RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 1 1 JULY 1990

Onset of valence and magnetic instabilities in the ferromagnetic semiconductor EuO at high pressures

M. M. Abd-Elmeguid* and R. D. Taylor

Physics Division, MS K764, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 22 March 1990)

Hydrostatic high-pressure ^{151}Eu Mössbauer measurements ($0 \leq p \leq 31$ GPa) on the ferromagnetic semiconductor EuO reveal, contrary to previous suggestions, no pronounced valence change of Eu ($Eu^{2+} \rightarrow Eu^{3+}$) even at highest pressures ($p = 31$ GPa). The magnetic ground state becomes unstable above 23 GPa, where the pressure-induced variation of the Curie temperature is consistent with theoretical predictions based on the volume-dependent competition between *sf*-exchange interactions and *sf* hybridization.

A fundamental issue connected with magnetism in local $4f$-moment systems is the question of the nature of the magnetic ground state when the electrons are able to fluctuate between the $4f$ level and the conduction band (intermediate valent *I-V* system). The search for a model system to study this problem has been the subject of much experimental and theoretical research. Among these systems the ferromagnetic (FM) semiconductor EuO is considered as a good $4f$-model system to study isotropic magnetic exchange interactions in solids (Heisenberg ferromagnet). This is due to its simple cubic fcc lattice structure and the pure spin magnetism of the localized $Eu^{2+}4f^7$ with $^8S_{7/2}$ ground state. The optical gap E_g between the $4f^7$ level and the bottom of the empty $5d$ conduction band (1.14 eV or 13200 K at room temperature) is found to decrease by applying external pressure p ($p < 1$ GPa) at a rate of 50 meV GPa^{-1} or 580 K GPa^{-1}.[1] It has thus been a challenge for experimentalists to reduce E_g towards zero by applying very high pressure ($p > 20$ GPa), thereby inducing both valence v and magnetic instabilities, possibly via a delocalization of the $4f^7$ configuration of the Eu^{2+} ground state.

From the theoretical point of view,[2] the reduction of E_g by increasing pressure not only causes a change of the transport properties of EuO but also strongly affects the magnetic properties: when E_g is reduced *both* the *sf* exchange interactions and the *sf* hybridization are enhanced. The competition between these two effects leads to a maximum of the Curie temperature T_C, followed by a breakdown of the magnetic order.[2]

Despite the fact that several high-pressure experiments have been performed on EuO,[3-7] the situation is still far from being clear. Pressure-volume data of EuO revealed either a sharp volume collapse near 30 GPa (Ref. 3) or a continuous one near 14 GPa.[4] Here the associated color change was taken as *evidence* for a semiconductor to metal transition which is driven by a valence transition $\Delta v(Eu^{2+} \rightarrow Eu^{3+})$ at high pressures.[3,4] Also *L*-edge measurements at high pressures suggested a valence shift of about 0.35 between $0 \leq p \leq 31$ GPa.[5] On the other hand, very recent high-pressure electrical resistivity data on EuO established the existence of the 14-GPa phase transition.[6] However, the analysis of the data shows the existence of a narrow E_g up to 25 GPa, suggesting instead a semiconductor-to-semiconductor phase transition.[6]

Regarding the effect of pressure on the magnetic properties of EuO, several groups have reported changes of the Curie temperature T_C with pressure, $T_C(p)$.[6-8] However, no experimental verification of the theoretical model[2] is yet available.

In the present work we have investigated the valence and magnetic instabilities in EuO at very high *hydrostatic* pressures ($0 \leq p \leq 31$ GPa) using the ^{151}Eu Mössbauer effect (ME) spectroscopy. This technique allows one to detect simultaneously pressure-induced *changes* of both the magnetic ground state [via the effective hyperfine (hf) field B_{eff}] and of the Eu mean valence (via the ^{151}Eu ME isomer shift S). $T_C(p)$ is obtained by measuring $B_{\text{eff}}(T)$ at different pressures.

Contrary to previous reports[3-5] we find no pronounced valence change of the Eu ions ($Eu^{2+} \rightarrow Eu^{3+}$) even at very high pressures ($p = 31$ GPa). The ferromagnetic state of EuO is found to be unstable above 23 GPa, where the behavior of T_C and $B_{\text{eff}}(0)$ in the whole pressure range is in qualitative agreement with theoretical calculations based on the volume-dependent competition between *sf* exchange interaction and *sf* hybridization.[2]

The high-pressure ^{151}Eu ME experiments were performed on a sample taken from a highly Ohmic stoichiometric EuO single crystal using a gasketed diamond-anvil cell (Merrill-Bassett type[9]) up to 31 GPa and at various temperatures between 300 and 4 K. The change of pressure between 300 and 20 K was typically about 5%.[9]

Some typical ME spectra of EuO are shown in Fig. 1 at (a) 300 K and (b) 4.2 K, respectively, at three different pressures. No Eu^{3+} impurities (e.g., Eu_2O_3) were detected. Spectra collected at low pressure at 300 K show a single line at a position corresponding to Eu^{2+}. All ME spectra ($0 \leq p \leq 31$ GPa) at 4 K display magnetic hf splitting (hf field) which reflects the ordering of the Eu^{2+} moments at low temperatures ($T < T_C$). The values of $B_{\text{eff}}(0)$ and S at ambient pressure are in a good agreement with previous results.[7]

We first discuss the stability of the Eu valence state in EuO at high pressures, until now the most contested point in previous works.[3-6] Here, the pressure- and temperature-induced change of the ^{151}Eu isomer shifts allows

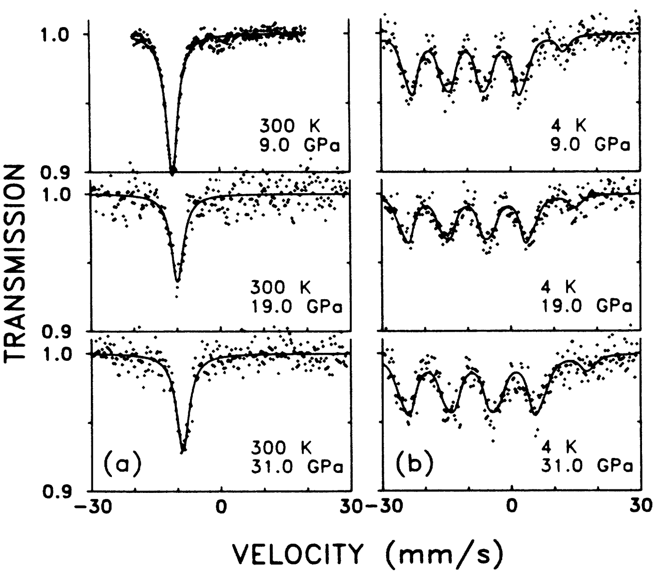

FIG. 1. Typical ^{151}Eu ME spectra of EuO at different pressures: (a) at 300 K, and (b) at 4 K. The source is ^{151}SmF$_3$ kept at the same temperature as the absorber.

us to detect any possible valence changes.[10,11] Figure 2 shows the values of S, obtained at different pressures up to 3 GPa and at different temperatures between 300 and 4 K, versus the relative volume change V/V_0 using the experimental pressure-volume relationship of Ref. 4. As shown in Fig. 2, S increases linearly with decreasing volume but with two different positive slopes where S is enhanced around 15 GPa. This increase of S reflects an increase of the s-electron density $\rho_s(0)$ at the Eu nucleus with pressure.

The pressure-induced increase of $\rho_s(0)$ in Eu^{2+} systems can be mainly caused by the following mechanisms:[12] (i) a compression of s-like electron shells (mainly $6s$); (ii) an increase of intra-atomic and interatomic $4f$ ($5d$,$6s$) exchange interactions; and (iii) a promotion of a $4f$ electron to the conduction band, i.e., a Eu$^{2+} \rightarrow$ Eu^{3+} valence change. In (iii) S is expected to be *strongly* temperature dependent, since the energy separation (excitation energy E_x) between the Eu^{2+} and Eu^{3+} configuration will be significantly reduced.[13] In our case, we observe a total pressure-induced shift of S between 0 and 31 GPa of $\Delta S = 2.6$ mm s^{-1} at 4 K or 2.68 mm s^{-1} at 300 K (see Fig. 2). However, such a shift of S cannot be fully attributed to a *real* valence shift towards Eu^{3+} unless: (a) the volume effect due isothermal volume compression is corrected, and (b) the temperature-induced change of S at different pressures $(\partial S/\partial T)_p$ is carefully analyzed (see below).

Following this basis, we obtain in the pressure range $0 \leq p \leq 15$ GPa a value of $\partial S/\partial \ln V = -9 \pm 1$ mm s^{-1}, typical for stable Eu^{2+} compounds.[14,15] Consistent with this we find a very small negative value of $(\partial S/\partial T)_p$ between 300 and 4 K (see inset of Fig. 2): $(\partial S/\partial T)_p \simeq -7\times10^{-4}$ mm s^{-1} K^{-1} at 9 GPa. The *negative* sign indicates that the electron density at the Eu nucleus decreases with increasing temperature. This must have originated from thermal lattice expansion since a thermal admixture of the Eu^{3+} configuration to the Eu^{2+} ground state would lead to a *positive* sign of $\partial S/\partial T$. In other words, below 15 GPa the $4f^7$ (Eu^{2+}) ground state is located well below the $4f^6$ (Eu^{3+}) state ($k_B T < E_x < 0$), so that no thermal admixture of the Eu^{3+} state can be observed between 4 and 300 K.

On the other hand, we find at higher pressures $15 \leq p \leq 31$ GPa a higher value of $(\partial S/\partial T)_p$: $(\partial S/\partial T)_p \simeq +2\times10^{-3}$ mm s^{-1} K^{-1} at 31 GPa. This has to be compared with the result at lower pressures (see above and inset of Fig. 2). The amount of deviation of the $\partial S/\partial \ln V$ values relative to the base line, which denotes the *pure* volume effect (extrapolated; dashed line in Fig. 2) allows us to determine the *real* pressure-induced valence changes.[16,17] This leads only to a small valence shift towards Eu^{3+} of $\Delta\nu \simeq 0.04$ or $\nu \simeq 2.04$ (at 4 K) and $\Delta\nu \simeq 0.07$ or $\nu \simeq 2.07$ (at 300 K). We obtain rough values of $E_x \simeq 510$ K (at 19 GPa) and 320 K (at 31 GPa). Consistent with these results, we obtain a positive value of $(\partial S/\partial T)_p$ in this pressure range (see inset of Fig. 2). The *positive* sign indicates a thermal admixture of the Eu^{3+} into the Eu^{2+} ground state. Thus, our analysis clearly proves an *onset* of a reduction of E_x above 15 GPa, at which the Eu ion begins to exhibit a weak *I-V* behavior.

This finding has to be compared with other macroscopic high-pressure results on EuO, e.g., optical reflectivity[4] and electrical resistivity,[6] where such an anomaly has been already observed around 14 GPa. However, the *interpretation* which has been presented in this former work[4] is in sharp contradiction with our results. Here, the pressure-induced change of the optical reflectivity and the pressure-volume relationship have been taken as an evidence of a *continuous* Eu$^{2+} \rightarrow$ Eu^{3+} valence change

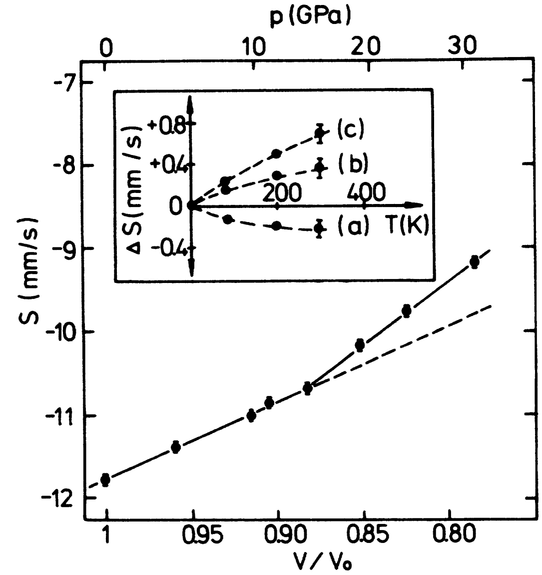

FIG. 2. Volume dependence of the isomer shift (S) at 4 K. The extrapolated dashed line denotes the pure volume effect (see text). Inset: temperature-induced changes of the isomer shift (ΔS) at different pressures: (a) 9 GPa, (b) 19 GPa, and (c) 31 GPa. The values of S are relative to ^{151}SmF$_3$. The error bars of all data points are the same as those shown for data points at 300 K.

which is driven by the onset of *ferromagnetic* ordering at 300 K. As mentioned above, we find neither a significant valence change of the Eu nor ferromagnetic order at 300 K [see Fig. 3(a) and the discussion below]. Thus, the ferromagnetic order cannot be the mechanism which triggers the phase transition at 14 GPa.[4] In contrast to the interpretation of the experimental results of this previous work,[4] recent high-pressure electrical resistivity ($p \leq 25$ GPa) measurements on EuO suggested a quite different physical behavior:[6] EuO exhibits a sudden but moderate drop in E_g at $p > 14$ GPa (300 K), with the persistence of a narrow hybridization gap up to 25 GPa, where the system is still *nonmetallic*.

Our high-pressure results on EuO are clearly consistent with those findings from electrical resistivity.[6] Here, we attribute the anomalous increase of S above 15 GPa to an onset of a reduced excitation energy (E_x) between the Eu^{2+} and Eu^{3+} states, at which we find a *weak I-V* behavior of the Eu ion.[18]

We now discuss the effect of pressure on the ferromagnetic state of EuO, i.e., on $B_{\mathrm{eff}}(0)$ and on T_C. In Figs. 3(a) and 3(b) we plot the values of (a) $B_{\mathrm{eff}}(0)$ (extrapolated to $T \rightarrow 0$ K) and (b) of T_C, obtained at different pressures versus the relative volume change (V/V_0) using the experimental pressure-volume relationship in Ref. 4. As shown in Fig. 3(a), the magnitude of $B_{\mathrm{eff}}(0)$ increases nonlinearly with decreasing volume ($0 \leq p \leq 23$ GPa), showing an enhancement above 15 GPa and then levels off with further decreasing volume ($23 \leq p \leq 31$ GPa). On the other hand, T_C increases rapidly from 69 to 195 ± 6 K with decreasing volume between $0 \leq p \leq 19$ GPa, passes a broad maximum of 200 ± 6 K at 23 GPa, and then falls rapidly between $23 \leq p \leq 31$ GPa to a value of 104 ± 4 K at 31 GPa.

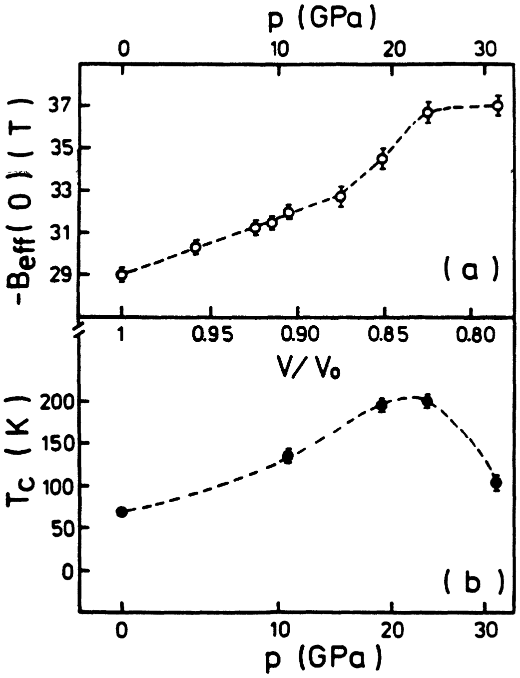

FIG. 3. Volume dependence of (a) the effective hf field $B_{\mathrm{eff}}(0)$ extrapolated to $T = 0$ K and (b) of the Curie temperature T_C in EuO.

To explain the increase of the magnitude of $B_{\mathrm{eff}}(0)$ with pressure, we describe B_{eff} at the Eu^{2+} nucleus in EuO by:[14] $B_{\mathrm{eff}} = B_c + B_{\mathrm{thf}}$, where B_c and B_{thf} denote the hf-field contributions from the spin polarization of the s shells by the Eu^{2+} ion itself and by Eu^{2+} neighboring atoms, respectively.[14] The pressure-induced enhancement of $B_{\mathrm{eff}}(0)$ observed in EuO [$0 \leq p \leq 23$ GPa; see Fig. 3(a)] is *similar* to that observed in *stable* divalent Eu compounds.[14,15] Here it has been shown that the magnitude of $B_{\mathrm{eff}}(0)$ increases with increasing pressure while B_c remains unchanged. The increase of $|B_{\mathrm{thf}}|$ with pressure is caused by the enhancement of *both* intra-atomic and interatomic $4f$ ($5d$,$6s$) exchange interactions. The enhancement of $B_{\mathrm{eff}}(0)$ above 15 GPa is similar to the behavior of S and originates from the onset of a reduced E_x as already discussed before (see above).

In agreement with the behavior of $B_{\mathrm{eff}}(0)$ with pressure, a similar enhancement of T_C in the same pressure range $0 \leq p \leq 23$ GPa is found [see Fig. 3(b)]. In fact, the enhancement of T_C with pressure is caused by the *same* mechanism responsible for the $B_{\mathrm{eff}}(0)$ enhancement, namely the increase of the $4f$ ($5d$, $6s$) exchange interactions. As mentioned before, at higher pressures $23 \leq p \leq 31$ GPa, T_C decreases sharply from 200 ± 6 to 104 ± 4 K and $B_{\mathrm{eff}}(0)$ levels off [see Figs. 3(a) and 3(b)]. Such a pressure behavior of T_C and $B_{\mathrm{eff}}(0)$ is consistent with that predicted from theoretical model calculations on EuO.[2] Accordingly, when the energy gap (E_g) is reduced with increasing pressure, *both* the $4f$ ($5d$,$6s$) exchange interactions and the $4f$ ($5d$,$6s$) hybridization are enhanced. These effects are competitive. In the moderate range, $p < 200$ GPa, T_C is strongly enhanced, whereas the Eu^{2+} magnetic moment is almost unaffected.[2] However, upon further increasing the pressure, the *competition* between these two effects leads to a sharp decrease of T_C after passing a maximum. This breakdown of magnetic order is caused by the reduction of the magnetic $4f$ moment.[2] We observe exactly the theoretically predicted pressure-behavior of T_C. Also the saturation value of $B_{\mathrm{eff}}(0)$ with pressure above 23 GPa is a consequence of the magnetic instability, which originates from the pressure-induced weak *I-V* state of the Eu ion ($v \simeq 2.04$ at 4 K and 31 GPa): a 4% admixture of the Eu^{3+} into the Eu^{2+} ground state should result in a 4% reduction of the Eu^{2+} magnetic moment and of $B_{\mathrm{eff}}(0)$. At the same time, $B_{\mathrm{eff}}(0)$ is still enhanced due to enhanced $4f$ ($5d$,$6s$) exchange interactions. These two effects act in opposite ways and thereby lead to a minor increase of $B_{\mathrm{eff}}(0)$.

In conclusion, the present results shed new insight into the nature of the high-pressure state of EuO. Contrary to previous reports,[3-5] we find no dramatic valence change of the Eu^{2+} ions ($\mathrm{Eu}^{2+} \rightarrow \mathrm{Eu}^{3+}$) even at very high pressures ($p = 31$ GPa). We further show that the pressure-induced changes of T_C and $B_{\mathrm{eff}}(0)$ verify theoretical calculations.

One of us (M.M.A.) wants to thank H. Micklitz, Ch. Sauer, and W. Zinn for helpful discussions. We thank J. G. Mullen for the loan of the $^{151}\mathrm{SmF}_3$ source. This work was supported by the U.S. Department of Energy.

*Present address: Institute für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany.

[1] P. Wachter, Solid State Commun. **7**, 693 (1969); see also M. R. Oliver, J. A. Kafalas, J. O. Dimmock, and T. P. Reed, Phys. Rev. Lett. **19**, 1064 (1970).

[2] M. Matlak and W. Nolting, Z. Phys. B **55**, 103 (1984); V. Eyert and W. Nolting, Solid State Commun. **60**, 905 (1986).

[3] A. Jayaraman, Phys. Rev. Lett. **29**, 1674 (1972).

[4] H. G. Zimmer, K. Takemura, K. Syassen, and K. Fisher, Phys. Rev. B **29**, 2350 (1984).

[5] J. Röhler, E. Dartyge, A. Fontaine, A. Jucha, K. Keulerz, and D. Sayers, in *EXAFS and Near Edge Structure III,* edited by K. O. Hodgson, B. Hedman, and J. E. Penner-Hahn (Springer-Verlag, Berlin, 1984), p. 385.

[6] D. DiMarzio, M. Croft, N. Sakai, and M. W. Shafer, Phys. Rev. B **35**, 8891 (1987).

[7] J. Moser, G. M. Kalvius, and W. Zinn, Hyperfine Interact. **41**, 499 (1988).

[8] R. D. Taylor and J. N. Farrell, J. Appl. Phys. **63**, 4108 (1988); R. D. Taylor, Hyperfine Interact. **47-48**, 502 (1989).

[9] M. Pasternak and R. D. Taylor, Hyperfine Interact. **47-48**, 415 (1989).

[10] J. Röhler and G. Kaindl, Solid State Commun. **37**, 737 (1981).

[11] E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. **30**, 1053 (1973).

[12] R. T. Bauminger, G. M. Kalvius, and I. Nowik, in *Mössbauer Isomer Shifts,* edited by G. K. Shenoy and F. W. Wagner (North-Holland, Amsterdam, 1978), p. 166.

[13] D. Wohlleben, in *Valence Fluctuations in Solids,* edited by L. M. Falcov, R. D. Handke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 1.

[14] U. F. Klein, G. Wortmann, and G. M. Kalvius, J. Magn. Magn. Mater. **3**, 50 (1976).

[15] M. M. Abd-Elmeguid, H. Micklitz, and G. Kaindl, Phys. Rev. B **23**, 75 (1981).

[16] M. M. Abd-Elmeguid, Ch. Sauer, and W. Zinn, Phys. Rev. Lett. **55**, 2467 (1985).

[17] D. Stöber, Ch. Sauer, W. Zinn, and M. M. Abd-Elmeguid, J. Magn. Magn. Mater. **69**, 144 (1987).

[18] The energy separation E_g between the local $4f^7$ level (Eu^{2+}) and the bottom of the $5d$ conduction band (Ref. 6) should be related to the excitation energy E_x between the Eu^{2+} and Eu^{3+} configurations derived from the Mössbauer data. A direct observation of E_x is reported in E. Zirngiebl *et al.*, Phys. Rev. Lett. **54**, 213 (1985).