with increase in Ta concentration, unlike what might intuitively be expected. This remains an open question which further experiments on single-crystal specimens should resolve.

We thank Dr. R. R. Hake, Dr. P. C. Hohenberg, Dr. L. Mattheiss, Professor J. C. Wheatley, Professor T. Ohtsuka, and Professor M. Levy for informative conversations, and express our appreciation to H. Nadler for preparing the specimens of Nb and V.

\*Present address: 4443 Whittier Street, Ventura, Calif. 93003.

†Present address: 1391 Thousand Oaks Boulevard, Thousand Oaks, Calif. 91360.

<sup>1</sup>T. McConville and B. Serin, Phys. Rev. 140, A1169 (1965); L. C. Skinner, II, R. M. Rose, and J. Wulff, J. Appl. Phys. 37, 2191 (1966); D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, Phys. Rev. 149, 231 (1966); T. Ohtsuka and N. Takano, J. Phys. Soc. Japan 23, 983 (1967); R. A. French, Cryogenics 8, 301 (1968).

<sup>2</sup>E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966), and references therein.

<sup>3</sup>D. R. Tilley, G. J. van Gurp, and C. W. Berghout, Phys. Letters 12, 305 (1964).

<sup>4</sup>W. A. Reed, E. Fawcett, P. P. M. Meincke, P. C. Hohenberg, and N. R. Werthamer in, Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, U.S.S.R., 31 August-6 September 1966 (VINITI, Moscow, 1967), Vol. IIA, p. 368.

<sup>5</sup>P. C. Hohenberg and N. R. Werthamer, Phys. Rev. 153, 493 (1967).

<sup>6</sup>V. K. Wong and C. C. Sung, Phys. Rev. Letters <u>19</u>,

1236 (1967); C. C. Sung, Phys. Rev. 187, 548 (1969). <sup>7</sup>L. Y. L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Letters 14, 1025 (1965).

<sup>8</sup>J. R. Carlson and C. B. Satterthwaite, Phys. Rev. Letters 24, 461 (1970).

<sup>9</sup>S. J. Williamson, Phys. Letters 23, 629 (1966), and references therein.

<sup>10</sup>L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 37, 833 (1959) [Soviet Phys. JETP 10, 593 (1960)]. It is shown in Ref. 2 that the trial gap function used by Gor'kov in this calculation is in fact the exact eigenfunction.

<sup>11</sup>L. Mattheiss, Phys. Rev. B 1, 373 (1970).

<sup>12</sup>S. J. Williamson, Rev. Sci. Instr. <u>40</u>, 1632 (1969).

<sup>13</sup>J. C. Wheatley, O. E. Vilches, and W. R. Abel, Physics 4, 1 (1968).

<sup>14</sup>C.-R. Hu and V. Korenman, Phys. Rev. <u>178</u>, 684 (1969).

<sup>15</sup>U. Brandt, Phys. Letters <u>29A</u>, 568 (1969).

<sup>16</sup>K. Maki and T. Tsuzuki, Phys. Rev. <u>139</u>, A868 (1965).

<sup>17</sup>P. Carsey, R. Kagiwada, M. Levy, and K. Maki, to be published.

<sup>18</sup>C. J. Gorter, Physica <u>30</u>, 2175 (1964); S. J. Williamson, Phys. Letters 28A, 665 (1969).

<sup>19</sup>S. J. Williamson, to be published.

<sup>20</sup>K. S. Nelson, J. L. Stanford, and F. A. Schmidt, Phys. Letters 28A, 402 (1968).

<sup>21</sup>Insensitivity of h(t) to strong-coupling effects in Nb and V has been predicted by N. R. Werthamer and W. L. McMillan, Phys. Rev. <u>158</u>, 415 (1967).

<sup>22</sup>T. Ohtsuka and Y. Kimura, in Proceedings of the International Conference on the Science of Superconductivity, Stanford, Calif., August 1969 (to be published).

## PRESSURE DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF EuO\*

M. R. Oliver, J. A. Kafalas, J. O. Dimmock, and T. B. Reed

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02139 (Received 13 February 1970)

The room-temperature electrical resistivity of EuO is reported as a function of pressure up to 10 kbar. For the higher resistivity samples the pressure coefficient corresponds very closely to the observed shift of the optical absorption edge with pressure. Both the temperature and pressure dependence of the electrical resistivity are explained in terms of a model in which electrons are distributed between a temperature- and pressure-sensitive conduction band and a localized stationary trap level.

The optical, electrical, and magnetic properties of the Eu chalcogenides, EuO, EuS, and EuSe, have been extensively investigated in recent years, both experimentally and theoretically.<sup>1</sup> These ferromagnetic semiconductors exhibit many interesting phenomena, among which is a large temperature dependence of the optical absorption edge characterized by a sizable red shift with decreasing temperature below the ordering temperature,  $T_c$ . Electrically conducting

materials also show a large temperature dependence of their electrical resistivity and a giant negative magnetoresistance in the vicinity of  $T_c$ .

Two models have been proposed to explain the temperature and magnetic field dependence of the electrical resistivity in lightly doped material.<sup>2-4</sup> In both of these models electrical conductivity at high temperature takes place through a thermally activated hopping process, and the large temperature and magnetic field dependence of the conductivity is ascribed to changes in electron mobility. The onset of band conductivity has been reported in more heavily doped samples of EuS in which the impurity states are considered merged to provide the conduction path.<sup>5</sup>

Recently, we have presented some evidence which indicates that the major part of the electrical resistivity variation near and below the Curie point in our undoped samples of EuO is due to changes in carrier density and not to mobility variations.<sup>6,7</sup> The observed dependence of the resistivity on temperature and magnetic field was found to be consistent with a model in which the conductivity occurs in an electron band which varies in energy in the same way as the optical absorption edge. In the model the carriers are thermally distributed between this conduction band and an electron trap state whose energy position is independent of temperature and magnetic field. The observed large changes in resistivity occur via a redistribution of electrons between the conduction band and the trap as the conduction band moves. In order to confirm this model we have measured the pressure dependence of the electrical resistivity of EuO at room temperature. The results agree with our model of band conductivity and a stationary trapping level and are in disagreement with predictions based on the hopping models.

The single-crystal EuO samples were grown in a closed tungsten crucible using Eu and Eu<sub>2</sub>O<sub>3</sub> as starting materials with a 20% excess of Eu above stoichiometry. The crucible was heated to 2050°C and slowly cooled at the rate of  $\sim 3^{\circ}$  per hour down to 1600°C, and at a slightly higher rate thereafter. The crystals used in this investigation were not intentionally doped, and the source of carriers was either residual impurities or small deviations from stoichiometry. However, mass-spectrographic analysis showed that trivalent rare-earth impurity concentrations were below 50 ppm and the results of thermogravimetric analyses indicated that the deviations from stoichiometry were probably less than 0.2%. Annealing studies, however, have shown that the conductivity can be greatly enhanced or suppressed by heating in excess Eu or in vacuum, respectively, indicating that the conductivity may be due in part to deviations from stoichiometry. The Curie points of similar samples were determined, by means of a moving coil magnetometer, to be within one degree of 69.5°K.

The electrical measurements were made using

the van der Pauw technique.<sup>8</sup> The samples were between 50 and 400  $\mu$ m thick and 1 to 3 mm on each side. The contacts were made using a La-Ag alloy. Hydrostatic pressure was applied using a cylindrical die and piston with pentane as the transmitting fluid. The pressure was monitored by measuring the resistance variation of a Manganin coil which was placed in the pressure chamber next to the sample. Pressures to 10 kbar were obtainable without damage to the system.

The resistivity-versus-pressure measurements were made at room temperature on a variety of crystals. The results for three representative samples are shown in Fig. 1. For the highest conductivity sample, the resistivity is independent of pressure. For the two highest resistivity samples, the pressure coefficient is given by

$$d \ln \rho / dP \simeq -0.20 \text{ kbar}^{-1}$$
.

If this variation is interpreted in terms of a pressure-sensitive electrical activation energy



FIG. 1. Resistivity versus pressure at room temperature for three EuO samples.



FIG. 2. Resistivity versus temperature curves for the three samples of Fig. 1.

we obtain

 $kTd \ln \rho/dP \simeq -5.2 \text{ meV/kbar},$ 

which is very close to the observed shift of the room-temperature optical absorption edge of  $-4.4 \text{ meV/kbar.}^9$ 

The temperature dependence of the resistivity for the same samples is shown in Fig. 2. The two highest resistivity samples have a very high peak in the resistivity near  $T_c$  and an activationenergy-type behavior well above  $T_c$  with  $\Delta E$  $\simeq 0.28$  eV. The higher conductivity sample 49-4 shows a peak in the resistivity near  $T_c$ , but above the peak the resistivity remains relatively constant out to 350°K. All of the curves show a large change in resistivity below  $T_c$  with a sharp break in slope near 50°K.

These results are consistent with a model which includes a conduction band whose energy

varies with temperature and pressure as does the observed optical absorption edge, and a trap level whose energy is constant and equal to that of the conduction-band minimum at  $50^{\circ}$ K and zero pressure. The proposed relative positions of the conduction-band edge and trap level are shown in Fig. 3. The observed change in resistivity with temperature and pressure is consistent with a change in the number of conduction electrons brought about by the change in the relative positions of the conduction band and the trap level.

Two different types of behavior of the electrical resistivity above the Curie point result from this model, both of which are observed experimentally. When the number of electrons  $n_e$  is greater than the number of trap levels  $n_t$ , the density of electrons in the conduction band will be equal to  $n_e - n_t$  until such temperatures are



FIG. 3. The proposed model for the conduction band and trap level as functions of temperature.

reached to thermally activate a significant additional number of electrons from the trap level. This would result in relatively little variation in resistivity above  $T_c$ , as observed in sample 49-4.

A second type of behavior is expected from this model if  $n_e < n_t$ . In this case the carriers in the conduction band are thermally activated and the conductivity above  $T_c$  should show an activation energy as observed in the higher resistivity samples 66-2-14 and 66-2-18. Similar activation-energy behavior above the Curie point has been observed by von Molnar.<sup>10</sup>

The resistivity variations with pressure shown in Fig. 1 strongly support the proposed model. In the high-resistivity case where the electrons are supplied to the conduction band by thermal activation, the resistivity decreases as the band edge is lowered toward the trap level and more electrons are thermally excited into the band. The observed behavior of sample 49-4 is also expected from the model in consideration of the lack of temperature dependence of its resistivity.

The fact that the resistivity variation with pressure is quite close to that expected from the observed pressure shift of the optical absorption edge supports the identification of the final state of the optical transition with the band responsible for the electrical conductivity. This requires that the energy of the trap level remain fixed relative to the initial state of the optical transition responsible for the absorption edge. This initial state is believed to be a highly localized Eu 4f state whose energy is not likely to be strongly dependent on temperature, pressure, or magnetic field.<sup>11</sup> If the trap level is also of a highly localized nature, its energy also should not depend strongly on temperature or pressure. Previous results on the temperature and magnetic field

dependence of the electrical resistivity were consistent with this model as are the present results on the pressure dependence.

We conclude that the observed pressure dependence of the electrical resistivity of EuO confirms a model in which the conductivity occurs in an energy band and the variation of the resistivity with temperature, magnetic field, and pressure is primarily due to changes in the number of conduction electrons in the band thermally excited from an electron trap. This variation is caused by changes in the relative positions of the band edge and trap level. Good agreement with experiment is obtained if the relative positions of the band edge and trap level are assumed to change with temperature, pressure, and magnetic field in the same way as the observed optical absorption edge. If the energy position of the localized electron trap level is assumed stationary relative to the localized Eu 4f state, which is the initial state of the optical absorption, then the conduction band in our model must shift as does the Eu 5d band which corresponds to the final state of the optical absorption edge in EuO. One is inclined, based on this argument, to tentatively identify the conduction band in our model with the Eu 5d band observed in optical absorption.

The authors would like to thank Dr. Edward B. Owens for making the mass spectrographic measurements. They would also like to thank Richard A. Westberg for technical assistance and Robert E. Fahey for his help in growing the crystals.

 $\ ^{*}\mbox{Work}$  sponsored by the U. S. Department of the Air Force.

<sup>1</sup>S. Methfessel and D. C. Mattis, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1968), Vol. 18 (Part 1).

<sup>2</sup>S. von Molnar and S. Methfessel, J. Appl. Phys. <u>38</u>, 959 (1967).

<sup>3</sup>T. Kasuya and A. Yanase, Rev. Mod. Phys. <u>40</u>, 684 (1968).

<sup>4</sup>T. Penney, in Proceedings of the Third International Conference on Photoconductivity, Stanford, Calif., 1969 (unpublished).

 $^5\mathrm{S.}$  von Molnar and T. Kasuya, Phys. Rev. Letters 21, 1758 (1968).

<sup>6</sup>C. E. Hurwitz, M. R. Oliver, J. O. Dimmock, and T. B. Reed, Bull. Am. Phys. Soc. <u>14</u>, 309 (1969).

<sup>7</sup>M. R. Oliver, J. O. Dimmock, and T. B. Reed, Bull. Am. Phys. Soc. <u>15</u>, 156 (1970), and to be published.

<sup>8</sup>L. J. van der Pauw, Philips Res. Rpt. <u>13</u>, 1 (1958). <sup>9</sup>P. Wachter, Solid State Commun. <u>7</u>, 693 (1969).

 $^{10}$ S. von Molnar, Bull. Am. Phys. Soc. <u>15</u>, 156 (1970), and to be published.

<sup>11</sup>See Ref. 1, p. 463 ff.