Behavior of the Curie temperature of EuO at pressures up to 20 GPa

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A sharp change has been detected in the behavior of the Curie temperature of EuO at 13 GPa. It is attributed to a transition of EuO to a mixed-valence state. The stability of the ferromagnetism in the mixed-valence phase of EuO is discussed.

Optical and x-ray structural experiments have shown that a gradual insulator-metal transition occurs in EuO at a pressure of 14 GPa and at room temperature. This transition is accompanied by a transition to a mixed-valence state.[1] The compound EuO is a ferromagnet with a Curie temperature T_c which increases from 69.4 K at atmospheric pressure to 124 K at 8 GPa (Ref. 2). Since Eu^{3+} has a nonmagnetic configuration, the transition to a phase with a mixed valence in EuO should (to some extent) promote a destabilization of the $4f$ moment and thus of the ferromagnetic order. In a study of the stability of ferromagnetism in a mixed-valence phase on the basis of a s-f model, Eyert and Nolting[3] found that T_c should reach a maximum at the transition of EuO to the mixed-valence state. Is it possible that T_c increases to 300 K, as Zimmer *et al.*[1] have suggested as a way of explaining the sharp decrease in the $4f$-$5d$ gap at pressures above 10 GPa? In this letter we report measurements of T_c of EuO at pressures up to 20 GPa.

For the measurements of T_c we use a high-pressure apparatus with diamond anvils and a system for measuring the initial *ac* magnetic susceptibility of ferromagnetic samples.[4] A single-crystal sample, with dimensions of $0.08 \times 0.08 \times 0.04$ mm, is positioned in an aperture in a metal spacer 0.15 mm in diameter. The medium which transmits the pressure is a 4:1 methanol-ethanol mixture. The anvil apparatus is cooled with nitrogen vapor to 130 K. The temperature is measured within $\pm$ 1 K by a copper-constantan thermocouple. The pressure is found from the shift of the ruby R lines at room temperature before and after the anvil apparatus is cooled to the temperature of interest. After cooling to 130 K, the pressure in the apparatus increases $\sim 8\%$ because of the plastic deformation of the spacer caused by the difference among the thermal expansion coefficients of the diamond anvils, the leucosapphire bearings and the metal cylinder. The pressure in the anvil apparatus exhibits a significant hysteresis as the applied force is increased and reduced. During the initial stage of the reduction of the applied force, the pressure decreases insignificantly, so the reduction of the load which occurs during warming leads to a pressure decrease of no more than 2% according to our estimates. Taking this circumstance into account, we carried out measurements of T_c during the warming of the anvil apparatus. The system used to measure the initial magnetic susceptibility of the ferromagnetic samples in the anvil apparatus is described in Ref. 4. In the present experiments we measured the voltage across the secondary coil as a function of the temperature with and without a sample

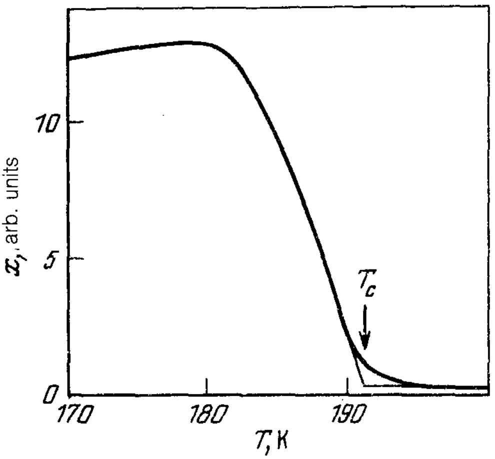

FIG. 1. Temperature dependence of the initial magnetic susceptibility of an EuO sample at $P = 11.7$ GPa.

in the anvil apparatus. A typical difference curve is shown in Fig. 1. The temperature at which the susceptibility increases sharply is adopted as T_c. The procedure for determining T_c is clear from this figure.

The pressure dependence of T_c found in these experiments is shown along with data from Ref. 2 in Fig. 2. As the pressure is raised, T_c increases in a nonlinear way, going through a maximum at 13 GPa and then decreasing.

A characteristic feature of the ferromagnetic semiconductor EuO, which determines its magnetic and optical properties, is the circumstance that the $4f$ levels lie between the valence band and the conduction band. Goodenough[5] has proposed an indirect-exchange model for this case, according to which the ferromagnetic-exchange constant is

$$J_1 = \frac{b^2 J_{fd}}{2S^2 U_{fd}^2} , \tag{1}$$

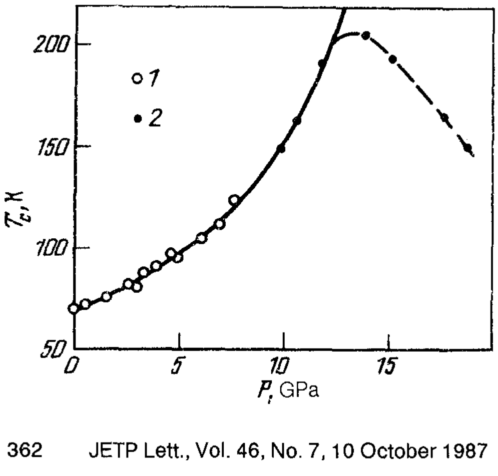

FIG. 2. Pressure dependence of the Curie temperature of EuO. 1—Data from Ref. 2; 2—data from the present study.

where b is the overlap integral of the $4f$-$5d$ orbitals of neighboring cations, J_{fd} is the exchange integral for intraatomic $4f$-$5d$ exchange, S is the resultant spin of the $4f$ shell, and U_{fd} is the difference between the energies of the $4f^7$ and $4f^6 5d$ states. The increase in the overlap of the $4f$ and $5d$ orbitals of neighboring cations and the increase in the $5d$ band in EuO, which are caused by the pressure, lead to an increase in b and a decrease in U_{fd} and thus an increase in J_1 and T_c. The solid curve in Fig. 2 was calculated from expression (1) with the help of the approximations for b and U_{fd} described in Ref. 1. We recall that expression (1) does not apply when the $4f$ levels overlap the conduction band. This point apparently explains the observed discrepancy between the calculated and experimental values at pressures above 12 GPa. Evidence in favor of this possibility comes from the results of Ref. 3, where a study was made of the Curie temperature of EuO in states with normal and mixed valence on the basis of an s-f model. The theoretical curves of T_c as a function of the position of the $4f$ level with respect to the bottom of the conduction band, for several parameters of the model, are similar to the experimental pressure dependence of T_c. On the other hand, we do not see a quantitative agreement. According to this model, the maximum of T_c results from a competition between the intensification of indirect exchange and the decrease in the localized $4f$ moment as the $4f$ level shifts toward the bottom of the conduction band. The maximum of T_c would correspond to a transition to a mixed-valence state. Unquestionably, a precise determination of the transition pressure will require further experiments (optical, x-ray structural, electrical-resistivity, etc.) over a broad temperature range.

The magnetic red shift of the absorption edge[6] in EuO should lead to a substantial decrease in the pressure of the insulator-metal transition as the temperature is lowered. The slope of the phase equilibrium line in the P-T plane should thus be positive. The results obtained in Ref. 1 and in the present experiments agree qualitatively with that conclusion.

It can be seen from Fig. 2 that ferromagnetism exists in the mixed-valence phase of EuO over a fairly wide pressure interval. The reason lies in the relatively weak dependence of the valence of the europium in EuO on the pressure. The valence found in Ref. 1 from the lattice constant by means of a linear interpolation is 2.5 at 35 GPa. It is interesting to estimate the critical valence, at which ferromagnetism would disappear in EuO. Unfortunately, the limited temperature interval which was possible in the present experiments prevented us from studying the behavior of T_c at higher pressures. A linear extrapolation of the experimental data yields a value of 30 GPa for the ferromagnet-paramagnet transition pressure at $T = 0$ K. However, it is clear from general considerations that T_c will fall off more sharply at pressures above 20 GPa. The critical valence thus lies between 2.2 ($P = 20$ GPa) and 2.4 ($P = 30$ GPa). This estimate shows that a comparatively slight deviation from an integer valence results in a suppression of the ferromagnetic order in EuO. This conclusion is not surprising since a nonmagnetic nature of the ground state is characteristic of most mixed-valence compounds over a broad interval of values of the mixed valence.[7]

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