Kondo Insulator: p-wave Bose Condensate of Excitons

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In the Anderson lattice model for a mixed-valent system, the $d-f$ hybridization can possess a $p$-wave symmetry. The strongly-correlated insulating phase in the mean-field approximation is shown to be a $p$-wave Bose condensate of excitons with a spontaneous lattice deformation. We study the equilibrium and linear response properties across the insulator-metal transition. Our theory supports the empirical correlation between the lattice deformation and the magnetic susceptibility and predicts measurable ultrasonic and high-frequency phonon behavior in mixed-valent semiconductors.

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Mixed valent compounds containing $f$-electrons in their insulating phase possess very distinctive electronic properties showing strong electron correlation, and are commonly called Kondo insulators, even though they are often not in the Kondo regime. The insulating state may be regarded as a condensate of the slave bosons which are used to simulate the high energy cost of too many $f$-electrons on the same ion site. Through the $f$-level and conduction band hybridization, this Bose condensate drives the condensation of $f$-hole-conduction-electron excitons, creating a band gap. This theory has been used to explain a number of thermal, transport, and optical properties.

In this paper, we adopt the same slave-boson treatment of the Anderson Lattice Model to explore the consequences of the $d$-character of the conduction electrons so that the $d-f$ hybridization at wave-vector $\mathbf{k}$ exhibits inversion antisymmetry, i.e.

$$V(-\mathbf{k}) = -V(\mathbf{k}) = V^*(\mathbf{k}).$$

(1)

This leads to odd-symmetry pairing of $d$-electrons and $f$-holes. (See below on how a $p$-wave symmetry can arise.) Coupling of the $d-f$ excitons to the lattice deformation leads to a structural phase transition known as the ferroelastic transition. We deduce the temperature dependence of the equilibrium properties (lattice distortion and phase diagrams) and of the linear responses (including the magnetic susceptibility, elastic constants, phonon frequency and damping). These properties show the characteristic dependence on the $p$-wave condensate and their observation can be used to distinguish the $s$- or $p$-wave nature of the Kondo insulator state. We shall make the case below that some of the $p$-wave characteristics have already been found in certain Kondo insulators. The establishment of the $p$-wave characteristics in a class of Kondo insulators could be of importance in providing a central framework for understanding their unusual properties in terms of the symmetry of the condensate.

The contrast between the $p$-wave condensate in the Anderson lattice and the $s$-wave condensate in the Falicov-Kimball model should also be noted. In the latter, the $d-f$ hybridization is neglected in comparison with the strong $d-f$ Coulomb attraction which is responsible for the exciton condensation. Since each $d-f$ exciton carries a dipole moment, the condensate behaves like an “electronic” ferroelectric. On the other hand, from symmetry considerations, the $p$-wave condensate does not produce a macroscopic electric polarization but can yield a finite lattice distortion. Responses to lattice vibrations induce coupling to the collective modes of the $p$-condensate, which are fundamentally different from the electronic ferroelectrics. When both the hybridization and $d-f$ interaction are present, the properties of the $s$ and $p$ wave coexist. Details will be presented in a long paper while here we concentrate on the limiting case when hybridization dominates, in contrast to the other limit.

We consider a model with one $f$-electron and one conduction electron per unit cell. For simplicity, we include only the one component each of the $d$ and $f$-bands which yield the hybridization obeying Eq. (1) and neglect the $f$ orbital degeneracy. To consider the formation of the condensate and the related dynamic response, we replace the onsite interaction in the Anderson model by the slave-boson constraints and further retain only zero-momentum slave bosons which are present in macroscopic numbers. The Anderson Hamiltonian is thus reduced to:

$$H = \sum_{\mathbf{k}\sigma} [\epsilon(\mathbf{k}) - \mu] d_{\mathbf{k}\sigma}^\dagger d_{\mathbf{k}\sigma} + (\epsilon_f - \lambda - \mu) \sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}^\dagger f_{\mathbf{k}\sigma}$$

$$+ \frac{1}{\sqrt{N_s}} \sum_{\mathbf{k}\sigma} \{V(\mathbf{k}) d_{\mathbf{k}\sigma}^\dagger f_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma}^\dagger + h.c.\} + \lambda \left( N_s - b_{\mathbf{k}\sigma}^\dagger b_{\mathbf{k}\sigma} \right),$$

(2)

where $d_{\mathbf{k}\sigma}, f_{\mathbf{k}\sigma}, b$ are annihilators for the conduction and $f$ electrons of wave vector $\mathbf{k}$ and spin $\sigma = \pm 1$, and slave-boson of zero momentum. The conduction band energy is denoted by $\epsilon(\mathbf{k})$ and the chemical potential by $\mu$. $\lambda$ is the Lagrange multiplier which enforces the constraint of at most one $f$-electron per cell for $N_s$ cells (on average).

The equations of motion for the $d-f$ exciton condensate are physically transparent upon expressing the density...
matrix in terms of a pseudo-spin vector $S_k$:

$$S_k^z = \frac{i}{2} S_k^y = \langle d_{k\sigma}^+ f_{k\sigma} \rangle,$$

$$S_k^+ = \langle d_{k\sigma} f_{k\sigma} \rangle.$$

(3)

In the mean-field approximation, the spin vector satisfies a Bloch equation [8]: $S_k = \Omega_k \times \Delta_k$, where the precession frequency is given by

$$\Omega_k = 2 \left[ \Re \left[ V^+(k) \frac{\langle b \rangle}{\sqrt{N_s}} \right] \right] + \left[ V^+(k) \frac{\langle b \rangle}{\sqrt{N_s}} \right], \xi(k), \xi(k) ,$$

where $\Re$ and $\Im$ denote the real and imaginary parts and $\xi(k) = \frac{1}{2}[\epsilon(k) - \epsilon_f + \lambda]$. The expectation value at a finite temperature of the slave-boson condensate $\langle b \rangle$ is driven by the exciton condensate $\langle d_{k\sigma}^+ f_{k\sigma} \rangle$:

$$i \partial_t \langle b \rangle + \lambda \langle b \rangle = \frac{1}{\sqrt{N_s}} \sum_{k\sigma} V(k) \langle d_{k\sigma}^+ f_{k\sigma} \rangle.$$ (5)

The zeroth-order (in the absence of external perturbation) solution of the above equations yield the thermal equilibrium state. The spin vector $S_k^{(0)}$ is a unit vector in the direction opposite to the zeroth order precession frequency $\Omega_k^{(0)}$, yielding the exciton order parameter:

$$\langle d_{k\sigma}^+ f_{k\sigma} \rangle^{(0)} = aV^+(k) [f(E_{k+}) - f(E_{k-})] / 2E_k,$$

where $f(E)$ is the Fermi distribution, $a = \langle b \rangle^{(0)} / \sqrt{N_s}$, and the quasi-particle energies are $E_{k\pm} = \frac{1}{2} [\epsilon_f - \lambda^{(0)} + \epsilon(k)] \pm E_k$, where $E_k = \sqrt{[\xi^{(0)}(k)]^2 + a^2 |V(k)|^2}$. From Eq. (6), the exciton order parameter being driven by the hybridization $V(k)$ must have the same symmetry. By Eq. (6), the pairing state is antisymmetric under inversion. More specifically, if $V(k)$ is one of the $p$ components of the hybridization matrix elements between the $d$ and $f$ states, the exciton order parameter would indeed have a $p$-wave symmetry.

To evaluate the mean field phase diagram from the zeroth order equations, we further adopt a simple model with the conduction band having a constant density of states with a bandwidth of $2W$. The hybridization is approximated by $V(k) = i V_0 \text{sgn}(k_z)$, where $V_0$ is a real constant. The vanishing gap case is avoided by choosing the energy surface $\xi^{(0)}(k) = 0$ not to intersect the plane where $V(k)$ vanishes. Some of the results are: (1) At $T = 0$ for arbitrary $\epsilon_f$, the ground state is always a $p$-wave condensate of excitons (correlated insulator). (2) For $\epsilon_f \geq 0$, there is no finite-temperature phase transition. (3) For $\epsilon_f < 0$, there is a second-order phase transition at finite temperature between the correlated insulator and a simple metal.

Figure 1 shows the temperature dependence of the slave boson condensate $a(T)$ for $\epsilon_f = -0.2 W$ and $V_0 = 0.3 W$. The resultant $k_B T_c = 0.123 W$ indicates this case to be in the intermediate coupling region. For the rest of this paper, the numerical results are reported for the same set of parameters.

Two immediate consequences of the odd symmetry exciton condensate are the absence of polarization and the possibility of lattice distortion. For a more quantitative study, we include in the Anderson model a coupling with the strain field $\theta$ through the deformation potential $\Xi(k)$ [9] by replacing $V(k)$ by $V(k) + \Xi(k) \theta$. From the form of the electron-phonon interaction we have included, the deformation potential $\Xi(k)$ arises from the change of the hybridization $V(k)$ to first order in the lattice displacement and, therefore, must have the same odd symmetry under inversion. The lattice deformation creates a stress:

$$s = C \theta + \frac{2}{\sqrt{N_s}} \sum_{k\sigma} \Xi(k) \langle d_{k\sigma}^+ f_{k\sigma} \rangle \langle b \rangle,$$

(7)

where $C$ is the bare elastic constant. The zeroth order terms show that the exciton condensate induces a spontaneous lattice deformation $\theta^{(0)}$. The feedback of the lattice distortion should be included in Eqs. (6) and (8). A tight-binding derivation shows that $\Xi(k)$ is the same order of magnitude as $V(k)$ and the distortion $\theta^{(0)}$ is always less than a percent (see below). Therefore, we may neglect the self-consistent inclusion of the lattice distortion in the determination of the exciton and slave-boson condensates.

Figure 1 also shows the temperature dependence of the lattice distortion $\theta^{(0)}$ in comparison with experiment on Ce$_3$Bi$_4$Pt$_3$, chosen as an example of a class of small-gap
correlated semiconductors \[10,11\]. The deformation potential is approximated in a similar way to the hybridization: \( \Xi(k) = i \Xi_0 \text{sgn}(k_z) \) where \( \Xi_0 \) is a real constant. To fit the experimental curve, we have chosen the parameters given for our simple model and used \( T_c = 350 \text{ K} \), which yields the conduction bandwidth of \( 2W \simeq 0.49 \text{ eV} \). The overall agreement of the calculated curve with the measured curve should not be taken too literally but the support of the spontaneous structural phase transition accompanying the exciton condensation in the mixed-valent system in our theory is noted. This structural transformation belongs to a well-known class of ferroelastic phase transitions \[3\].

By adding a perturbing term to the equations of motion, we can calculate the first-order changes. To calculate the Pauli spin susceptibility, we use the perturbation

\[
H_B = -\mu_B \sum_{k,\sigma} (g_\sigma d_{k\sigma}^d d_{k\sigma} + g_f \sigma f_{k\sigma}^f f_{k\sigma}) B, \tag{8}
\]

where \( B \) is the magnetic field in a fixed direction, \( \mu_B \) is the Bohr magneton, and \( g_\sigma \) and \( g_f \) are phenomenological gyromagnetic ratios for \( f \) and \( d \) electrons. The Pauli susceptibility is

\[
\chi = \mu_B^2 \sum_k |2aV(k)|^2 (g_f - g_d)^2 \frac{[f(E_{k-}) - f(E_{k+})]}{(2E_k)^3} + (2\mu_B^2/k_BT) \sum_{k,s=\pm} g_s^2 f(E_{ks}) \left[ 1 - f(E_{ks}) \right], \tag{9}
\]

where \( g_{\pm} = g_d A_{\pm}(k) + g_f A_{\pm}(k) \) is the effective gyromagnetic ratio for quasiparticles in the mixed \((\pm)\) bands with spectral weights \( A_{\pm}(k) = \frac{1}{2} \{ 1 \mp \xi^{(0)}(k)/E_k \} \). The first sum at the right-hand-side of Eq. (8) is due to interband mixing proportional to \( a^2 \) of the slave-boson condensate, while the second sum is from the individual band contributions. Figure 2 and its inset show the temperature dependence of the spin susceptibility \( \chi \) and its relation with the lattice deformation as well as comparisons with the experimental results for Ce\(_3\)Bi\(_4\)Pt\(_3\) \[10\].

The observed low-temperature upturn of the susceptibility was sample dependent and was ascribed to magnetic impurities. Excluding that feature, the calculated temperature dependence of the spin susceptibility resembles the observation. Fisk et al. \[10\] found an empirical correlation between the lattice distortion and the spin susceptibility, which is intriguing since \( \chi T \) measures the effective moment squared of an isolated magnetic ion. Our theory of this functional correlation provides an alternative explanation in which both properties are driven by the same condensation phenomenon. Moreover, the theory predicts a low-temperature indirect gap of \( |a(0)V_0|^2/W \simeq 44 \text{ K} \), in good agreement with the experimental activation energy of 42 K determined from transport measurement \[11\].

\[
\text{FIG. 2. Temperature dependence of static Pauli spin susceptibility and its correlation with lattice deformation (inset) for } g_d = 2.38, g_f = 1.55 \text{ for the same model as in Fig. 1. Squares are experimental results from Ref. 10 for Ce\(_3\)Bi\(_4\)Pt\(_3\).}
\]

Since the exciton condensation is intimately connected with the structural transformation, one would expect corresponding changes in elastic constants and phonon properties. With the addition of the deformation terms in Eqs. (8) and (9), to first order in the external stress in Eq. (8), the dynamics of the pseudospin and the boson condensate is governed by a set of five coupled linear equations. The linear response deduced from them involves the collective mode in general \[12\]. The elastic constant \( C = C_{\text{cond}} \), with the second being from the response of the condensate. At the high-frequency sound wave limit, where \( \omega \gg \Gamma \) (the linewidth of the collective mode, taken to be of the order of the indirect gap) but \( \omega \ll 2aV_0 \) (the direct gap), the response involves the collective mode and the dynamic elastic constant is

\[
C_{\text{cond}} = 4a^2 N_s \Xi_0^2 \times \frac{4D_2 - 4\lambda D_1 + \lambda^2 D_0 + 24aV_0^2(D_0 D_2 - D_1^2)}{(1 + 4V_0^2 D_1)^2 - V_0^4 D_0(16V_0^2 D_2 - 2\lambda)}, \tag{10}
\]

where \( \lambda = \chi^{(0)} \) for short, and

\[
D_i(\omega) = \frac{1}{N_s} \sum_k \xi^{(0)}(k) f(E_{k-}) - f(E_{k+}) \frac{E_k}{2E_k(\omega^2 - 4E_k^2)}. \tag{11}
\]

The relative velocity change \( \Delta v_s/v_s = \Re(C_{\text{cond}})/2C \) is plotted in the inset of Fig. 3 for our simple model. For the parameters of Fig. 1, the unit of relative change is \( N_s \Xi_0^2/CW \simeq 0.26\%. \) It is evident that its temperature dependence reflects the second-order phase transition and differs greatly from the typical anharmonic effect. In the static or low-frequency limit (\( \omega \ll \Gamma \)), the elastic response is decoupled from the collective mode and is given by the quasi-particle contributions. There is a characteristic step-like drop \[3\] in the inverse static

\[
\text{FIG. 3. Temperature dependence of } \Delta v_s/v_s \text{ in a Ce\(_3\)Bi\(_4\)Pt\(_3\) mixed-valent system.} \]

3
elastic constant at $T_c$, with the magnitude of the drop proportional to $\Xi_0^2$. The static elastic constant is qualitatively different from the high-frequency one.

In the study of high-frequency phonons, we have taken, for simplicity, the electron-phonon interaction to be given by the same deformation potential as above. A phonon, with energy greater than the direct gap ($\omega > 2aV_0$) but limited by the Debye frequency ($\sim 0.1$ eV), can break particle-hole pairs which contribute to the imaginary part of $C_{\text{cond}}$. This is the well-known Landau damping. The relative phonon linewidth contains a term $-3|C_{\text{cond}}|/2C$. Correspondingly, the relative phonon energy change is given by $\Re[C_{\text{cond}}]/2C$. Figure 3 presents the numerical results for such a high-energy phonon within our simple model. The resonance behavior in both the frequency change and damping occurs when the phonon frequency equals the temperature-dependent direct gap. Neutron scattering by phonons should be able to detect such resonances. Similar behavior in superconductors has been predicted and observed.

We have also considered a two-dimensional square lattice with unit cell size $d$ and a conduction band $\epsilon(\mathbf{k}) = -V_W(\cos k_x d + \cos k_y d)$. For hybridization $V(\mathbf{k}) = iV_0 \sin(k_x d/2)$ between a $d$-electron at the corner and an $f$ in between, the ground state is a fully gapped insulator, similar to our simple model presented above. For hybridization $V(\mathbf{k}) = iV_0 \sin(k_x d)$ between $d$-f electrons at neighboring corners the exciton condensate contains nodes in the excitation spectrum. Nevertheless the numerical results for $a(T)$ and consequently the lattice deformation resemble those in Fig.1. Its interesting low-

![FIG. 3. Relative phonon energy change and intrinsic linewidth in units of the dimensionless factor $N_k^2/\omega^2$ for a phonon of unrenormalized frequency $\omega/W = 0.2 + i10^{-4}$ for the simple model described in the text. Inset: Relative velocity change for the case of lattice softening for ultrasound of $\omega/W = 10^{-6}$.](image)

In summary, the additional consideration of the rotational symmetry of the hybridization between $d$ and $f$ electrons to the finite-temperature, mean-field solution of the periodic Anderson lattice using the slave-boson technique reveals the correlated insulator state to be a $p$-wave exciton condensate as well as the existence of a concomitant structural transformation. Theoretical deduction of the temperature dependence of the spontaneous lattice distortion and of the Pauli spin susceptibility have some experimental support. In particular, the empirical correlation between the lattice distortion and the spin susceptibility in the correlated insulator $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ can be explained in terms of the temperature dependence of exciton condensation. Moreover, intimate relation between the symmetry of the exciton condensate and the lattice distortion leads to theoretical predictions of (1) characteristic static elastic constant jump across the phase transition, (2) temperature dependence of the high-frequency ultrasound velocity, and (3) resonance behavior of phonon frequency and damping as the gap parameter varies with temperature. All these consequences of the theory could be easily subjected to further experimental tests in mixed-valent correlated insulators.

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[1] G. Aeppli and Z. Fisk, Comm. Condens. Matter Phys. 16, 155 (1992).
[2] P. A. Lee, et al., Comm. Condens. Matter Phys. 12, 99 (1986).
[3] C. M. Varma, Phys. Rev. B 50, 9952 (1994).
[4] A. Auerbach and K. Levin, Phys. Rev. Lett. 57, 877 (1986); A. J. Millis and P. A. Lee, Phys. Rev. B 35, 3394 (1987).
[5] P. S. Riseborough, Phys. Rev. B 45, 13984 (1992); A. J. Millis in Physical Phenomena at High Magnetic Fields (ed. E. Manousakis et al.), p. 146 (Addison-Wesley, Redwood City, 1992).
[6] A. Bulou, M. Rousseau and J. Nouet, Key Engineering Materials 68, 133 (1992).
[7] T. Portengen, Th. Ostreich, and L. J. Sham, Phys. Rev. Lett. 76, 3384 (1996).
[8] A nonzero expectation value for $b$ would violate a local gauge symmetry. Higher orders of perturbation theory beyond the mean-field level will ensure $\langle b \rangle = 0$ and a power law dependence to the correlator $\langle b(t)b(0) \rangle$ [see, e.g. N. Read, J. Phys. C 18, 2651 (1985)] — there is no true Goldstone mode for this condensate, but the insu-
lating gap, which depends on $b^4$, persists at low temper-
atures.

[9] See, for example, L. J. Sham and J. M. Ziman, *Solid State Phys.* **15**, 221 (1963).

[10] Z. Fisk et al., *J. Alloys Comp.* **181**, 369 (1992).

[11] M. F. Hundley et al., *Phys. Rev. B* **42**, 6842 (1990).

[12] T. Portengen, Th. Östreich, and L. J. Sham, *Phys. Rev. B*, in press.

[13] J. D. Axe, *Physica* **137B**, 107 (1986).

[14] V. M. Bobetic, *Phys. Rev.* **136**, 1535 (1964); P. B. Allen, *Phys. Rev. B* **6**, 2577 (1972).