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Bound Magnetic Polarons and the Insulator-Metal Transition in EuO†

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A new model is presented for the insulator-metal transition in Eu-rich EuO: At low temperatures the electrons are only very weakly bound to oxygen vacancies and conduction is metallic; near and above T_c the electrons *localize* and form bound magnetic polarons by ordering the Eu^{2+} spins neighboring the vacancy, thereby gaining exchange energy. Magnetic-susceptibility data are presented which support this model.

The conductivity behavior typical of Eu-rich EuO is shown by the solid curve in Fig. 1. As the temperature is lowered below 300 K, the conductivity decreases with an activation energy of typically 0.3 eV, similar to an ordinary semiconductor. Between 120 and 70 K the conductivity is too low to be measured. However, below the ferromagnetic ordering temperature of 69 K, the conductivity suddenly increases by more than 13 orders of magnitude and becomes nonactivated, or metallic, below 50 K. This insulator-metal transition was first discovered by Oliver[1] and has since been examined by a number of authors.[2-7] For comparison, the dashed curve in Fig. 1 is the conductivity for an oxygen-rich sample, which has an activation energy of typically 0.6 eV and shows no insulator-metal transition.[7] Therefore, the transition is not intrinsic in origin, but involves the extra electrons in Eu-rich EuO, which are presumably associated with oxygen vacancies.[1,4,7] In this Letter we propose a new explanation for the insulator-metal transition in EuO[8,9] and present new magnetic-susceptibility data which favor this model over earlier models.

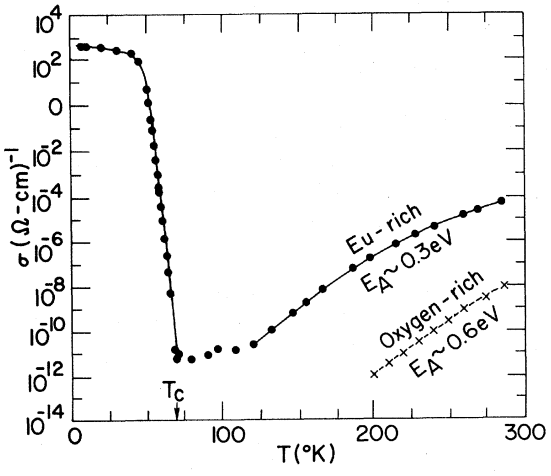

FIG. 1. Conductivity of Eu-rich EuO (after Ref. 5) and oxygen-rich EuO (after Ref. 7).

Oxygen vacancies hold two electrons and, hence, are much more complicated than one-electron donors. The basic assumption and the new feature of the model described here, the bound magnetic polaron (BMP) model, is that oxygen vacancies in EuO are *shallow* donors, as in CdO,[10] ZnO,[11,12] and possibly BaO.[13] This implies that one of the electrons is loosely bound. In this paper we shall concentrate on the effects of this electron and neglect the other, more tightly bound electron. Thus, the ground state in

the absence of magnetic interactions is a rather delocalized electron in a large-radius molecular orbital around an oxygen vacancy. For moderate vacancy concentrations ($\gtrsim 0.1\%$), these states will exhibit nonactivated, or metallic, conduction.

We must now include the effects of the exchange interaction between this electron's spin and the $4f^7$ spins, which are localized on the Eu^{2+} ions. If the electron, in its orbit around the vacancy, overlaps n Eu^{2+} ions equally, the exchange energy is[14]

$$E = -\sum_i^n \frac{2I\vec{\sigma}}{n} \cdot \vec{S}_i = -IS\frac{\langle S^z\rangle_n}{S}, \quad (1)$$

where $\vec{\sigma}$ is the spin of the orbiting electron, $\langle S^z\rangle_n$ is the average z component of the spin of the n Eu^{2+} ions, and $S=\frac{7}{2}$. The factor $1/n$ enters because the orbiting electron spends that fraction of its time on each Eu^{2+} site. The magnitude of the exchange interaction, I, depends strongly on whether the orbiting electron has primarily $5d$, $6s$, or $6p$ character.[15] Infrared measurements[8,16] as well as conductivity data[5] indicate that the appropriate value is the atomic $5d$ value, $I_{df}=+0.1$ eV (ferromagnetic),[15] giving $IS\approx 0.35$ eV.

At lowest temperatures, all the Eu^{2+} spins are ordered and $\langle S^z\rangle_n/S=1$. From Eq. (1) the orbiting electron can gain an energy $IS\approx 0.35$ eV if it aligns its spin parallel to the Eu^{2+} spins. Since this will require no change in its molecular orbital, the electron will remain as delocalized as in the absence of the magnetic interaction. For moderate concentrations of oxygen vacancies ($\gtrsim 0.1\%$), the orbitals overlap sufficiently that the conductivity should be nonactivated, as is observed in the metallic phase at lowest temperatures (Fig. 1).[1,3-7] For smaller concentrations, hopping conductivity is observed,[2,7] as expected.

In the paramagnetic region ($T>69$ K), the Eu^{2+} spins are disordered and we might expect no magnetic energy. However, the orbiting electron can *cause* the Eu^{2+} spins in its orbit to order partially and thereby gain some of the magnetic energy: From Eq. (1) each of the n Eu^{2+} spins in the orbit sees an effective magnetic field $H\propto I/n$, which can give rise to a finite value of $\langle S^z\rangle_n$. Furthermore, if the electron were in a smaller orbit, with a smaller n, the effective field, $\propto I/n$, would be larger. $\langle S^z\rangle_n$ would then be larger and a larger fraction of the magnetic energy (0.35 eV) would be gained. In addition, the cost in entropy (proportional to n) would be decreased if the orbit were smaller. The orbit then shrinks until the Eu^{2+} spins are ordered. Thus, the electron gains magnetic free energy by *localizing* and concentrating on ordering a smaller number of Eu^{2+} spins, thereby forming a magnetic polaron.

The formation of this magnetic polaron and the localization mechanism just described are basically the same as for the free magnetic polaron, i.e., for a conduction-band electron with no Coulomb interaction (no donor). This problem has been studied quantitatively by Kasuya and coworkers.[14,17] Since the polaron we have described in EuO is bound to an oxygen vacancy, it is called a bound magnetic polaron (BMP). This case has also been briefly discussed by Kasuya.[18] Although the free magnetic polaron is stable only very close to T_c,[14,17] the BMP remains localized over a much wider temperature range[18] as a result of Coulomb attraction of the donor. Note that the donor is assumed *shallow* relative to the magnetic energy. The case of the relatively *deep* donor is the magnetic impurity state (MIS) of Kasuya and Yanase.[15] The BMP model, therefore, lies in between these two, more well-studied limits and has some of the properties of each.

The observed conductivity in EuO is associated with electrons activated from the oxygen vacancies up into conduction-band states.[1,4,5] In the paramagnetic region the weakly bound vacancy electrons localize, form bound magnetic polarons, and gain magnetic energy. Conduction-band electrons, on the other hand, have too much kinetic energy to form magnetic polarons[14,17] (except very near T_c) and cannot gain the magnetic energy. Thus, the BMP electrons have a magnetic binding of ~ 0.35 eV with respect to the conduction band. The difference between the observed activation energy (~ 0.3 eV) and the magnetic energy (0.35 eV) is probably the kinetic energy associated with the more localized orbit of the BMP. Below T_c, however, the conduction-band electrons begin to gain magnetic energy, and the magnetic contribution to the activation energy gradually disappears and the material becomes metallic.[9] Since this decrease in energy of the conduction-band electrons will follow the long-range magnetic order, the predicted temperature dependence of the activation energy is in agreement with the detailed experimental results of Penney, Shafer, and Torrance.[5]

The model[19] previously used to describe EuO is the He-like model,[17,4,3] where an oxygen vacancy is considered a relatively deep donor (~ 0.3 eV). In the paramagnetic region, the two vacancy electrons have a He-like ground state. Above

this singlet state are conducting triplets and singlets. Below T_c, the exchange interaction gives rise to an effective exchange field, which splits the conducting triplets. At a sufficiently low temperature, this field drives the lowest conducting triplet below the ground singlet, giving rise to the insulator-metal transition.

The major difference between this model and the BMP is in the paramagnetic region: In the He-like model, the two electrons in the oxygen vacancy have their spins antiferromagnetically aligned and all the Eu^{2+} spins are disordered; in the BMP model, on the other hand, the two electronic spins are ferromagnetically aligned, as are the Eu^{2+} spins neighboring the oxygen vacancy. Thus, one ground state is a nonmagnetic singlet, while the other is a ferromagnetic cluster of spins. In order to experimentally distinguish between these two models, we have made careful magnetic-susceptibility measurements on samples with and without oxygen vacancies. While the He-like model would predict no difference in the susceptibility between samples, the BMP model predicts an increase in χ for samples with vacancies, due to the ferromagnetic clusters. In this Letter we discuss the results for three representative samples[20]: Sample A was approximately stoichiometric; sample B had ~0.3% oxygen vacancies, and Sample C had ~0.5% oxygen vacancies. The samples were grown and characterized as described in Ref. 7. In Fig. 2(a) the inverse of the magnetic susceptibility is plotted versus temperature for the three samples. Although there are only small differences between samples, the data indicate that $\chi_c > \chi_B > \chi_A$, i.e., the susceptibility is *increased* due to the presence of vacancies. This increase is predicted by the BMP model, while incompatable with the simple He-like model.[21]

In order to examine the susceptibility data more quantitatively, we have attempted to fit χ_M by a Curie-Weiss law,

$$\chi_M(y,T) = C_M(y)/[T-\theta(y)], \qquad (2)$$

where y is the vacancy concentration, $C_M(y)$ is the molar Curie constant, and $\theta(y)$ is the paramagnetic Curie temperature. Between ~200 and 600 K, the data fit (2) with the same value of $C_M = 7.74 \pm 0.05$ for all samples. This value agrees favorably with typical values of 7.7 for Eu^{2+} in other compounds. Equation (2) and the sample independence of C_M suggest that the differences in χ_M between samples may be viewed as due to differences in $\theta(y)$. In order to magnify and examine these small differences, we have used Eq. (2) to transform the χ_M data into $\theta(y,T)$ as shown in Fig. 2(b). The dashed lines correspond to the mean value of $\theta(y)$ at high temperatures, and the error bars indicate our estimated ~0.3% random error.[20]

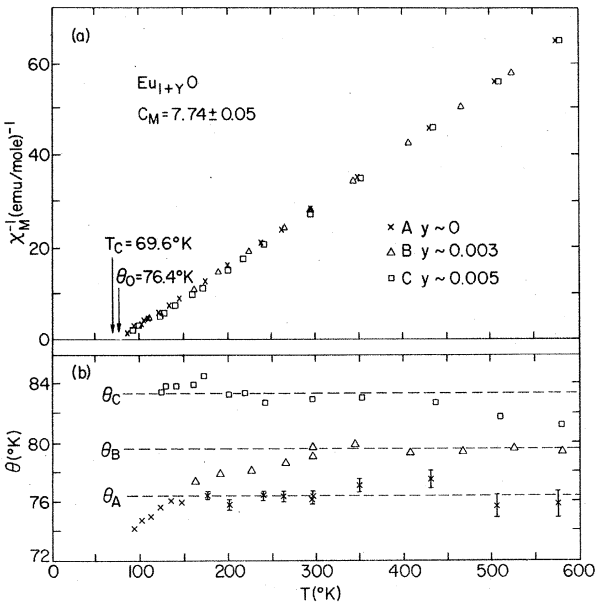

FIG. 2. (a) Inverse susceptibility for three samples with different concentrations of oxygen vacancies; (b) same data replotted using Eq. (2).

The most important feature of Fig. 2(b) is not the exact shape of the $\theta(y,T)$ data, but the fact that θ is larger for samples with oxygen vacancies. This increase may be veiwed as an increase in the strength of the exchange interactions caused by the electrons in the BMP.[20] More quantitatively, the magnetic properties of a BMP should be similar to those of a ferromagnetic spin cluster of a MIS.[15] Using those results we can calculate[20] an effective $\theta(y,T)$ for Eu-rich EuO. This theoretical θ increases slowly with T, but between ~300 and 600 K we find $\theta(y) \sim \theta_0 + 3500y$. For $y \sim 0.004$, an increase in θ of ~15 K is predicted. This value compares favorably to the observed ~3–7-K increases, considering the uncertainties in calculating $\theta(y)$ and in determining y.

Besides these measurements, there are two more experiments which favor the BMP model. In EuS the static dielectric constant is less than half of that of EuO. The He-like model would then predict a donor significantly *deeper* than in EuO and, hence, no insulator-metal transition (since the electrons would then be deeper than

the magnetic energy). Recent conductivity measurements[22] on Eu-rich EuS, however, reveal an activation energy in the paramagnetic region of ~0.05 eV (far less than in EuO) and a *large* resistivity anomaly near T_c. These data support the basic assumption of the BMP model, i.e., that chalcogenide vacancies are *shallow*, not deep, donors. A third group of experiments supporting the BMP model is the infrared measurements in the paramagnetic region of Eu-rich EuO, first reported in Refs. 7 and 8. It does not appear possible to understand this spectrum in terms of the He-like model. However, using the BMP model, we have successfully interpreted the spectrum as due to magnetic and orbital excitations of bound magnetic polarons.[16]

Thus, although both the bound magnetic polaron and He-like models well describe the insulator-metal transition in Eu-rich EuO, the BMP model alone is consistent with (i) the magnetic susceptibility measurements,[21] (ii) conductivity data on EuS, as well as (iii) infrared measurements on EuO. Several authors[23] have used the model of a free magnetic polaron to interpret their experiments. Free magnetic polarons, however, exist only near T_c.[14] We suggest that if the Coulomb interaction were included in these models (making the polarons *bound* magnetic polarons), the polarons would then be stabilized and the description would be fine. Furthermore, we expect that BMP will be found in many magnetic semiconductor systems.

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Note added in proof.—Recently Leroux-Hugon[24] has calculated the linear response properties of an electron gas which is coupled both by an exchange interaction to localized spins and by a Coulomb interaction to donors. We believe that this model is essentially equivalent to our BMP description of EuO, although the two approaches are entirely different.

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[21]*Compensated* He-like states would be MIS states and should increase χ and θ. However, our estimate (Ref 16) of the *maximum* compensation of ~5% gives an increase in θ of only ~0.4 K for y ~0.004, much smaller than the observed increases.

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