$EuAl_2$ at Pressures up to 41 GPa: A Localized Magnet Exhibiting Highly Nonlinear Electronic Effects

A. Gleissner, W. Potzel, J. Moser, and G. M. Kalvius

Physik-Department E15, Technische Universität München, D-8046 Garching, Germany

(Received 21 December 1992)

^{151}Eu Mössbauer studies under hydrostatic pressures up to 41 GPa coupled to x-ray diffraction measurements show that—contrary to expectations—the $4f$ electrons in $EuAl_2$ remain fully localized even under a reduction of unit cell volume of ~30%. However, strongly nonlinear effects are observed for the conduction electron polarization, for the s-electron density $\rho(0)$ at the ^{151}Eu nucleus, the Néel temperature T_N, and the transferred hyperfine field B_{thf}. With reduced volume, $\rho(0)$ increases hyperbolically; T_N and B_{thf} are quadratically connected to $\rho(0)$. The latter results can be described quantitatively within the RKKY formalism.

PACS numbers: 76.80.+y, 62.50.+p, 75.30.−m

Hybridization and exchange interaction involving $4f$ electrons in rare earth compounds are of fundamental interest, in particular in intermediate valent (IV) systems, where a valence electron is shared by the $4f$ level and the conduction band [1,2]. In Eu the $4f$ electron core is stable in two configurations, $4f^6$ and $4f^7$; the latter represents a half-filled $4f$ shell. These two configurations correspond to the charge states Eu^{3+} and Eu^{2+}, respectively, found in ionic compounds. Although in conducting systems Eu is neutral, it has become customary to speak of trivalent and divalent charge states to express the similarity of the $4f$ core to that in the pure ions. These two states differ dramatically in magnetic behavior: Eu^{3+}, $4f^6(^7F_0)$ is nonmagnetic, Eu^{2+}, $4f^7(^8S_{7/2})$ shows pure spin magnetism. Hence Eu intermetallics are well suited to gain information on magnetic properties of IV systems. With ^{151}Eu (21.6-keV) Mössbauer spectroscopy the charge states can be identified by their isomer shifts as well. The difference in shift at ambient pressure between Eu^{2+} and Eu^{3+} is ~14 mm/s, about 10 times the experimental width of the resonance lines.

Of particular interest is the cubic Laves-phase intermetallic $EuAl_2$ [3]. It orders antiferromagnetically at 27 K under ambient pressure. Our x-ray data gave a bulk modulus of $B_0=53.8(1.8)$ GPa and its pressure derivative $B_0'=4.18(0.16)$, i.e., a volume compressibility between those of $CeAl_2$ and $YbAl_2$. Since the latter is a known IV case [4], $EuAl_2$ also might be an IV system.

In addition, under a large reduction of unit cell volume, the magnetic hyperfine field, the Néel temperature, and the conduction electron density are expected to show *nonlinear* volume dependencies. In the past they could not

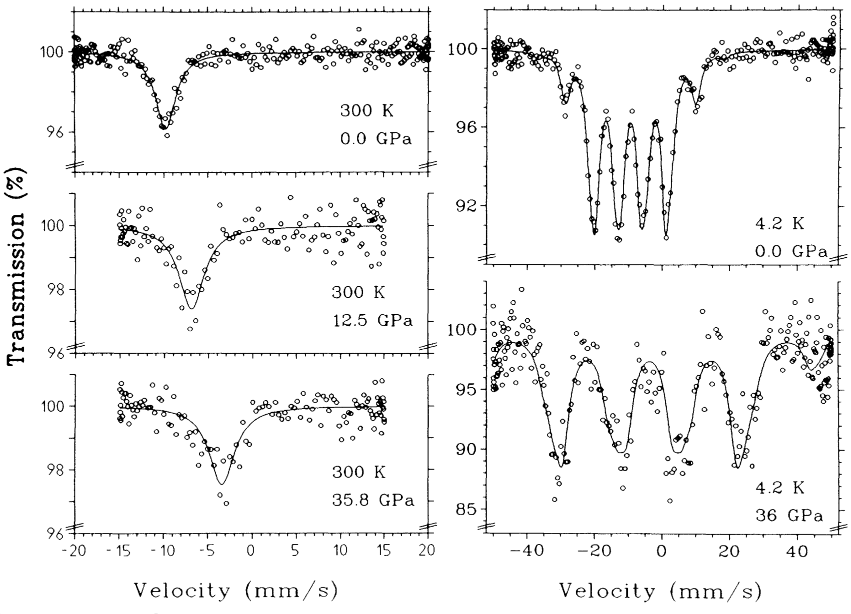

FIG. 1. ^{151}Eu Mössbauer spectra of $EuAl_2$ at 300 K, 4.2 K, and various pressures. The source is kept at the same temperature as the absorber.

be observed well since volume reductions of more than ~10% were not achieved [2,3]. Here we report ^{151}Eu Mössbauer studies of magnetic parameters (i.e., hyperfine field, Néel temperature) and isomer shift of $EuAl_2$ in the presence of quasihydrostatic pressures up to 41 GPa, corresponding to a volume reduction of ~30%, and temperatures down to 4.2 K.

The experiments were carried out in transmission geometry with a 320-mCi $^{151}Sm_2O_3$ source. Pressure is applied to the $EuAl_2$ absorber by a diamond anvil cell based on a design described earlier [5]. Important modifications allowed us to reach the regime of 50 GPa for a sample diameter of 0.3 mm at temperatures between 4.2 and 340 K. Details will be presented in a forthcoming publication [6].

Spectra recorded at 300 K and low pressures exhibit a single line with an isomer shift corresponding [7] to metallic Eu^{2+}. Figure 1 gives examples. When pressure is increased the resonance line moves towards more positive velocities corresponding to an increase of s-electron density $\rho(0)$ at the Eu nucleus [$S=\alpha\Delta\rho(0)$ with $\alpha=0.35a_0^3$ mm/s (Ref. [7])]. Spectra at 4.2 K ($T \ll T_N$) show at all pressures magnetic hyperfine splitting reflecting the ordering of the Eu moments. Figure 2 displays the volume dependence of isomer shift. The solid line is a fit to a hyperbolical dependence of S on volume reduction. It explains the data well. A linear fit (dashed line) works only up to a volume change of 10%, which is the typical range of most high-pressure Mössbauer experiments in such systems up to now [2,3]. Clearly, if larger volume reductions are involved a linear fit is insufficient.

The increase of $\rho(0)$ when volume is reduced will mainly originate from three mechanisms [7,8].

(i) Uniform compression of s-like conduction electrons, mainly $6s$ electrons. According to $\Delta\rho(0) \approx -\rho(0)(\Delta V/V)$, this leads to a hyperbolic change of $\rho(0)$ (or S) with reduced volume.

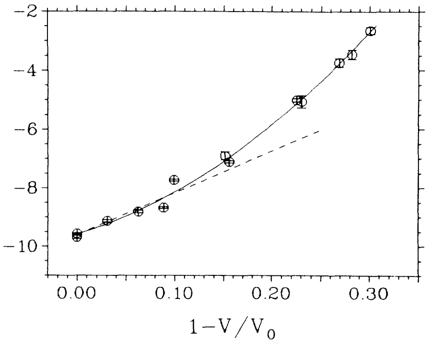

FIG. 2. Volume dependence of the isomer shift S at 300 K. The solid line is a least-squares fit where S depends hyperbolically on the volume change: $S(V)=C_1+C_2[(1/V)-(1/V_0)]$, where C_1 and C_2 are constants and V_0 is the unit cell volume at ambient pressure. The dashed line is a linear fit to the data points up to a volume change of 0.10.

(ii) Increase of intra- and interatomic exchange interaction between $4f$ and $5d$, $6s$ and $6p$ electrons due to increased hybridization. This leads to a reduced shielding of s-electron densities by the $4f$ electrons and also increases $\rho(0)$. To make predictions of the resulting dependence of $\rho(0)$ on volume would require relativistic self-consistent field calculations which unfortunately are at present not available.

(iii) Promotion of a $4f$ electron into the conduction band, i.e., a valence change from Eu^{2+} to Eu^{3+}. This process is known to cause a *strong* temperature dependence of $\rho(0)$ [9].

At a particular temperature T, the isomer shift S or its variation with pressure is determined relative to the $^{151}Sm_2O_3$ source. Both source and absorber are kept at the same temperature T. We observe a total pressure-induced difference in S of 6.93 mm/s between 0 and 41 GPa at 4.2 K. At all pressures the variation of S between 4.2 and 300 K is ≤ 0.5 mm/s and at some pressures even of opposite sign. The charge state of Eu which is close to $v=2$ is stable, i.e., it does not move towards $v=3$, even for a volume reduction of 30% within the limit $\Delta v \leq 0.05$. The causes for the large pressure-induced change of S have to be (i) and (ii). The hyperbolic dependence of S on volume reduction (Fig. 2) strongly suggests that (i) is the dominant mechanism.

The Néel temperature T_N derived from the onset of hyperfine splitting rises from 27.1(1.9) K at ambient pressure to 340(10) K at 41 GPa. Because of thermal contraction of cell material the pressure acting on the sample for a fixed setting of the cell is dependent on temperature. Hence in the determination of the pressure dependence of T_N (as well as for the temperature dependence of S) careful pressure calibrations were carried out. The more than tenfold increase of T_N is strongly correlated to the change ΔS of isomer shift as demonstrated by Fig. 3 (top) where $\Delta(T_N^{1/2})$ vs ΔS is plotted. The straight-line fit gives $\Delta(T_N^{1/2})$ in $K^{1/2}$ and ΔS in mm/s:

$$\Delta(T_N^{1/2}) = 1.865(36)\Delta S + 0.43(15) . \qquad (1)$$

Our value $T_N=27.1(1.9)$ K at ambient pressure is in disagreement with earlier results [10] claiming two different ordering temperatures ($T_N=15$ K and $T_N'=30$ K). A detailed study of the $EuAl_2$-$EuAl_4$ system shows that $T_N=15$ K for $EuAl_4$ whereas $T_N=27.1(1.9)$ K is the Néel temperature of pure $EuAl_2$ [6].

The magnetic hyperfine field B_{hf} at the Eu nucleus shows the largest variation in magnitude observed so far. It increases by more than a factor of 2, that is, from $-26.8(1)$ T at ambient pressure to $-68.7(6)$ T at ~41 GPa. B_{hf} can be written as the sum of four terms [3], since the orbital contribution to B_{hf} vanishes for Eu^{2+}:

$$B_{hf} = B_C + B_{cep} + B_{thf} + B_{dip} . \qquad (2)$$

B_C is the core polarization field arising from the $4f$ elec-

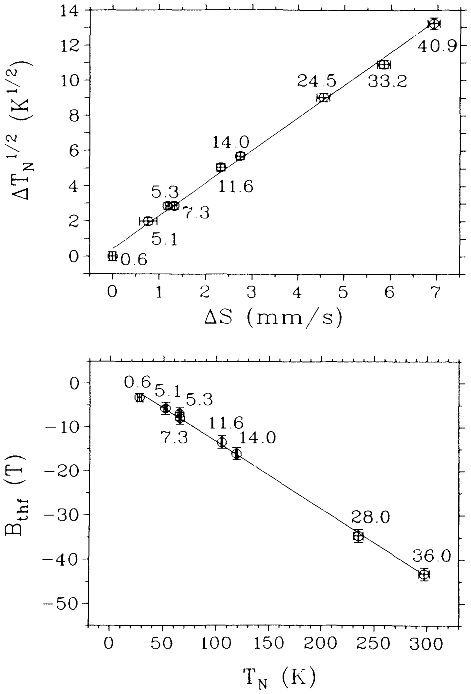

FIG. 3. Linear relations between the change of $T_N^{1/2}$ and the change of S (top) and between $B_{\rm thf}$ and T_N (bottom) when the volume of the unit cell is reduced. At each data point the pressure (in GPa) is indicated. Because of thermal contraction of the pressure cell the pressure given for high T_N values differs from that at 4.2 K where $B_{\rm thf}$ is determined. The fits show that T_N as well as $B_{\rm thf}$ are quadratically connected to the s-electron density $\rho(0)$ at the ^{151}Eu nucleus.

trons, $B_{\rm cep}$ is the self-polarization field due to polarization of the conduction electrons local to the ion by $4f$-conduction-electron exchange, and $B_{\rm thf}$ is the transferred hyperfine field felt by the nucleus due to conduction-electron polarization by neighboring magnetic sites. The dipolar field $B_{\rm dip}$ can safely be neglected. At ambient pressure the following values are deduced [11] for EuAl$_2$:

$$B_C = -34.0(2.0)\ \mathrm{T};\quad B_{\rm cep} = +10.5(2.0)\ \mathrm{T};$$

$$B_{\rm thf} = -3.3(0.5)\ \mathrm{T}.$$

The enormous increases of T_N and $|B_{\rm hf}|$ with pressure demonstrate—in agreement with the already mentioned results for the isomer shift—that the $4f^7$ electronic configuration is highly stable. As a consequence, the local moment of Eu^{2+} in EuAl$_2$ is saturated at the $S=\frac{7}{2}$ free ion value and the pressure dependence of B_C must be negligibly small. The question of the pressure dependence of $B_{\rm cep}$ is complex and has been discussed in some detail [3,12,13]. In Ref. [13] it was argued that, in contrast to EuPt$_2$ and EuZn$_2$, the pressure dependence of $B_{\rm cep}$ is not significant in EuAl$_2$. Therefore the move of $B_{\rm hf}$ to more negative values with increasing pressure is in good approximation solely caused by the volume dependence of $B_{\rm thf}$. This transferred hyperfine field turns out to be strongly correlated with T_N, as shown in Fig. 3 (bottom). The straight-line fit gives for $B_{\rm thf}$ (in T):

$$B_{\rm thf} = -0.162(4)T_N + 2.52(58)\,. \tag{3}$$

Clearly, via relations (1) and (3) the transferred hyperfine field $B_{\rm thf}$ is correlated quadratically to the increase of the s-electron density at the nucleus, $\rho(0)$.

The volume dependence of the magnetic properties and their correlations to the s-electron density can well be explained within the RKKY model. $B_{\rm thf}$ and T_N can then be expressed as [14]

$$B_{\rm thf} = -2a_s\langle s_Z\rangle_s - 2a_{ns}\langle s_Z\rangle_{ns}\,, \tag{4}$$

$$T_N = \frac{S_{\rm Eu}(S_{\rm Eu}+1)}{3k_B\langle S_Z\rangle_{\rm Eu}}(\Gamma_{4f\text{-}s}\langle s_Z\rangle_s + \Gamma_{4f\text{-}ns}\langle s_Z\rangle_{ns})\,, \tag{5}$$

where one has for the hyperfine interaction constants for s and non-s conduction electrons $a_{ns}\approx -0.1a_s$ and for the exchange integrals $\Gamma_{4f\text{-}s}\approx\Gamma_{4f\text{-}ns}\approx\Gamma_{4f}$. $S_{\rm Eu}$ is the $4f$ spin of Eu and k_B is the Boltzmann constant. The spin polarization of s-like and non-s-like conduction electrons is given by [14]

$$\langle s_Z\rangle_s + \langle s_Z\rangle_{ns} = -\frac{9\pi Z^2}{4E_F}\Gamma_{4f}\langle S_Z\rangle_{\rm Eu}\sum_i F(\mathbf{k}_f\mathbf{R}_i)\cos\mathbf{q}\cdot\mathbf{R}_i\,, \tag{6}$$

where E_F is the Fermi energy, Z is the number of conduction electrons per atom, and $F(x)=(x\cos x - \sin x)/x^4$; $\mathbf{k}_F$ is the Fermi vector, $\mathbf{q}$ the wave vector of the antiferromagnetic structure, and $\mathbf{R}_i$ the position vector of the spin i. At ambient pressure we have for EuAl$_2$, $B_{\rm thf}=-4.5$ T, $T_N=27.1$ K. Using $a_s=375$ T/(spin $\frac{1}{2}$) and $\Gamma_{4f}=0.16$ we obtain $\langle s_Z\rangle_{ns}=-0.0143$ and $\langle s_Z\rangle_s=+0.004457$, i.e., ferromagnetic polarization of non-s electrons and antiferromagnetic polarization of s electrons [14]. The polarization of non-s electrons plays an important role. From (5) and (4) we get

$$\frac{B_{\rm thf}}{T_N} = -6k_B\frac{\langle S_Z\rangle_{\rm Eu}}{S_{\rm Eu}(S_{\rm Eu}+1)}\frac{a_s}{\Gamma_{4f}}\frac{\langle s_Z\rangle_s - 0.1\langle s_Z\rangle_{ns}}{\langle s_Z\rangle_s + \langle s_Z\rangle_{ns}}\,. \tag{7}$$

In Eq. (6) the sum is pressure independent. Since E_F is not very sensitive to pressure, the exchange integral Γ_{4f} has the same pressure dependence as the conduction-electron polarization.

Experimentally we observe that the ratio $B_{\rm thf}/T_N$ is independent of volume (Fig. 3, bottom). Assuming the pressure dependence of the non-s and s conduction-electron polarizations to be alike, it follows from Eq. (7) that a_s must have the same volume dependence as Γ_{4f}. This conclusion is in disagreement with Ref. [3] where a_s was considered to be volume independent. Since our data cover a volume change of 30%, it would be very difficult indeed to keep $B_{\rm thf}/T_N$ constant over this large range of volume change unless a_s and Γ_{4f} do have the same dependence on volume. To connect magnetic properties

(T_N, B_{thf}) with the s-electron density $[\rho(0)]$, we combine Eqs. (5) and (6):

$$T_N = \frac{S_{\text{Eu}}(S_{\text{Eu}}+1)}{3k_B \langle S_Z \rangle^2_{\text{Eu}}} \frac{4E_F}{9\pi Z^2} \frac{1}{\sum_i F(\mathbf{k}_F \mathbf{R}_i) \cos \mathbf{q} \cdot \mathbf{R}_i} \times (\langle s_Z \rangle_s + \langle s_Z \rangle_{ns})^2 . \tag{8}$$

It is to be expected under the conditions outlined that the polarization of conduction electrons (ce) is proportional to their density, ρ_{ce}, which again is proportional to the density of ce at the nucleus, $\rho_{\text{ce}}(0)$. We obtain

$$T_N \propto \rho^2_{\text{ce}}(0) , \tag{9}$$

the same relation that has been found previously for a Np intermetallic compound [15] using the Rudermann-Kittel-Arrott (RKA) model for localized f spins. Clearly, $T_N^{1/2} \propto \rho_{\text{ce}}(0)$ and $\Delta(T_N^{1/2}) \propto \Delta\rho_{\text{ce}}(0) \propto \Delta S$. The linear relation between $\Delta(T_N^{1/2})$ and ΔS holds for EuAl$_2$ over the whole pressure range [Eq. (1) and Fig. 3, top]. The intercept in Eq. (1) is due to a small systematic error in determining T_N.

Since B_{thf}/T_N is constant, obviously also

$$B_{\text{thf}} \propto \rho^2_{\text{ce}}(0) . \tag{10}$$

The fulfillment of relations (9) and (10) can be considered characteristic of localized f-electron systems. However, they are only observable in the absence of an orbital field, that is, for S-state ions.

In conclusion, our high-pressure Mössbauer data show EuAl$_2$ to be a typical divalent Eu system which retains its localized magnetic properties up to volume changes of ~30%. The width of the 4f state might increase because of hybridization with conduction electrons. It is, however, reflected neither in the isomer shift nor in the magnetic parameters B_{thf} and T_N. The s-electron density $\rho(0)$ increases hyperbolically with reduced volume, a behavior expected if the conduction electrons behave like a free electron gas. An increase of magnetic order—although not as drastic as for EuAl$_2$—and of isomer shift S has been found upon application of high pressure in the ferromagnetic compound EuO [8]. At ~15 GPa an increase of the slope of S was observed and interpreted as the onset of weak IV behavior. Unfortunately, since EuO is a semiconductor it does not seem to be feasible to compare the pressure behavior, especially of the isomer shift, for the two compounds. Our data prove that at least in metallic systems the assumption of a linear volume dependence of isomer shift is not sufficient at large volume reductions. Fully relativistic self-consistent theoretical calculations are highly desirable to establish this volume relation for $\rho(0)$. T_N as well as $|B_{\text{hf}}|$ increase drastically when pressure is applied. It is demonstrated for the first time that both magnetic quantities are quadratically connected with $\rho(0)$. An explanation is given within the RKKY formalism.

We would like to thank Dr. M. M. Abd-Elmeguid, Ruhr-Universität, Bochum, and H. Karzel, W. Schiessl, and M. Steiner, Technische Universität München, Garching, for helpful discussions.

[1] A. Stratkötter and W. Nolting, J. Phys. C **20**, 1103 (1987).

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

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

[4] A. Palenzona and S. Cirafici, High Temp.-High Press. **17**, 547 (1985).

[5] W. A. Bassett, T. Takahashi, and P. W. Stook, Rev. Sci. Instrum. **38**, 37 (1967).

[6] A. Gleissner, W. Potzel, J. Moser, and G. M. Kalvius (to be published).

[7] E. R. 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. 661.

[8] M. M. Abd-Elmeguid and R. D. Taylor, Phys. Rev. B **42**, 1048 (1990).

[9] D. K. Wohlleben, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 1.

[10] W. M. Swift and W. E. Wallace, J. Solid State Chem. **3**, 180 (1971).

[11] I. Nowik, B. D. Dunlap, and J. H. Wernick, Phys. Rev. B **8**, 238 (1973).

[12] R. A. B. Devine, Phys. Rev. B **25**, 7052 (1982).

[13] M. M. Abd-Elmeguid, H. Micklitz, G. Kaindl, and D. Wagner, Phys. Rev. B **25**, 7055 (1982).

[14] H. Kropp, W. Zipf, E. Dormann, and K. H. J. Buschow, J. Magn. Magn. Mater. **13**, 224 (1979), and references therein.

[15] W. Potzel, J. Moser, G. M. Kalvius, C. H. de Novion, J. C. Spirlet, and J. Gal, Phys. Rev. B **24**, 6762 (1981).