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Insulator-Metal Transition and Long-Range Magnetic Order in EuO[†]

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Several aspects of the insulator-metal transition below the magnetic-ordering temperature in EuO have been examined. The conductivity above 50 K is shown to be thermally activated, with an activation energy which depends linearly on the long-range magnetic order. Below 50 K the conductivity is metallic. This insulator-metal transition is observed only in samples which are slightly oxygen deficient, presumably in the form of vacancies. The magnitude of the exchange interaction between the conduction electron and localized spins is shown to be about 0.1 eV.

INTRODUCTION

The conductivity of EuO may increase by many orders of magnitude as the temperature is decreased below the ferromagnetic-ordering temperature ($T_c = 69.3$ K). This behavior has been reported by Oliver, Kafalas, Dimmock, and Reed[1-3] and by Petrich, von Molnar, and Penney.[4] We have grown additional crystals and extended our measurements to cover a wider range of conductivities, both with and without an applied magnetic field. Typical data are shown in Fig. 1. It is evident that the insulator-metal transition below T_c is related to the onset of magnetic order. It is our purpose to explore the nature of this relationship. Furthermore, we shall discuss the preparation and stoichiometry of EuO and show that the crystals which exhibit the insulator-metal transition are oxygen deficient, probably in the form of oxygen vacancies.

The conductivity σ shown in Fig. 1 may be divided into four regions. Between room temperature and 125 K, $\log\sigma$, if plotted against $1/T$, shows thermally activated conduction with a 0.285-eV activation energy. Between 125 and 70 K the conductivity was masked by leakage currents. Below T_c, there is a 13-order-of-magnitude increase in σ which we may well call an insulator-metal transition. Below 50 K, conduction is essentially metallic.

Hall-effect measurements have been made at 5 K and near room temperature, but could not be made in the 50–70 K region due to the very large magnetoconductance. The results for three samples (89B, 89A, and 73) showing the insulator-metal transition are summarized in Table I. The expression $\sigma(T)$

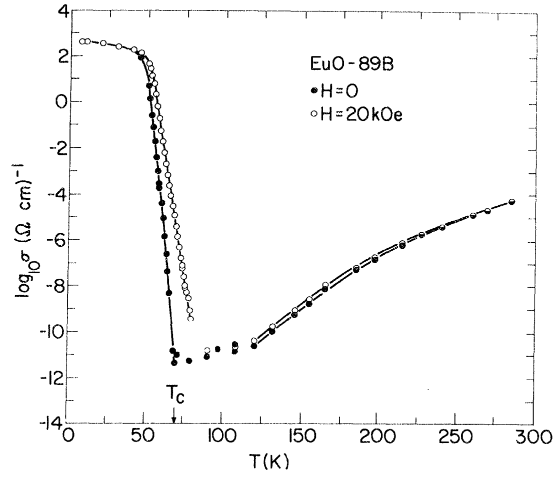

FIG. 1. Conductivity vs temperature for EuO sample 89B in 0 and 20 kOe.

$=\sigma_\infty e^{-E/kT}$ defines σ_∞ and $E(T)$ in terms of the data $\sigma(T)$. Hall measurements on sample 73 between 225 and 295 K show that it is the carrier concentration n that is changing exponentially near room temperature. The results, assuming a single band, give a carrier concentration of $10^{19}/\text{cm}^3$ at 5 K and $10^{13}/\text{cm}^3$ at room temperature. The sharp increase in conductivity, $\sigma = ne\mu$, below 70 K is, therefore, due to a change in n. Oliver[2,3] has compared the infrared free-carrier absorption $\alpha \sim n\lambda^2/m^*\tau$ to the conductivity $\sigma = ne^2\tau/m^*$, and has argued that the large change in σ below 70 K is due to a change in n and not mobility $\mu = e^2\tau/m^*$, assuming m^* is temperature independent and τ is the same in both expressions.

In EuO the optical-absorption edge shifts several tenths of an eV to lower energy with decreasing temperature. This red shift begins well above T_c and follows the short-range magnetic order $\langle \vec{S}_i \cdot \vec{S}_j \rangle$.[5,6] Oliver *et al.*[1-3] take the view that the optical-absorption edge corresponds to a transition from a europium $4f^7$ level lying in the band gap to the conduction band. Therefore, the conduction band decreases in energy, relative to these tightly bound atomiclike levels, following the red shift. They postulate that there are trap states associated with oxygen vacancies whose energy is independent of magnetic order. They propose, then, that the activation energy E to promote electrons from the traps to the conduction band decreases by several tenths of an eV following the red shift and, hence, the short-range order. The decrease in E causes an exponential increase in n and σ according to

$$n(T)/n(0) = \sigma(T)/\sigma(0) = e^{-E/kT} \tag{1}$$

in the region of the insulator-metal transition. We have tested this model and find that the data are consistent with Eq. (1), but E decreases with the long-range magnetic order $\langle S \rangle$ rather than the short-range order $\langle \vec{S} \cdot \vec{S} \rangle$.

TABLE I. Hall and conductivity data.

	89B	73	89A
σ (287 K) $(\Omega\ \text{cm})^{-1}$	5.3×10^{-5}	1×10^{-4}	6.17×10^{-5}
μ (287 K) cm^2/V sec	8	14	11
n (287 K) cm^{-3}	4×10^{13}	4.5×10^{13}	3.5×10^{13}
E (287 K) eV	0.285	0.30	0.30
σ_∞ $(\Omega\ \text{cm})^{-1}$	3.5	21	12
σ (5 K) $(\Omega\ \text{cm})^{-1}$	4.3×10^{2}	5.0×10^{2}	7.7×10^{2}
μ (5 K) cm^2/V sec	0.7×10^{2}	1.3×10^{2}	1.7×10^{2}
n (5 K) cm^{-3}	4×10^{19}	2×10^{19}	3×10^{19}

CONDUCTIVITY AND LONG-RANGE ORDER

The values of $\sigma(T)$ at $H=0$ from Fig. 1 may be used with Eq. (1) to determine experimental values for $E(T)$. In order to test the relationship between $E(T)$ and $\langle S \rangle$ we need $\langle S(T) \rangle$. The hyperfine field $h(T)$ is proportional to $\langle S(T) \rangle$ and has been measured using the Mössbauer effect by Petrich[4] on sample 73. It is given by

$$\langle S(T) \rangle / S = h(T)/h(0) = 1.13 \times (1 - T/69.3)^{0.36} \tag{2}$$

in the range 40–70 K.[7] The data of Fig. 1 used with Eqs. (1) and (2) determine the dependence of the activation energy for conduction on the long-range order $\langle S \rangle$. The results, as shown in Fig. 2 (dots), are (i) $E(T)$ vs $\langle S(T) \rangle$ is a straight line; (ii) the intercept at $\langle S \rangle = 0$ is 0.30 eV; (iii) $\langle S \rangle / S = 0.77$, where $E \to 0$.

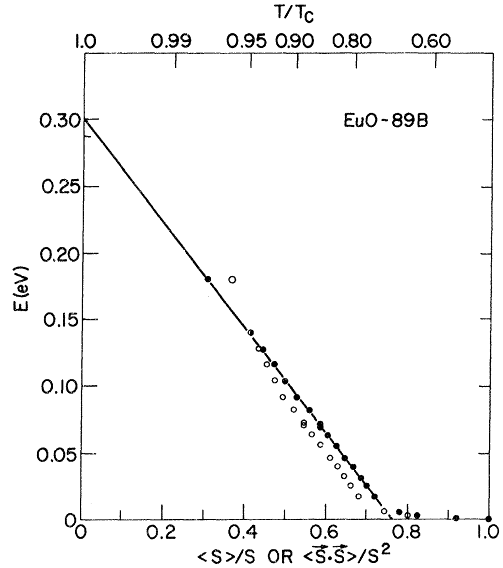

FIG. 2. Activation energy vs magnetic long-range order $\langle S \rangle$ (dots) and short-range order $\langle \vec{S} \cdot \vec{S} \rangle$ (circles) for EuO sample 89B.

The first result shows that the activation energy E is linearly dependent on long-range order $\langle S \rangle$. A plot of E vs the short-range order $\langle \vec{S} \cdot \vec{S} \rangle$, as determined by Argyle, Miyata, and Schultz,[8] also shown on Fig. 2 (circles) deviates from straight-line behavior as $T \rightarrow T_c$ and $\langle \vec{S} \cdot \vec{S} \rangle$ deviates from $\langle S \rangle$. We find, therefore, that the enormous increase in n and σ below T_c is caused by a decrease in E which is linearly proportional to the increase in $\langle S \rangle$. The second result indicates that the Fermi level E_F extrapolated from $\langle S \rangle \neq 0$ to $\langle S \rangle = 0$ lies about 0.30 eV below the conduction band for temperature where $\langle S \rangle = 0$, that is, $T \geq T_c$. In fact the $\sigma(T)$ data above 130 K where $\langle S \rangle = 0$ have a slope of 0.285 eV on a $1/T$ plot—in remarkable agreeement with the 0.30-eV value extrapolated from the low-temperature data. The third result gives a measure of the exchange coupling J between band electrons and the europium $4f$ spins S, as we shall see. The point where $E \rightarrow 0$ corresponds to the knee at about 50 K in Fig. 1. Below this temperature, since $E = 0$, the conduction is no longer thermally activated but metallic, as observed. These results may be summarized by the following expression for the activation energy:

$$E = E_0 - A \langle S \rangle = 0.30 - 0.39 \langle S \rangle / S \text{ eV}. \qquad (3)$$

MAGNETIC FIELD DEPENDENCE

Referring again to Fig. 1 the magnetoconductivity in the neighborhood of T_c is very large, the ratio $\sigma(H = 20 \text{kOe})/\sigma(0)$ at T_c being about 10^6. As we shall see, this very large effect may be explained by Eq. (3). It follows that a magnetic field increases $\langle S \rangle$, decreases E, and therefore increases σ exponentially. In order to test this idea, Eq. (3) may be used to determine $\langle S \rangle$ once E has been obtained from the conductivity and Eq. (1). The values of $\langle S \rangle$ vs T thus obtained for both 0 and 20 kOe are given in Fig. 3. For comparison, $\langle S \rangle$ as determined from magnetization measurements is given for a sphere of the same material in 20 kOe. Also shown is $\langle S \rangle$ for a disc perpendicular to the external field as calculated from the sphere data. The fit of the zero-field resistivity data (dots) to the magnetization data is equivalent to the fit of the data in Fig. 2 to the straight line. However, as we shall argue below, the fit of the resistivity data at 20 kOe (open circles) to the magnetization of a disc is a confirmation of the validity of Eq. (3) in an applied field and an explanation of the large magnetoconductance effect. The actual sample used was a rectangular parallelopiped $0.75 \times 0.85 \times 0.25$ mm with the field parallel to the 0.85-mm edge and four contacts on the largest face. Since the sample is not an ellipsoid it will not have a uniform magnetization. Throughout the sample the magnetization may vary between a maximum, which is that applicable for a disc parallel to H, and a minimum, which is that applicable for a disc perpendicular to H. Equations (1) and (3) show that the variations in M will cause exponential variations in σ. The average σ which is measured along a constant current path will correspond to an average of $\sigma^{-1} = \rho = \rho_0 \exp(E_0 - A\langle S \rangle)$, according to Eqs. (1) and (3). This highly nonlinear average can be approximated by using the maximum $E = E_0 - A \langle S \rangle$, that is, the minimum magnetization rather than an average magnetization since the conductivity will be limited by the regions of highest resistance. The magnetization predicted by the σ (T, 20 kOe) data is, therefore, close to the minimum possible value, that is, a disc perpendicular to H as shown in Fig. 3.

The conductivities at $H = 0$ for $70 < T < 125$ K and at $H = 20$ kOe for $80 < T < 125$ K do not fit Eqs. (1) and (3) as do the rest of the data. These very low values correspond to some other weak conduction process or to current leakage on the sample surface or sample holder.

EXPERIMENTAL DENSITY OF STATES

In Ref. 4, both Mössbauer and conductivity measurements were reported for samples made from the same crystal run (73). Assuming compositional gradients are small for this run, as we believe, T_c,

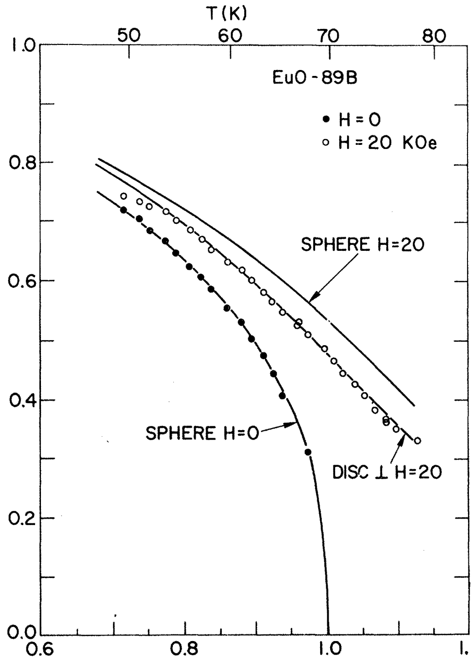

FIG. 3. $\langle S \rangle$ vs T (solid lines) for a sphere in $H = 0$ and $H = 20$ kOe as well as $\langle S \rangle$ calculated for a disc perpendicular to a 20-kOe magnetic field. The predicted values of $\langle S \rangle$ from the conductivity data are shown for $H = 0$ (dots) and $H = 20$ kOe (circles).

$\langle S(T)\rangle$, and $\sigma(T)$ are all known for similar crystals. A plot similar to Fig. 2 gives the following results: E vs $\langle S\rangle$ is a straight line; the intercept at $\langle S\rangle = 0$ is 0.29 eV; and $\langle S\rangle/S = 0.72$, where $E \rightarrow 0$. These three results are similar to those for sample 89B. The room-temperature activation energy for sample 73 is 0.30 eV, in good agreement with the low-temperature extrapolation of 0.29 eV. A fourth result is that the isomer shift (IS) is changing approximately linearly with $\langle S\rangle$ over the region $\langle S\rangle/S = \frac{1}{4}$ to $\frac{3}{4}$, before conduction becomes metallic.[4] The observed change in IS corresponds to an increase in the electron density at the Eu nuclei. This result means that above 50 K, where the number of carriers in the band is changing exponentially, the electron configuration is changing roughly linearly with $\langle S\rangle$.

These four results are consistent with the density of states shown in Fig. 4. Electrons above the mobility edge in the band states B are conducting (n type) and have mobilities of order 10^2 cm^2/V sec at low temperature and 10 cm^2/V sec at high temperature. The energy difference ΔE between the mobility edge and some impurity state I decreases linearly with $\langle S\rangle$. For $\langle S\rangle/S$ less than 0.75 (above 50 K) conduction occurs in the band by carriers thermally excited from I to B. Below 50 K a band state is the ground state and metallic conduction occurs. On the diagram the crossing of B and I, which causes the knee in the conductivity, is labeled $\Delta\sigma$. The states I' below the mobility edge are included to explain the change in isomer shift. If the energy difference $I' - I$ also decreases with increasing $\langle S\rangle$, then the change in IS will begin at the point labeled ΔIS and continue until I is empty.

The high-temperature ($\langle S\rangle = 0$) position of the Fermi level E_F will depend on the concentration of compensating defects. However, once I' begins to cross I and the IS begins to change, E_F will be pinned at the partially empty donor levels I. Therefore, the activation energy E measures the actual separation ΔE of the mobility edge and the donors I. Since E extrapolates to 0.30 eV at $\langle S\rangle = 0$ and the separation E_F and B at high temperature is 0.285 eV, E_F must be pinned at I at high temperature as well. The fact that the Fermi level is always pinned at I indicates the presence of compensators.[9] At low temperature the electrons are divided between the states I' and B in this model. We expect, therefore, that the number of uncompensated states I will be somewhat greater than the values of n (5 K) given in Table I.

The picture presented in Fig. 4 and Eq. (3) is that of nonlocal conducting states above the mobility edge approaching the nonmagnetic donor states I with a linear dependence on the long-range order $\langle S\rangle$. On the other hand, the optical-absorption edge red shifts following the short-range order $\langle\vec{S}\cdot\vec{S}\rangle$.[5] It is then clear that the final states of the optical absorption and the conducting states are not the same since they have different dependences on the magnetic order.

MICROSCOPE MODELS AND ESTIMATIONS OF EXCHANGE

Kasuya[10] has proposed a specific model in which the trap state associated with the oxygen vacancy contains two electrons. Since the oxygen vacancy differs by two charges from $O^{=}$, the trap may be thought of as a helium-like defect rather than the common hydrogenic defect suitable for Gd^{3+} substituted for Eu^{2+} or a halide, such as Cl^-, substituted for $O^{=}$. The lowest helium-like state is a nonmagnetic singlet ^1S with configuration $1s\uparrow 1s\downarrow$. The first excited states are magnetically active triplets, $^3S(1s\uparrow 2s\uparrow)$. The exchange field, if sufficiently large, will split the ^3S so that the lowest branch ^3S $(1s\uparrow 2s\uparrow)$ falls below the ^1S $(1s\uparrow 1s\downarrow)$ and the electronic configuration will change. If some of the ^3S states are merged with the bottom of the conduction band, conduction will result. In this model I in Fig. 4 is the ^1S state and I' is the excited ^3S state broadened by the random-potential fluctuations of the oxygen vacancy. The conducting states B are a hybrid of band states and the higher ^3S states.

Oliver, Dimmock, McWhorter, and Reed[11] have independently adopted the He model calling it a magnetic double donor. Kasuya[12] and Oliver *et al.*[11] have pointed out that if one electron in a band state has an exchange energy E_{ex}, the remaining electron in the more localized state will have a smaller exchange energy αE_{ex}. Since we have shown the band-edge shift is proportional to $\langle S\rangle$ we may write the exchange energy for a conduction electron $\vec{s}$ as

$$E_{ex} = -2J\vec{s}\cdot\langle\vec{S}\rangle. \qquad (4)$$

Then the difference in magnetic energy between the parallel-spin excited state and the antiparallel-spin ground state is

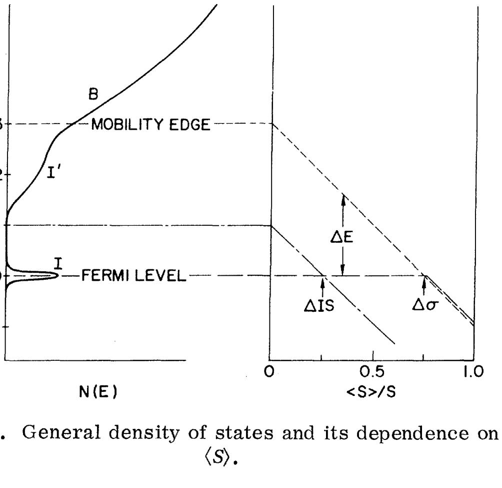

FIG. 4. General density of states and its dependence on $\langle S\rangle$.

$$\Delta E_{ex} = -J(1+\alpha)\langle S\rangle. \quad (5)$$

We have determined, Eq. (3), that $\Delta E_{ex} = -0.39$ eV for $\langle S\rangle = S = \frac{7}{2}$ and, therefore,

$$J = 0.11/(1+\alpha) \text{ eV or } 0.055 < J < 0.11 \text{ eV} \quad (6)$$

for $0 < \alpha < 1$, as one would expect. In this model the ^1S ground state is independent of $\langle S\rangle$ because it has oppositely paired spins. No magnetic cluster will form around it at $T > T_c$, but if one electron is removed to a compensator a spin cluster may form at $T > T_c$.

Another model which has been successful in describing the magnetically dependent thermally activated conduction in doped EuS and EuSe is the magnetic-impurity-state model of Kasuya and Yanase.[13,14] In this case an electron may be trapped at a defect by the combined Coulomb and exchange interactions. In the paramagnetic region a cluster of Eu spins in the neighborhood of the bound electron may be ordered by the exchange interaction J. Conduction may occur by thermally activated hopping or thermal activation to the band. Below T_c as the whole crystal orders magnetically the contribution of the exchange to the binding energy of the localized state disappears. If in EuO the Coulomb energy alone is not sufficient to bind the electron then nonthermally activated band conduction will result. In such a model the magnetic binding energy will depend on the difference $\Delta\langle S\rangle$ between the average spin in a cluster around the defect and the average spin $\langle S\rangle$ throughout the crystal. In Fig. 4 this magnetic impurity state is the state I and its change in magnetic binding energy will be $-J\Delta\langle S\rangle$ and we would expect a value for J of order 0.1 eV as in the He-like model.

A major difference between the He model and the magnetic-impurity-state model for the oxygen vacancy is that the ground state is, respectively, orbitally nondegenerate and nonmagnetic or orbitally degenerate and magnetic. Kasuya[12] has pointed out that the ground state is nonmagnetic if the Eu-derived 6s band lies well below the 5d band as expected.[13,15] However, the ground state will be magnetic if the opposite is true. Rather than argue the merit of the He or magnetic-impurity models, we have presented the conditions which must be satisfied by any model.

The magnitude of J derived from experiment is somewhat model dependent but for the case of the He model ranges from 0.055 to 0.11 eV. These values are very close to the s-f and d-f values $I_{sf} = 0.025$ eV and $I_{df} = 0.1$ eV for the free-ion Eu^+.[13] von Molnar and Shafer[16] have measured the spin-disorder scattering in metallic EuO doped with Gd and find $Jm^* \approx 0.05$ eV or $J \approx 0.05$ eV, assuming $m^* \approx 1$.

SAMPLE PREPARATION

Systematic studies of the crystal growth, microstructure, infrared absorption, and conductivity in the europium-oxygen system have shown strong relationships between the physical properties and stoichiometry of EuO. The details of these studies are being published elsewhere.[17] However, a summary of the results and the data pertinent to the preparation and composition of the crystals reported in this paper are given below.

The composition of the rock-salt EuO phase is variable and extends > 0.5% on the Eu-rich side and about 2–3% on the oxygen-rich side of the stoichiometric compound. The two parameters which determine whether a crystal is Eu or oxygen rich are the Eu pressure under which it is grown and the temperature. However, because of the tendency of EuO to lose europium at high temperatures, the crystals are normally grown in sealed crucibles with an excess of Eu metal. Such a method eliminates possible large variations in the Eu pressure during growth and also limits the control one has in regulating it. Consequently, the temperature parameter becomes the convenient one to relate to stoichmetry. Crystals grown at temperatures greater than 1825 °C are Eu deficient and highly insulating. As the growth temperature is lowered by the addition of Eu metal, the crystals become more stoichiometric and those grown in the 1780–1825 °C range have a Eu/O ratio of very nearly one and remain highly insulating. Crystals grown just below 1780 °C are slightly oxygen deficient, probably in the form of oxygen vacancies, and show insulator-metal transitions. Crystals grown much lower than 1600 °C are metallic.[17] From this result we conclude that the insulator-metal transition is associated with oxygen deficiencies probably in the form of vacancies as suggested by the models.

The crystals discussed in detail in this paper were all grown below 1780 °C, but by three slightly different methods. Crystal 89B, used to obtain the data in Fig. 1, was produced by cooling Eu_2O_3 pellets in Eu vapor from 1650 to 1350 °C in a double-crucible arrangement. An open inner crucible containing the Eu_2O_3 pellets, and subsequently the EuO crystal, was placed inside a sealed crucible containing a large excess of Eu metal. In this arrangement the liquid metal was never in contact with the EuO crystal. The techniques to grow the other two crystals were similar in that the excess Eu metal was mixed with Eu_2O_3 (89A) and with EuO powder (73) and sealed in single tungsten crucibles. They were then heated to slightly above 2000 °C to ensure a complete reaction, and then cooled. The quantity of excess Eu metal determined the crystallization temperature and for both crystals that quantity was sufficient for the crystals to grow below 1780 °C. After growth, which was 16-20 h, the crystals were rapidly cooled to room temperature. The similarity in conductivity behavior observed in all three crystals, grown by different methods but in the same temperature range, shows the importance of the growth temperature in determining the physical properties of EuO. All crystals were chemically analyzed [by EDTA (ethylenediamine tetraacetic acid) titration] for total europium and for their impurtiy content by a mass spectrometer. The analysis showed all three to contain a probable excess of europium, of the order of 0.1 at.%.

The conductivity measurements were made using the four-probe van der Pauw technique.[18] Lanthanum-silver contacts were alloyed into the material under an inert He atmosphere and provided good Ohmic contacts. Current leakage on the surface of the sample and sample holder limited our measurements to about 10^{13} Ω corresponding to bulk conductivities of about $10^{-11}(\Omega \text{ cm})^{-1}$.

CONCLUSION

We have examined the insulator-metal transition in EuO and have shown that the large change in conductivity below T_c may be understood in terms of carriers thermally activated into a conduction band. Furthermore, the activation energy is linearly dependent on long-range magnetic order, both with and without an external magnetic field. The data are not consistent with an interpretation based on short-range order. The low-temperature data, when plotted as activation energy vs long-range order, and extrapolated to $\langle S \rangle = 0$, give a value for the activation energy which is in good agreement with the measured high-temperature values of 0.3 eV. The low-temperature conductivity data were used to estimate the exchange coupling J, between a conduction electron and the Eu $4f$ spins. J lies in the range 0.05–0.11 eV, using the He-like model for oxygen vacancies. These values are in order-of-magnitude agreement with a previous determination made from resistivity measurements in degenerate EuO and the free-ion values for Eu$^+$. The insulator-metal transition was found only in samples which are slightly oxygen deficient, probably in the form of vacancies.

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