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LETTER TO THE EDITOR

Excitons at a van Hove singularity

R S Markiewicz
Physics Department and Barnett Institute, Northeastern University, Boston, MA 02115, USA

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Abstract. At a van Hove singularity, there can be an instability towards a saddle-point excitonic phase. Here, the excitonic binding energy is calculated for a model of $La_{2-x}Sr_xCuO_4$, and the crossover from spin density wave to charge density wave with increasing doping is demonstrated.

At the saddle-point van Hove singularity (VHS) of a two-dimensional energy band, the carriers cross over from hole-like to electron-like and the density of states (DOS) has a logarithmic singularity. It has been proposed that high-temperature superconductivity is associated with this VHS [1–4]. Here, it is demonstrated that the divergence involves the formation of excitons which couple the two degenerate VHS. This, in turn, can drive an 'excitonic instability' [5] into a spin or charge density wave.

In a semiconductor, excitons [6] are bound states of holes near the top of the valence band and electrons near the bottom of the conduction band. The negative electron mass near a band maximum translates into a positive hole mass, and positive mass electrons and holes attract one another. Usually, the exciton binding energy E_B is $\ll E_G$, the energy gap, so the electrons and holes must be created by thermal or photoexcitation across the gap. However, if E_G is small, it is possible that $E_B > E_G$. In this case, an electron and hole would lower their energy by binding into an exciton, and the gap spontaneously collapses into an excitonic ground state [5]. This state may involve the formation of either a spin- or charge-density wave (S/CDW). Ordinarily, the residual electron–electron interaction is repulsive, so an SDW is favoured, but an odd-parity exciton can couple to phonons, and if the electron–phonon coupling is strong enough, the instability will favour a CDW.

In $La_{2-x}Sr_xCuO_4$ (LSCO), there are two degenerate VHS, at the X and Y points of the Brillouin zone, which coincide with the Fermi level near the doping of highest T_c (corresponding to $x \approx 0.17$). A quasiparticle near one of these VHS has highly unusual properties, having a negative mass in one direction and a positive one in the other. A quasielectron at one VHS and a quasihole at the other VHS have an interaction that is attractive when they are separated in a direction in which their masses are both positive, but repulsive when the carriers have negative mass. If the carriers have opposite masses, the interaction is very curious: both carriers are accelerated in the *same* direction. However, the two particles are still attracted (repelled) if their reduced mass is positive (negative). This is not a violation of Newton's third law, since the interaction is not really a two-body interaction, but includes the response of the crystalline lattice. To see if there

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can be a net attraction, the usual calculation of exciton binding must be generalized to account for this angular-dependent Coulomb interaction. For an s-wave exciton, the attractive and repulsive forces cancel, leading to no exciton formation. However, a p-wave exciton can take advantage of the purely attractive regions, and thereby form a net bound state.

To simplify the calculation, the screening effect of other carriers will initially be ignored, reducing the problem to a two-body problem that can be solved in the effective mass approximation [6]. If the CuO_2 plane energy band is approximated by

$$E = -2t_0(\cos(k_x a_0) + \cos(k_y a_0)) - 4t_1 \cos(k_x a_0)\cos(k_y a_0) \tag{1}$$

then the dispersion near the X-point VHS is quadratic in k, with anisotropic effective mass

$$1/m_e = \cos^2\theta/m_y - \sin^2\theta/|m_x| \tag{2}$$

where

$$1/m_{x,y} = (\mp 1 - \tau)/m_0$$

$\tau = 2t_1/t_0$ and $m_0 = \hbar^2/2a_0^2 t_0$. A *hole* at the Y-point has the same dispersion, but with $|m_x|$ and m_y interchanged. The value of τ varies in the range -0.5 to -0.7 in different materials, corresponding to the VHS falling at an excess hole doping of ≈ 0.15–0.25 holes per CuO_2 plane. The relative mass

$$1/\mu = 1/m_e + 1/m_h = 2\cos(2\theta)/m_0 \tag{3}$$

changes sign at $\theta = 45°$. In an effective mass formalism, this mass is kept positive, and the sign of the charge adjusted to give the correct response of the quasiparticle to an electric field. The excitonic binding energy can be estimated by a variational calculation. For a p-exciton, the envelope wavefunction is assumed to be $\psi = x\exp(-\sqrt{\rho^2/a^2 + z^2/b^2})/\sqrt{\pi a^4 b}$, with a chosen to minimize the energy (b is left unspecified). For this wavefunction, the variational energy is found to be

$$E = 2\hbar^2/5m_0a^2 + U_0 \tag{4a}$$

$$U_0 = -3e^2/8\varepsilon a. \tag{4b}$$

The minimum energy is found to be

$$E_x = (45/512)e^2/2\varepsilon a_B \tag{4c}$$

$$a \equiv a_1 = (32/15)a_B \tag{4d}$$

and $a_B = \hbar^2\varepsilon/m_0e^2$.

The excitonic binding energy E_x, depends on the renormalized band mass and the background dielectric constant. However, the effective dielectric constant is a function of the exciton radius. For small a, screening by phonons is ineffective, so the large static dielectric constant $\varepsilon_0 \simeq 84$ [7] should be reduced to the smaller high-frequency value, $\varepsilon_\infty \simeq 6$. As a is further reduced, $\varepsilon \to 1$. For a first approximation, then, it will be assumed that $\varepsilon \simeq \varepsilon_\infty$, and $m_0 \simeq 5$ (in units of the free electron mass) [8] in which case $E_x \simeq 170$ meV and $a = 0.13$ nm. Choosing an envelope function with different radii, a, along the x- and y-axes would enhance E_x by a factor of about two. However, the Bohr radius is so small (a is less than the Cu–O separation) that this result is only qualitative.

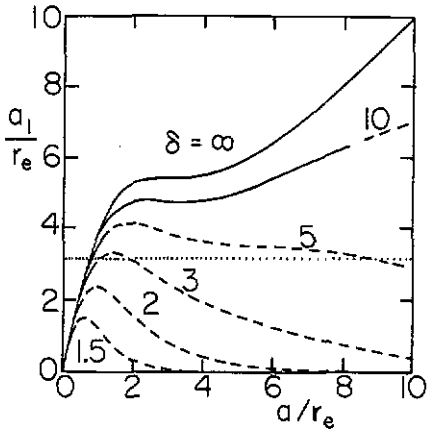

Figure 1. Renormalization of exciton radius due to screening and short-range cutoff of dielectric constant. Dotted line shows calculated a_1 value.

An improved estimate of the binding energy can be made by using a distance-dependent dielectric constant and incorporating free carrier screening, replacing U_0 by

$$U = -U_0 e^{-a/\lambda}[1 + (\varepsilon_\infty - 1)e^{-a/r_e}] \tag{5}$$

where λ is the screening length and r_e is the short-distance cutoff of ε_∞. Writing $y = a/\lambda$, $y_1 = a_1/\lambda$, and $\delta = 1 + \lambda/r_e$, the minimum y is found to be the solution of

$$y_1 = y[\exp(-y)(1 + y) + (\varepsilon_\infty - 1)\exp(-\delta y)(1 + \delta y)] \tag{6}$$

which is plotted in figure 1, for several values of δ.

In analysing these results, it is simplest to begin by neglecting free-carrier screening ($\lambda \to \infty$). The parameter r_e may be estimated from the Coulomb integrals, which have been calculated for LSCO. The values of Hybertsen *et al* [9] are used: $U_d = 10.5$ eV, $U_p = 4$ eV, and $V = 1.2$ eV. These can be interpreted in terms of (5) as follows. The parameter r_e is found by fitting the Cu-on-site Coulomb repulsion U_d to (5), assuming that the average separation of two Cu d-electrons is equal to the Goldschmidt radius [10] of Cu^+, $a_d = 0.053$ nm. This then gives the nearest-neighbour repulsion $V = 1.29$ eV, when the Cu–O separation 0.189 nm is used in (5). Similarly, the O-on-site repulsion U_p is fit by assuming $a_p = 0.091$ nm, somewhat smaller than the Goldschmidt radius of O^{--}, 0.132 nm.

Figure 1 shows how the short-range cutoff, r_e, reduces the excitonic radius from a_1 ($4d$) to a (6). The $\delta = \infty$ curve refers to the situation with no free-carrier screening. For the physical parameters ($a_1 = 0.13$ nm) it is found that the minimum $a < a_d$. Thus, the lowest allowed exciton state corresponds to $a = a_d$. That is, *the exciton is a bound state of an electron and hole on the same Cu site*. This is a microscopic description of the Mott insulating state. The excitonic binding energy corresponding to $a = a_d$ is 0.4 eV.

What happens as the material is doped? I propose that doping introduces excess holes, which screen the excitons, leading to a greatly reduced binding (or unbinding) of the excitons. This is illustrated in Figure 1, which shows the renormalized exciton radius for several values of the screening length. For finite λ, there are two solutions to (6) for each value of a_1: the lower (upper) value of a corresponds to a minimum (maximum) of E_x. Some of the minima are only metastable: the broken parts of the curves in figure 1

correspond to $E_x > 0$. For LSCO, the Thomas–Fermi screening length can be estimated from the Hall density as

$$\lambda^2 = E_F/6\pi ne^2 = \hbar^2 c/6e^2 m_0$$

or $\lambda \simeq 0.064$ nm for $c = 1.32$ nm. For this value, it can be seen (figure 1) that the excitons are marginally unstable. However, an improved calculation (e.g., anisotropic in-plane exciton radius) could find that they are metastable.

Just how doping introduces free carriers is a subtle problem. The picture that is emerging [10] is that this is an effect of band structure renormalization by on-site Coulomb repulsion. As the material is doped toward half-filling, the large U_d drives a Mott transition, in which the Cu and O bands decouple. Since τ arises from O–O hopping, the effective τ value in the Cu band is renormalized towards zero [11]. This result may be restated to say that the VHS remains pinned near the Fermi level as the doping is varied [12].

For τ equal to zero, the Fermi surface is square at half filling, so the excitonic instability would 'gap' the entire Fermi surface, leading to an insulating state. For non-zero τ, there will be a curved Fermi surface, with 'ungapped' parts of the Fermi surface [3]. These portions correspond to a second population of carriers, which are not bound into excitons, and dominate the transport properties of these materials including screening of the excitonic interaction.

This leads to the following picture of the excitonic phase. Near half filling, τ is renormalized to a small value, so the Fermi surface is nearly square and there is little screening charge. Hence, the excitonic binding is strong, and these materials are unstable with respect to an excitonic instability [5], in which the conduction band collapses into an insulating state via the creation of a spin or charge density wave. Since the excitonic radius is so small, electron–phonon coupling is weak [6], so the Coulomb interaction is repulsive, and the spin-density wave instability predominates [5], as previously proposed [13].

As the material is doped, τ increases, leading to additional screening charge, which reduces the excitonic binding energy while increasing a_B. As the Bohr radius increases, the electron–phonon coupling becomes stronger [6], and this will ultimately change the instability from spin to CDW [5]. This CDW is associated with a soft mode of a phonon which would split the two VHS peaks, driving one below the Fermi level (pure hole), the other above (pure electron). Such long-range CDW order has been observed [14] in $La_{2-x}Ba_xCuO_4$, where it strongly suppresses the superconducting transition. In other materials, there is no long-range CDW order, but strong short-range fluctuations. In the excitonic picture, this corresponds to the unbinding of the excitons by free-carrier screening. The short-range order indicates that the excitons survive as long-lived resonances, similar to the M1-excitons found in the optical absorption spectra of ordinary metals [15]. The reduced excitonic binding energy in doped materials may be compared with the energy of the mid-infrared anomaly [16] in these materials, $\simeq$44 meV, which has been interpreted as a manifestation of short-range change-density wave order [3, 17].

Rice and Scott [18] showed that the electron gas in the presence of a VHS is susceptible to a peculiar form of nesting instability, wherein only the large density-of-states associated with the VHS is driven under the Fermi level. The present letter provides a clear interpretation of that instability, which can lead to quantitative calculations of the excitonic binding energy. The excitonic model also provides a possible resolution to a long-standing problem: why is the physics dominated by spin-correlations near half filling, but by charge correlations (and strong electron–phonon coupling) near the VHS?

In the present picture, this is due to the cutoff of electron–phonon interaction at the short-length scale of the excitonic radius.

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