r}) \hat{\rho}_v^{(1)}(\mathbf{r}') + \hat{\rho}_v^2(\mathbf{r}, \mathbf{r}') \} \quad (3)$$

where Z_v is the long range charge associated with an ion, and $g(\mathbf{r}, \mathbf{r}')$ represents the corrections to pure Coulombic behavior originating with core electrons. In a similar way the term $f(\mathbf{r}, \mathbf{r}')$ represents the non-local pseudopotential modifications to point-ion behavior. The familiar band-structure problem emerges from one-electron approximations to (3) when the masses of the nuclei are infinite and the one- and two-particle density operators are the c -numbers corresponding to coordinates simply taken as the fixed sites of a perfect crystalline structure.

Though the Hamiltonians are modified (in proceeding from (1) to (3)) the same basic physical questions clearly obtain with respect to the nature of both equilibrium and non-equilibrium states of \hat{H} , and of states of order or broken symmetry. Once more the possibility of spontaneous magnetic order is evident (this again residing predominantly in the valence electron structure). Hamiltonians (1), (2), and (3) can immediately be generalized to multielement systems, and the known states of broken electronic symmetry then include spin-density and charge-density wave phases, ionic systems, and so on. These might be referred to as states of diagonal long range order, a familiar classical concept.

3. THE OCCURRENCE OF SUPERCONDUCTING ORDER

The pertinent issue here concerns the possibility of off-diagonal long-range electronic order in the valence electron system, especially in the

lighter elements and in their combinations. Of particular importance is the role played by the choice of average density or equivalently the average inter-ion spacing. To approach this problem for the valence electrons, note that underlying (3) is the quite standard quantum mechanical problem obtained by replacing fixed ions by a rigid, continuous and uniform charge distribution, $e\bar{\rho}_v = eNZ_v/V$.

The result, see also (2a), is

$$\hat{H}_v = \hat{T}_v + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ \hat{\rho}_v^{(2)}(\mathbf{r}, \mathbf{r}') - 2\hat{\rho}_v^{(1)}(\mathbf{r})\bar{\rho}_v + \bar{\rho}_v^2 \} \quad (4)$$

the much studied interacting electron gas problem. The constants of this Hamiltonian (\hbar, m_e, e) define the familiar atomic unit of length $a_0 = \hbar^2 / m_e e^2$, in terms of which the standard linear measure r_s of average inverse valence electron density (through $(4\pi/3)r_s^3 a_0^3 = 1/\bar{\rho}_v$) emerges. Though formally independent of spin (4) admits of magnetically ordered states for sufficiently dilute conditions (or large r_s). It also takes up prominent states of continuous symmetry (the Fermi liquid for $r_s \sim O(1)$) and, again for sufficiently large r_s , states of broken translational symmetry (the Wigner crystal, or a Wigner crystal with a basis). The central issue for the viewpoint to follow is whether states of (4) can be found that spontaneously break a gauge symmetry in the presence of a magnetic field. As will be seen this may well be the case and the question can therefore be posed again, first for Hamiltonian (3) representing the particular static periodic system for which $\langle \bar{\rho}_e^{(1)}(\mathbf{r}) \rangle$ conforms to this symmetry, and then finally for (1). According to chosen conditions the latter can again represent a periodic system but only on time scales long compared with mean phonon periods. As noted above a control parameter is implicit in this analysis and it is mean density, this presently being an experimental variable of some consequence.

An *in principio* answer to the fundamental question on the symmetry of the ground state of the interacting electron gas was provided in 1965 by Kohn and Luttinger [8] who argued that pairing ground states for the homogeneous interacting electron gas might well be preferred over the normal Fermi liquid (but in energetic measures not greatly). In terms of static interactions their argument was centered in part on the presence of

Friedel oscillations (and hence attractive regions) in effective electron-electron interactions. More formally, the kernel of the Eliashberg equation contains contributions (especially from ladder diagrams) that can very much favor formation of a paired state [9-11]. In fact this may even be seen as the second of two possible symmetry breakings actually 'detected' by the presence of a vector potential, \mathbf{A} . The first involves its role in detecting an insulator to metal transition. Thus when (4) is augmented to include the effects of \mathbf{A} , it can be shown [12] that the consequent ground-state energy per electron (i.e. $\langle H_v \rangle / N$) satisfies

$$\left(\frac{d}{dr_s} \right) \left(\frac{\langle \hat{H}_v \rangle}{N} \right) + \frac{1}{r_s} \left(\frac{\langle \hat{T}_v \rangle}{N} + \frac{\langle \hat{H}_v \rangle}{N} \right) = \frac{1}{r_s} \left(\frac{V}{N} \right) \frac{\mathbf{A} \cdot \mathbf{J}}{c} \quad (5)$$

where \mathbf{J} is the current density in the presence of \mathbf{A} . Precisely the same result obtains [12] for a charged two-component system (corresponding, for example, to (1)); the result is exact and, importantly, it holds independent of the symmetry of the states actually taken up, in particular for states displaying off-diagonal long-range-order. But among such phases might well be in insulating states, in which case $\mathbf{J} = 0$, necessarily. If so then so far as the energy is concerned, and for the limiting case of a system with the Kamerlingh-Onnes ring topology mentioned earlier, an insulating state will then not detect the presence of \mathbf{A} , an important distinction first emphasized by Kohn [13]. As has been emphasized in Ref [12], a transition from insulating to metallic state can actually be viewed as the breaking of a global gauge symmetry (and the condensation of gauge bosons). Accordingly given the breaking of a gauge symmetry associated with formation of the superconducting state in the presence of a magnetic field, it may be interesting to seek a deeper connection between superconductivity and the metal-insulator transition [12].

This notion evidently gains more prominence when the same question is asked of Hamiltonian (3); in a one-electron approximation this eventually leads, as noted, to band-structure. For the light elements, or those dominated by s - p character, treatments of (3) involving structural perturbation theory have been generally successful in accounting for observed atomic arrangements. Nevertheless, the possibility of inherent electronic instability was recognized, particularly by Overhauser [14], and notably that the states could be susceptible to exchange driven electronic transitions leading either

to spin-density waves or charge-density waves. Utilizing a Hubbard approach, at fixed static structure, Siringo et al [15] observed that commensurate charge-density-waves might even develop in the alkali series leading to a metal-insulator transition at high compression. But when full relaxation of nuclear coordinates is permitted, very significant structural complexity seems to occur, at least for infinitely massive nuclei. This has been predicted to be the case for lithium and sodium [16, 17], and is even observed to be the case in the higher s-p alkali series.

Yet the primary issue still remains, namely whether full restoration of electron-electron interactions can again lead to pairing ground-states for the valence electrons but now under far more general conditions, and especially whether periodicity in the underlying lattice, and the possible occurrence of complex structures just mentioned, can enhance this prospect. Kohn and Luttinger's question in a band context has quite interesting features since the effective interaction can be appreciably modified in a system with discrete translational symmetry [18]. This is notably so in multi-band systems [19-23] and especially the case when electron and hole bands are both prominent in the single-particle electronic structure. Indeed, the most effective situation appears to be the case where the system is compensated; here fluctuations are necessarily of a compensated correlated form, and these actually lead to attractive contributions to the effective electron-electron interaction [24]. When applied to the case of a proton-paired metallic phase of hydrogen, the enhancements to the predicted transition temperatures are significant [25].

Thus, the simplest and earliest approach to the inclusion of many-electron effects is the Thomas-Fermi (TF) method, and it is immediately useful in the scale it sets when electron-electron interactions are restored. In a BCS viewpoint the measure of direct electron-electron repulsion is

$$\mu = \langle N_0 v_c(\mathbf{k}' - \mathbf{k}) \rangle \quad (6)$$

the average being taken over a spherical Fermi surface whose diameter is $2k_F$. In the above $N_0 = (1/4\pi^2)k_F^3 / \varepsilon_F$ is the (intensive) density of states per unit volume, for a given spin, evaluated at the Fermi energy ε_F . When many-body effects are treated in the TF approximation, and wavevectors are normalized to $2k_F(\mathbf{x} = \mathbf{k} / 2k_F)$, and $(k_0^2 / 2k_F) = \gamma = (4/9\pi^4)^{1/3} r_s$, where k_0 is the Thomas-Fermi wave-vector), then

$$N_0 v_c(\mathbf{x} - \mathbf{x}') = (\gamma^2/2) / \left((\mathbf{x}' - \mathbf{x})^2 + \gamma^2 \right) \quad (7)$$

the average of this over a sphere of unit diameter then giving $(\gamma^2/2) \ln(1+1/\gamma^2)$. Inclusion of retardation effects then leads to a first estimate for the Coulomb pseudopotential namely;

$$(1/\mu^*) = \left[(\gamma^2/2) \ln(1+1/\gamma^2) \right]^{-1} + \ln(\hbar\omega_{p,e}/\hbar\omega_p) \quad (8)$$

where $\hbar\omega_{p,e}$ is the electron plasmon energy and $\hbar\omega_p$ is the corresponding quantity for the ions. Standard estimates for these are already sufficient to yield the well known values $\mu^* \sim 0.1$; for μ itself the figure is ~ 0.2 .

Detailed inclusion of electron dynamics (well beyond TF) can lead to further reductions in μ^* . Intrinsic pairing (i.e where the effective electron-electron interaction acquires no additional enhancements from, for example, phonon based fluctuations) has been studied in some detail for single-band systems as noted [9-11], but only modestly for multi-band situations. The pairing tendencies also seem very much enhanced when dimensionality is reduced [25,26]. Included under this broad rubric would be the electronic fluctuation that arises from the charge corresponding to the class of electron states classified above as localized and specifically associated with bound states. Though localized plasmons might exist in principle for such states (these attributable to dynamic monopoles) a further important class of excitations (they are also propagating) is the set of polarization waves associated with localized charge but periodically arranged [28] (these attributable to dynamic multipoles). The energies of these are formally contained within appropriate ground state functionals, but it is known now that their development requires a non-local treatment of such functionals (Van der Waals attraction, the most prominent manifestation of such effects, mandates correlated dipolar fluctuations). For the present it may be noted that quantized waves of polarization are coherent and are clearly synthesized from such correlated fluctuations.

4. NUCLEAR AND ELECTRONIC FLUCTUATION COMBINED.

These correlated fluctuations themselves ‘ride’ on a further set of coherent fluctuations taking place at a much lower frequency scale and normally attributed to the phonons, the traditional exchange Bosons associated with superconductivity. Real systems are never devoid of ionic or nuclear motion, and at the very least it is now Hamiltonian (3) (and eventually its extension to alloys) that applies for a full discussion of superconductivity; density fluctuations in the nuclear coordinates are omnipresent and of course their effects on electronic ordering have been evident for quite some time. An elementary estimate of the relative importance of (monopole) polarization arising from phonons and the (multipole) equivalents arising from internal fluctuations, primarily of a dipole character, can now be easily given.

First, valence and core electrons are formally identical; however, the separation of valence and core electron density is dictated by the standard view of atomic physics. Thus for an ion at j , coordinates $\mathbf{r}_{j,i}$ are assigned to the $Z_a - Z_v$ electrons designated as core electrons, the understanding being that the states of the system are such that $\langle \mathbf{r}_{j,i}^2 \rangle^{1/2}$ is a small quantity ($\leq a_0$). Thus if \mathbf{u}_j is the displacement of an ion at site j arising from phonons, then the one-electron density operator is approximated by

$$\hat{\rho}_e^{(1)}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_{e,i}) + \sum_j \sum_i \delta(\mathbf{r} - \mathbf{R}_j - \mathbf{u}_j + \hat{d}_j/e) \quad (9)$$

where the second term is taken to account for electronic density that will reside in localized states, and the first corresponds to the valence electron density. In the above \mathbf{R}_j is a lattice site, and the dipole operator \hat{d}_j for site j is written as

$$\hat{d}_j = \sum_i (-e) \mathbf{r}_{j,i} \quad (10)$$

It is useful to re-emphasize at this point that the generalized Kohn-Luttinger question is being asked for the case where all the \mathbf{R}_j are

rigorously zero (i.e. for the possibility of intrinsic pairing in the valence electrons arising from fluctuation in both itinerant and localized charge).

But next, consider the characteristic scales of \mathbf{u}_j and \hat{d}_j ; these follow from noting that

$$\langle u_j^2 \rangle^{1/2} \sim (m_e/m_n)^{1/2} \left(\frac{e^2/2a_0}{\hbar\omega_D} \right)^{1/2} a_0 \quad (11)$$

where $\hbar\omega_D$ is a typical phonon energy, whereas

$$\langle \hat{d}_j^2 \rangle^{1/2} / e \sim \left(\frac{\hbar\Omega}{e^2/\alpha^{1/3}} \right)^{1/2} \left(\frac{\alpha}{a_0^3} \right)^{1/3} a_0 \quad (12)$$

where $\hbar\Omega$ is a typical excitation of an ion (or ion complex) whose polarizability is α . Though the time scales of the two classes of excitations differ appreciably (as they do between electrons and phonons) it should be noted, once again, that both are coherent in a crystalline environment. The main point, however, is that typical excitation energies $\hbar\Omega$ may be a notable fraction of an atomic unit, and for ions with significant core spaces the dipole polarizability can also reach appreciable fractions of a_0^3 . Thus depending on system $\langle \mathbf{u}_j^2 \rangle^{1/2}$, and $\langle \mathbf{d}_j^2 \rangle^{1/2} / e$ can be comparable and it is apparent that interference between these terms will not always be constructive (this could well be the case in a simplified view of the noble metals, for example, where a tight-binding view of the d -electrons is taken).

With the scale of lattice displacement approximately established it is also useful to recall that phonons have been the traditional and indeed dominant mechanism for pairing, and a supporting argument for this is usually to be found in the normal state transport properties, for example the static resistivity. Thus in the static resistivity common arguments hold that at low temperatures and in three-dimensions the number of phonons available to scatter electrons rises as T^3 . Of these a fraction $\sim T^2$ will satisfy the constraint restricting scattering to a (Fermi) surface. For normal scattering processes, the quasi-classical Boltzmann equation introduces a factor $(1 - \cos\Theta) \sim q^2 \sim T^2$ into the determination of the actual current density. Here Θ is the angle between velocity vectors before and after scattering. Finally, the

electron-phonon interaction leads to a scattering rate $\sim q \sim T$ and hence for normal processes to an overall T^5 rise in resistivity (the Bloch-Grüneisen ‘law’). Note, however, that for strong interband or Umklapp processes, and a Fermi surface in many sheets (and possibly with varying effective masses) the factor $(1 - \cos\Theta) = 2\sin^2\Theta/2$ will lead instead to averages close to a constant (the velocities which are normal to the constant energy surface now suffer large relative changes in the scattering event).

This last argument may be of particular relevance to a layered or near two-dimensional system, for here the Fermi surface can become a sequence of Fermi cylinders, and of the now order T^2 phonons only a measure $\sim T$ will satisfy the constraints to lie on these cylinders. And if the degree of doping is such that the Fermi curves again lie in several zones, and if again the scattering is strong, the factor $(1 - \cos\Theta)$ for transitions between different bands will once more average to an approximate constant. Finally, for scattering that is being dominated by electron-phonon interactions favoring such interband effects, the corresponding scattering rate is once more proportional to K (a reciprocal lattice vector). Overall in near two-dimensional system, the resistivity should therefore be roughly proportional to T (also the high temperature limit) but with minor corrections anticipated to account for the expected departure from absolute Fermi curves in what is a strictly three-dimensional environment, these clearly being dependent on the degree of doping. When conditions are such that normal process do eventually dominate, it is clear that a higher dependence on T will again be expected (possibly T^4), but over a relatively small range of temperatures.

It is evident that if intrinsic electronic effects are insufficient to bring about a superconducting instability, then additional contributions to pairing may be sought in these phonon terms whose presence should be revealed in normal state transport, as described above. Traditionally the measure of possible phonon attractive contributions, $\langle N_0 V_{ph} \rangle = \lambda$, originating with screened electron-phonon coupling $g_q(\mathbf{k}', \mathbf{k})$ associated with the scattering of an electron from \mathbf{k} to \mathbf{k}' , by a phonon of wave-vector \mathbf{q} . In this case the average is required of

$$-N_0 2 |g_q(\mathbf{k}', \mathbf{k})|^2 / \hbar \omega(\mathbf{k}' - \mathbf{k}) \quad (13)$$

where for a Debye spectrum and longitudinal modes for nuclei of mass Am_n

$$g_q(\mathbf{k}', \mathbf{k}) = \frac{4\pi e^2 f(\mathbf{k}', \mathbf{k})}{((\mathbf{k}' - \mathbf{k})^2 + k_0^2)} i(\mathbf{k}' - \mathbf{k}) \cdot \left(\frac{\hbar}{2cq} \cdot \frac{N/V}{Am_n} \right)^{1/2} \quad (14)$$

Here the actual sound speed will be written as $c = \alpha v_F \{3m_e/Z Am_m\}^{1/2}$ the role of the dimensionless α being to correct the standard Bohm-Staver estimate. For *normal* intraband ($\mathbf{k}' - \mathbf{k} = \mathbf{q}$) processes, the contribution to $\langle N_o V_{ph} \rangle$ follows from an average on a sphere of unit diameter (but with the restriction $q = |\mathbf{k}' - \mathbf{k}| < k_D$, also normalized) of

$$-N_o v_c(\mathbf{x} - \mathbf{x}') \left\{ \frac{f^2(\mathbf{x}', \mathbf{x})}{\alpha^2} \cdot \frac{\gamma^2}{(\mathbf{x}' - \mathbf{x})^2 + \gamma^2} \right\} \quad (15)$$

The quantity α is < 1 ; for elevated densities f increasingly reflects the short range repulsive region of the pseudopotential and it can become appreciable. As is well known, depending on system the phonon mechanism may well prevail over the direct electron repulsion term but that inclusion of Umklapp terms ($\mathbf{k}' - \mathbf{k} = \mathbf{q} + \mathbf{K}$, with \mathbf{K} a reciprocal lattice vector) can increase the likelihood considerably. From the definition of N_o , (and for NZ electrons in a volume V) it follows that $|g_q(\mathbf{k}', \mathbf{k})|^2 \sim (V/ZN)(\epsilon_F \cdot \hbar \omega_D)$ and g is therefore proportional to the geometric mean of the electron and phonon energy scales. The coupling can therefore be large and, again depending on system, the phonon-term $\lambda = (N_o V_{ph})$ may then approach the strong-coupling values ~ 1 .

For a full discussion of the theory underlying determinations of T_c from phonon based mechanisms, particularly within the Eliashberg framework, the reader is directed to the review by Allen and Mitrovic [29]. Here the issue devolves on the essential input, arising from the interactions defining the problem at hand (and subsequently entering the kernel of the linearized Eliashberg equations) and on the role of average density with its ability to alter the relative contributions of valence electron coupling to the various excitations discussed above. In the quest for off-diagonal-long-range-order for the valence electrons (and hence in formulating the establishment of the overall effective electron-electron interaction) the sources to be examined are (i) the valence electrons themselves, but in a periodic arrangement and in multiple bands, (ii) the internal dynamics of the core states and their coherent excitations emerging once more from a time average periodic

environment, and (iii) the phonons which are traditionally treated within an approximation of rigid, or near rigid ions. It is to be emphasized again that in atomic complexes, with sizable spatial scales, the contributions from (ii) may be especially significant. The time scales of these excitations are quite disparate and this is already encountered in the comparison of electron plasmon frequencies and typical Debye frequencies. Likewise there is a significant difference between the times scales of phonons and polarization waves, but not especially between polarization waves and plasmons. It should be noted that all the excitations suffer damping. And it should also be particularly noted that spin fluctuations in the valence electron system can also be important to the pairing problem.

5. PRESSURE, ELECTRONIC STRUCTURE, AND OFF-DIAGONAL-LONG-RANGE-ORDER

On the basis of an assessment of the rankings in energy of the various terms entering (1), or its reductions in a periodic system, it has been suggested [18] that the problem of superconductivity could be approached via Eliashberg theory by starting first with such fluctuational attraction as may arise from *all* electrons in a crystalline space, and only later augmenting these with the additional interactions arising from phonons and, as indicated above, from internal fluctuations of localized electronic charge. The simplest cases to consider are systems where the latter can be neglected (generally where $\hbar\Omega$ is large but α is compensatingly small). This viewpoint can change considerably however when the system is constructed from such elements in combination.

The case $Z = 3$, lithium, conforms well to this approximation, for which (1) reads

$$\hat{H} = \hat{T}_n + \hat{T}_v + (1/2) \int_v d\mathbf{r} \int_v d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ 9\hat{\rho}_n^{(2)}(\mathbf{r}, \mathbf{r}') - 6\hat{\rho}_n^{(1)}(\mathbf{r})\hat{\rho}_e^{(1)}(\mathbf{r}) + \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') \} \quad (16)$$

and (3) represents an effectively monovalent system described by

$$\hat{H} = \hat{T}_n + \hat{T}_v + (1/2) \int_v d\mathbf{r} \int_v d\mathbf{r}' v_c(\mathbf{r}, \mathbf{r}') \{ g(\mathbf{r}, \mathbf{r}') \hat{\rho}_n^{(2)}(\mathbf{r}, \mathbf{r}') - f(\mathbf{r}, \mathbf{r}') \hat{\rho}_n^{(1)}(\mathbf{r}') \hat{\rho}_v^{(1)}(\mathbf{r}) + \hat{\rho}_v^{(2)}(\mathbf{r}, \mathbf{r}') \} \quad (17)$$

In the supposed limit $m \rightarrow \infty$ and for crystalline symmetry, the one-electron approximation to (17) leads at standard densities to the familiar band structure description of metallic lithium, originally studied at high density by Boettger and Trickey [29]. Recent total energy treatments [16] of (17) (via density functional methods) show that at one atmosphere the ground-state structure taken up conforms to 9R ($\delta - Sm$); at progressively higher pressures fcc is first preferred, in agreement with experiment. However, at around 40 GPa several quite complex structures are predicted to become competitive, and indeed complex structures are found experimentally [30]. Most interestingly for the subsequent problem of broken electronic symmetry, the valence bands are *diminishing* in width at the corresponding densities, an effect attributable to valence-core orthogonalization which progressively diverts valence electron density into interstitial regions.

Elementary arguments now strongly suggest [16] the possible onset of off-diagonal-long-range-order in the valence electrons once \hat{T}_n is restored, high dynamical energies then being expected at elevated densities. First, as a consequence of band narrowing the density of states is expected to increase. Second, steady reduction in inter-ion separation carries with it the expectation that the repulsive core region of the pseudopotential will gain increasing prominence; in other words the factor f in (17) will lead to a generally stronger electron-ion interaction and hence a stronger electron-phonon interaction. This is not unlike the situation encountered in dense hydrogen, which leads to the prediction of elevated superconducting transition temperatures for metallic states. Here the same arguments prevail, except that should lithium take up a complex structure with an *even* number of ions per cell, then the ensuing complex compensated metallic system further favors pairing through the intrinsic mechanisms discussed above. Experimentally, lithium now seems to be an element with one of the highest of transition temperatures, this first being measured (with a resistive technique) by Shimizu et al [31], and later with an inductive technique by Struzhkin et al [32], and later still with an inductive method in a near hydrostatic environment by Deemyad and Schilling [33]. The measurements show a clear progression of phases clearly illustrating the role of pressure in tuning both structure and the contributions to pairing from nuclear and electronic sources. But Deemyad and Schilling [33] also report that above 67 GPa the observation of superconductivity abruptly disappears, and if substantiated this raises the prospect of further changes in symmetry,

including even the possibility of a transition from a metal to an insulator upon *increase* of density [16].

It is evident that the arguments just outlined for lithium (these being invoked even earlier for hydrogen) can also be invoked for certain light elements in combination. The most interesting class appears to be those hydrogen rich compounds that are actually dominated by hydrogen, these eventually being driven metallic by steady increase in density. Attention is then focussed on the Group IVa hydrides which, among chemically simple systems are among the most hydrogen dominant as may be found [22]. Further, upon an assumption of overlapping bands, they will contain 8 electrons per cell in simple structures, exactly as is the case for MgB_2 at one atmosphere. What endows these systems with especial physical interest is the fact that prior densification of hydrogen is being attained through the presence of other constituents; it is a form of chemical pre-compression. As a commentary on the likely role of the lower modes in these alloys it may be noted that tin and lead as pure constituents are among the strong coupling superconductors, and silicon and germanium also have notable superconducting transition temperatures when, impelled by pressure, they enter the metallic state.

The Group IVa hydrides include methane, silane, germane, stannane and plumbane, the last being marginally stable but nevertheless an important candidate for study at high pressures. These encompass a considerable spread in mass and hence through systematic deuterations they offer, in metallic states, a possibly unique opportunity to assess broken gauge symmetry and the theory of strong coupling superconductivity in general. An equally important point is that the pressure required to attain a metallic state with r_s typically around 1.5 is considerably less than is required for pure hydrogen itself [34] providing only that there is no disproportionation. Given the fact that an even number of electrons will be found in unit cells, the metals will be compensated and again this presents a situation especially favorable to a reduction in Coulomb pseudopotentials.

Arguments for considering *ternary* Group IVa hydride alloys can also be advanced [34] in order to maximize the contributions of lower modes. An interesting question then centers on symmetry; will such arrangements favor stoichiometric arrangements or, reverting to the initiating example (the quenched ammines) will disorder continue to play an as yet unexplained microscopic role in superconductivity? From the example of the Group IVa hydrides given above it would appear that if the relatively small gaps separating the Li 2s bands and the hydrogen bands (as reported by Kohanoff

et al. [35]) could be closed by application of pressure, then the common bands should begin to exhibit a degree of similarity to the hydrides. In particular the hydrogens are now in an environment of itinerant electrons. Accordingly for $Li(NH_3)_4$ and indeed for many of the metal amines, a case can be made for the presence of high temperature superconductivity at higher densities. Note that the remnant polarizability associated with the molecular order can still be expected to be large.

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