Coulomb Gap in Sodium Tungsten Bronzes

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Recent photoemission experiments on sodium tungsten bronzes, $Na_xTa_yW_{1-y}O_3$, have revealed a depletion of the density of states near the chemical potential in insulating samples. We propose that this depletion is a Coulomb gap, and that these experiments represent the first direct measurement of a Coulomb gap in a disordered insulator. Our conclusion is supported by physical estimates and numerical calculations of the density of states for a classical model of $Na_xTa_yW_{1-y}O_3$. The width and shape of the calculated bands agree well with the experiments.

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In a disordered semiconductor, the chemical potential lies at an energy where the electronic states are localized by the disorder. Because these states cannot carry a current, they are unable to screen the electron-electron interaction which retains its long-range $1/r$ form. Coulomb interactions consequently have a large effect on the electronic structure of disordered insulators.[1] One of the most significant results of the interactions is the Coulomb gap[2,3] in the density of single-particle states $n_1(E)$, which is that for adding an extra electron or hole to the ground state and allowing no relaxation of the localized electrons. The Coulomb gap is a depletion in $n_1(E)$ near the chemical potential μ; it is a "soft" gap, meaning that $n_1(E)$ vanishes only at $E=\mu$. According to a mean-field theory,[3,4]

$$n_1(E)=\alpha(E-\mu)^2, \quad \alpha=(3/\pi)(e^2/4\pi\epsilon_0\kappa)^{-3}, \quad (1)$$

near $E=\mu$ in three-dimensional systems. The only parameter in α is κ, the static dielectric constant of the material; apart from this, the value of α is universal.

While much numerical work has confirmed this remarkable result,[5-8] the experimental status of the Coulomb gap is less clear. The main problem is that the gap is strictly in $n_1(E)$, which is *not* the density of states probed by measurements of optical absorption or specific heat, for example. The Coulomb gap is expected to modify the activated electrical conductivity at low temperatures, but the effects of interaction on transport are not well understood. Tunneling experiments measure $n_1(E)$ directly, but cannot be interpreted quantitatively when the sample is not a good conductor.[9] Photoemission is better, because an electron is ejected rapidly from an occupied level and processes involving relaxation of the localized electrons should make a negligible contribution to the observed density of states. Unfortunately, this method has inadequate energy resoltuion to detect a Coulomb gap in conventional doped semiconductors.

Photoemission experiments have recently been performed on a different class of materials,[10,11] sodium tungsten bronzes. The most striking features of the results are apparent in insulating samples: (i) There is a depletion of the density of states near the chemical potential. (ii) The occupied part of the conduction band has a width almost independent of the degree of filling, and has a symmetric density of states. We argue in this paper that the long-range Coulomb interaction is responsible for both these features, and that (i) represents the first direct experimental measurement of a Coulomb gap. To gain further evidence, we have developed a classical model of insulating tungsten bronzes. The density of states, calculated numerically, exhibits both features (i) and (ii). In addition we demonstrate that (ii), which is in complete contradiction to the rigid-band model, is a natural outcome of the Coulomb interactions in disordered insulators in which the localized electrons are distributed on a lattice.

Sodium tungsten bronzes, which may be compensated with tantalum, have formula $Na_xTa_yW_{1-y}O_3$ and show a metal-insulator transition[10-13] as the doping is varied. Sodium is an interstitial donor, giving up its outer electron to the conduction band of the host. This is composed predominantly of W $5d$ orbitals, with some admixture of O $2p$ orbitals. Band-structure calculations[14] show that the Na $3s$ wave functions lie so high in energy that they make a negligible contribution to the conduction band, and NMR experiments[15] support this picture. Tantalum is believed to act as an acceptor, taking an electron from the conduction band. Thus the density of electrons remaining in the conduction band is $x-y$ per unit cell. A metal-insulator transition occurs[12,13] as this is lowered through $x-y \approx 0.18$. Although these compounds are very different from conventional doped semiconductors, they may also be expected to have a Coulomb gap in their density of single-particle states. The requirements for a Coulomb gap are a long-range $1/r$ interaction, and that the participating electronic states are so well localized that they have negligible overlap in space. We expect these conditions to be met in sufficiently lightly doped

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tungsten bronzes. The density of impurities is much higher than in doped semiconductors, and the dielectric constant is lower, which means that typical Coulomb energies in the impurity band are larger. The Coulomb gap should have a width of roughly 1 eV, large enough to be investigated by photoemission.

Photoemission experiments have recently been carried out[10] on a family of samples of $Na_xTa_yW_{1-y}O_3$ with a resolution of about 0.25 eV. We assume (following Ref. 10) that there are no problems with assigning the chemical potential, nor with a straightforward interpretation of the intensity of photoemission as proportional to the density of states of the bulk. The experiments on insulating samples reveal an impurity band whose density of states is depleted near the chemical potential. It was suggested[10] that this depletion might be a Hubbard gap, but we believe instead that it is a Coulomb gap. The experimental evidence against a Hubbard gap is that photoemission shows a gap at the chemical potential both in compensated[10] and in uncompensated[10,11] ($y=0$) samples. A Hubbard gap coincides with the chemical potential only if there is exactly one electron per site. This is *never* the case in compensated materials, and the nature of the impurity band in tungsten bronzes means that it is not the case here *even when they are not compensated*; we explain this in more detail later. In contrast[16] to a Hubbard gap, a Coulomb gap is tied to the chemical potential, as seen in the experiments. Its form is known from Eq. (1), which fits the experimental measurements well. To make this identification more precise, we have calculated $n_1(E)$ for a simplified model of $Na_xTa_yW_{1-y}O_3$.

The original numerical calculations[5-8] of $n_1(E)$ that were made to investigate the Coulomb gap used a classical model of an impurity band. To derive densities of states in the same way for comparison with the experiments,[10,11] we introduce a highly simplified, classical model of $Na_xTa_yW_{1-y}O_3$. The Na and Ta impurities generate a random electrostatic field which distorts the bottom of the WO_3 conduction band and localizes the electronic states there. This can be exploited, when the system is well within the insulating phase, to model the lowest part of the conduction band as a classical impurity band with the following features:

(i) The basic structure is a simple cubic array of W atoms; the O's are ignored.

(ii) A fraction y of these atoms are replaced at random by Ta. These become negatively charged (with electrons donated by Na) and behave only as fixed negative point charges.

(iii) A fraction x of interstitial sites are occupied randomly by Na^+ ions, which again behave simply as fixed point charges.

(iv) The remaining $x-y$ electrons per unit cell are distributed over the W atoms. Their eigenstates are localized on single sites, with negligible tunneling between neighbors. No more than one electron may occupy a W site, and occupation of the Ta sites is forbidden.

It is essential for this model that the wave functions of the donor Na atoms make no contribution to the impurity band, as was pointed out above. This is in sharp contrast to a conventional doped semiconductor like Si:P where the wave functions of the impurity band, as well as the electrons, are contributed by the donors. The total number of states per spin in the impurity band is therefore $1-y$ per unit cell, the number of remaining W atoms, rather than x, the number of donors. This in turn means that for the band to be half filled, which is the condition for a Hubbard gap to lie at the chemical potential, the number of electrons $(x-y)$ must be equal to the number of W atoms $(1-y)$, i.e., $x=1$. This is far from the region in which we are interested, so that a Hubbard gap can play no role in the insulating phase of $Na_xTa_yW_{1-y}O_3$ *even in uncompensated material* ($y=0$).

The fourth of the classical model's features is the least well founded. In crystalline WO_3 the wave functions in the conduction band form a "tubular" structure along the W-O-W directions. We expect that the random field from the Na^+ and Ta^- ions is powerful enough to disrupt this structure and to localize electrons on individual sites. This random field has a magnitude of several electronvolts (see the results later) which is comparable with the width of the conduction band[14] (about 2.5 eV). A classical model fails for systems too close to the metal-insulator transition, where the weakly localized wave functions acquire a large radius. Our particular model also fails for very lightly doped tungsten bronzes, where a different basis of localized states becomes appropriate. We are unable to offer precise limits on the validity of the model because this would involve a detailed treatment of the complex conduction band of WO_3. The rest of the band structure of this "host," comprising states for more than one electron per site, has been ignored. It plays no important role provided that it does not overlap the occupied part of the impurity band, which is all that is needed for comparison with the experiments. On the other hand, we do not expect the part of the conduction band that we are describing with the classical model to be separate from the rest of the band.

After these simplifications, only the Coulomb interactions remain in the problem, and these determine all the energies in the impurity band. The ground state of the classical model is defined as the arrangement of the $x-y$ electrons over the $1-y$ W atoms that minimizes the total energy. We used a computer program described previously[8] to calculate $n_1(E)$. In terms of the lattice spacing a_0 and the Coulomb energy between adjacent sites $E_0=e^2/4\pi\epsilon_0\kappa a_0$, the Coulomb potential

energy becomes $E_0 a_0/r$. In our case, $a_0 \approx 0.38$ nm and $E_0 \approx 0.76$ eV with use of an estimate[17] $\kappa = 5$. A brief description of the program is as follows. The Ta and Na atoms are distributed at random in the way described above. The electrons are thrown in randomly on the W atoms and then moved one at a time to lower the total energy until no favorable transition remains. The resulting "pseudoground state" is stable against moving any one electron, but is not expected to be a true ground state. Previous work[5,8] showed that there was little difference between $n_1(E)$ for pseudoground states and true ground states, and we assume that this result holds here. We used lattices of $10 \times 10 \times 10$ sites, which were found[5,8] to be large enough to avoid finite-size effects. Fluctuations from sample to sample were rather stronger in our present calculations, which we attribute to the different source of the random field, but the effect is barely visible in our densities of states.

Figure 1 shows the densities of single-particle states derived from the pseudoground states. All the curves have a prominent Coulomb gap at the chemical potential, to which the parabola (1) is a good fit. The occupied parts of the bands ($E < \mu$) are all of nearly identical width and are symmetric in shape, as seen in the experiments. Note that the experimental densities of states[10] are broadened by the resolution of about 0.25 eV. For $x = 0.25$, $y = 0.20$ [Fig. 1(a)] the computed band of occupied states is about $1.3E_0$ wide (≈ 1.0 eV). This is in excellent agreement with the experiments (Ref. 10, Fig. 6), which give a width of about 1.1 eV.

Experimental measurements on two samples, both with the same value of $x - y = 0.15$ but differing in x and y separately, yielded densities of states that were indistinguishable (Ref. 10, Fig. 6). We find the same [Figs. 1(b) and 1(c)]. This value of $x - y$ is, however, rather too close to that at the metal-insulator transition for our classical model to be very reliable.

For $x = 0.1$, $y = 0$ [Fig. 1(d)] the calculated band is narrower, only about $1.1E_0$ (≈ 0.8 eV), which again agrees closely with the experimental curves for these values (Ref. 10, Fig. 5; Ref. 11, Fig. 6). This system is uncompensated, which implies a much lower density of ions; this in turn leads to a weaker random field and explains the narrower peaks in $n_1(E)$. The comparison with experiment is unfortunately not as straightforward in this case because the cubic crystal structure, which we have used for our calculations, is not stable at these values of x and y, but we do not expect this to have a significant effect on the shape or energy scale of the impurity band.

A striking feature of the occupied bands measured in insulating samples,[10,11] and seen in the simulations, is that their width is almost independent of their degree of occupation ($x - y$), in strong disagreement with the rigid-band model (which works well for metallic samples). This strange behavior can be explained very simply by the classical model and the theory[3] of the Coulomb gap. Consider a filled site i and an empty site j in the ground state, with single-particle energies E_i and E_j. The energy required to move the electron from i to j is $E_j - E_i - E_0 a_0/r_{ij}$, which includes the change in Coulomb energies caused by the moving of the electron. Because the system was originally in the ground state, the difference in energy must not be negative. If i and j are neighbors, in which case the Coulomb energy takes its maximum value of E_0, this inequality becomes $E_i \leq E_j - E_0$. Since the lowest value of E_j is μ, there must be values of E_i at least as low as $\mu - E_0$. This implies a minimum bandwidth of E_0 for the occupied states, regardless of the fraction of the band that is occupied. It also follows from this argument that the bottom of the occupied band, as well as the top, is influenced by the Coulomb gap, so that the band tends to be symmetric as observed. These features should help to identify bands that are dominated by Coulomb interactions in disordered semiconductors with a lattice. They do not apply to conventional doped semiconductors like Si:P, where the sites of the impurity band are distributed very nearly at random through space.

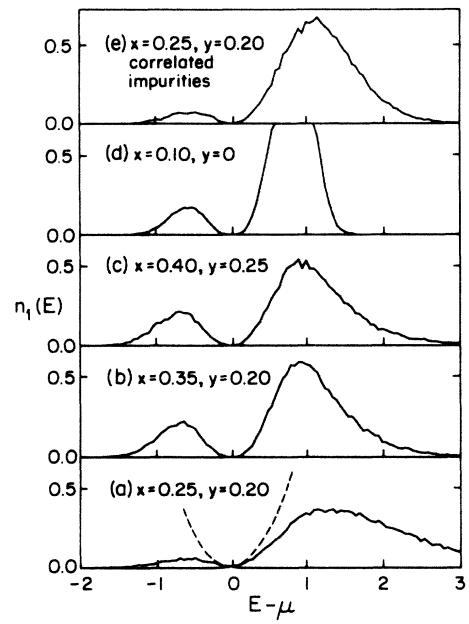

FIG. 1. Density of single-particle states $n_1(E)$ for the classical model of $Na_xTa_yW_{1-y}O_3$ for various values of x and y. The results are for systems of $10 \times 10 \times 10$ sites, averaged over 50 samples. For clarity, the points of the histograms have been joined by straight lines. The parabola predicted by Efros (Ref. 4) is also shown in (a). The sites in (e) were correlated so that every Ta^- ion had a Na^+ ion in an adjacent interstitial site. Energies are measured in units of E_0.

It is possible that correlation between the positions of the Na^+ and Ta^- ions might arise during the preparation[13] of the samples, because of the Coulomb forces between the ions. This would tend to narrow the density of states by reducing the magnitude of the random electrostatic field, and might also be important in explaining the puzzling observation[12,13] that the metal-insulator transition depends only on $x-y$, the density of electrons in the conduction band, and not on x and y separately. We investigated the effect of such correlation on $n_1(E)$ for $x=0.25$, $y=0.20$ by performing a further simulation in which every Ta^- has a Na^+ in one of the interstitial sites immediately next to it. The result of this pairing is shown in Fig. 1(e): the occupied band is narrowed by about 20%. It would be difficult to detect the existence of correlation between the impurities without better experimental resolution.

It has been pointed out[18] that the electron-phonon interaction might also give rise to an apparent gap in the density of states measured by photoemission, through the creation of polarons. Such a gap would also occur at the chemical potential. If this were the case, the electrical conductivity ought to show an activation energy related to the apparent gap. The present measurements[13] are inadequate to rule this out conclusively. However, it is difficult to see how the symmetric shape and constant width of the band could arise solely from polaronic effects.

In conclusion, we have identified the gap in the density of states of $Na_xTa_yW_{1-y}O_3$ measured by means of photoemission[10,11] as a Coulomb gap. This identification is strengthened by calculations of the density of states using a simplified, classical model. We hope to see further experiments on these materials, in particular inverse photoemission to probe the unoccupied side of the Coulomb gap. It is also important to elucidate the effect of the Coulomb gap on other properties such as transport, and to study more closely the effect of compensation. There are other compounds where photoemission might reveal the presence of a Coulomb gap, of which doped Fe_3O_4 and Ti_4O_7 are examples, and experiments on these would also be valuable.

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