

Comments on the crystal-field splitting of the localized Gd^{3+} moments in Au single crystals

K. Baberschke and Y. v. Spalden

*Institut für Atom- und Festkörperphysik, Freie Universität Berlin,
D-1000 Berlin 33, Germany*

(Received 30 November 1978)

New ESR experiments on Au single crystals doped with Gd impurities yield a positive crystal-field splitting parameter $b_4 = +30.5 \pm 1.0$ G corresponding to $+28.5 \times 10^{-4} \text{ cm}^{-1}$. A fully resolved spectrum is observed. At higher concentrations an exchange-narrowed line appears, produced by interacting impurity spins. Previously published data showed a superposition of a single-ion spectrum and a "cluster" line. The positive sign is in agreement with a recent interpretation of lanthanide S states splitting in metals.

I. INTRODUCTION

A great deal of interest in electron-spin resonance in metals has been spent on the "fine structure" splitting of S -state ions in nonmagnetic host metals. The first observation of a resolved "fine structure" in metals was reported in 1971 by Chock *et al.*¹ for Gd^{3+} in Au single crystals.

The crystal-field splitting of S -state ions is several orders of magnitude smaller than for non- S -state ions and, because of the "higher-order effects," difficult to calculate from first principles. However, a relative comparison should be possible of host metals with different ligand charge, different lattice parameters, or change of host spin-orbit coupling. Following other experimental results on Gd in Pt,² Pd,^{3,4} Ag,⁵ and Eu^{2+} in $LaAl_2$,⁶ we tried to show recently⁷ that an extra "metallic" contribution is needed to explain the crystal electric field (CEF) splitting of S -state ions in cubic and noncubic (Mg,⁸ Sc,⁹ Y,¹⁰ and Lu¹¹) metals. For Gd^{3+} and Eu^{2+} in cubic host metals (and intermetallic compounds) b_4 seems to be positive. There exists only one "exception" in the literature: for Au:Gd $b_4 = -20 \pm 1$ G.^{1,12} This induced us to repeat the experiments. In Sec. II we report the results. A full analysis using the theory of Barnes¹³ is given in Sec. III. According to the theory the transverse dynamic susceptibility is calculated including impurity spin-spin interactions.¹⁴

II. EXPERIMENTAL RESULTS

We have grown by the Bridgman method single crystals of Au doped with Gd concentrations of 300, 100, and approximately 20 ppm. The concentration was determined by saturation-magnetization measurements which agree with the relative intensities of the ESR signals. The crystals for the ESR experiments at

35 and 9 GHz were produced by spark cutting followed by chemical etching. In these small samples there exists a concentration gradient of approximately 10 to 20%. Two different microwave frequencies of 35 GHz ($\cong 1.7$ K) and 9 GHz ($\cong 0.43$ K) were used. For 35 GHz and $T = 1.3$ K most of the Zeeman levels are depopulated. The only populated ones yield two transitions, $-\frac{7}{2} \leftrightarrow -\frac{5}{2}$ and the exchange-narrowed $-\frac{5}{2} \leftrightarrow -\frac{3}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$; this spectrum is easy to interpret. Figure 1 shows the experimental results for approximately 20-ppm Gd. The crystal was rotated in the (101) plane. Using first-order perturbation theory¹⁵ the separation of the two lines yields approximately $31b_4$ in the [100] and $\frac{2}{3} \times 31b_4$ in the [111] direction. The spectrum determines b_4 to be positive, $b_4 \cong +30$ G, which is in contradiction

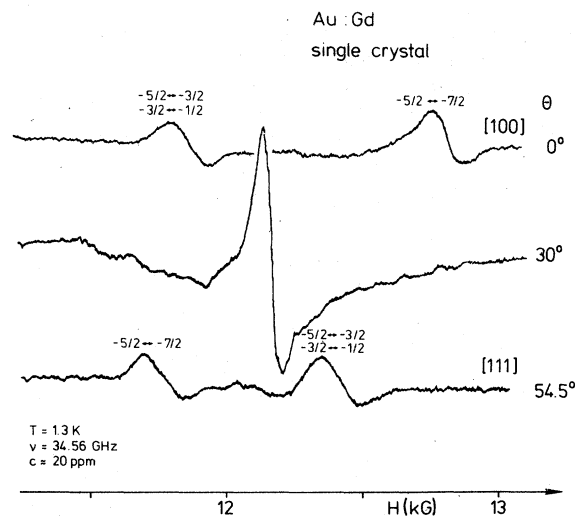


FIG. 1. Q-band ESR spectrum. A small signal at $g = 2$ produced by the empty cavity was subtracted.

with Ref. 1. At 9 GHz more levels are populated and one expects to detect also the $+\frac{1}{2} \leftrightarrow +\frac{3}{2}$, etc. transitions. In Fig. 2 we show the corresponding spectrum. In the [100] direction clearly three weak lines and a "central" transition are observed. The concentration of this sample is 100 ppm. For 300 ppm only the central transition appears. This concentration dependence of the central transition leads to the following conclusion: For concentration $c < 50$ ppm all Gd ions act as independent ions. Depending on temperature and microwave frequency 2, respectively 3, transitions appear and no $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is expected from theory (see Sec. III). For higher concentrations (100 to 300 ppm) some of the Gd ions are strongly coupled and produce an exchange-narrowed single-line spectrum. At 300 ppm and higher concentration only this line is observed. The spectrum in Ref. 1 shows, in our interpretation, the central "cluster" line, and only the low-field bump can be attributed to the single-ion spectrum.

For all samples the full angular dependence of the 2 (Q-band), or 3 (X-band), resonance lines was

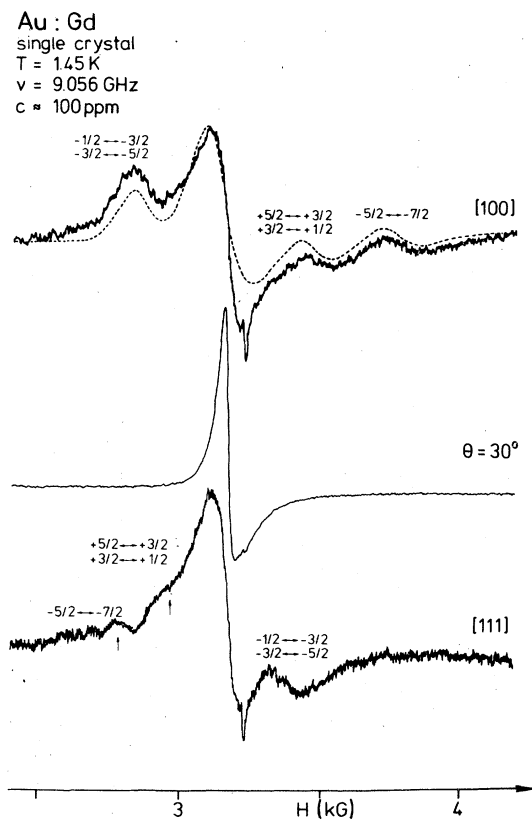


FIG. 2. ESR spectrum for different orientations in the (101) plane. The dashed line is a theoretical fit. A single-ion spectrum and a "cluster" line were superposed—see Fig. 5 and Sec. III.

measured. Figure 3 shows the resonance field versus angle θ . Open circles indicate a resolved spectrum, full dots an exchange-narrowed single-line spectrum. This exchange narrowing is produced by the coupling between one impurity and the conduction electrons and has to be distinguished from the exchange narrowing which is produced by impurity-impurity interaction and is therefore concentration dependent. For the collapsed angle $\theta = 30^\circ$, we determined the thermal broadening of the linewidth $\Delta H = a + bT$, $a = 28$ G, $b = 9.8$ G/K. The thermal broadening is in agreement with values published previously and is independent of the Gd concentration and of the purity of the host metal, indicating that no bottleneck is observed. The g factor in this simple analysis yields $g = 2.041$. The full lines in Fig. 3 show the calculated resonance field, H_{res} , as a function of orientation in

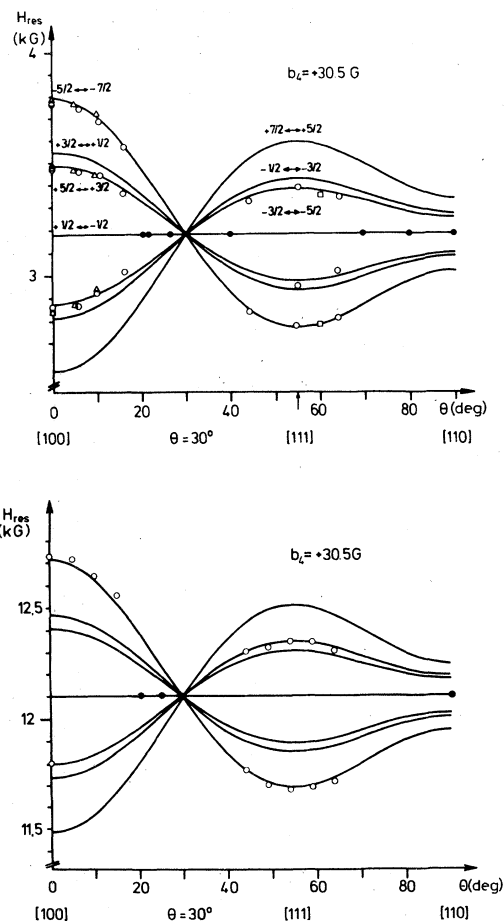


FIG. 3. Resonance field as a function of orientation, θ being the angle between H_0 and the [100] direction. Open circles, triangles, and squares indicate different samples. Full dots are plotted, where only one exchange-narrowed line was detected.

first-order perturbation theory, neglecting the coupling with the conduction electrons.¹⁵ These experimental results evidently show without any further computer analysis that (i) the crystal-field splitting of Gd in Au is in accord with those in other systems, namely positive; (ii) already for 100 ppm Gd approximately 50% of the impurity spins are coupled together. This dynamic "clustering" will of course depend on the sample preparation technique, etc. In Sec. III we will give an accurate analysis of the results taking into consideration impurity-conduction-electron coupling as well as impurity-impurity coupling. It is worthwhile to mention that no conduction-electron spin-resonance signal was observed. In view of the high sensitivity which enables us to detect 20 ppm of Gd one would expect to see this resonance even by reflection techniques.

III. ANALYSIS

Up to now there exist only few examples showing a resolved fine structure and very little theoretical work has been done. In principle one expects, for a coupled system with a local spin $S = \frac{7}{2}$ and a conduction-electron spin $s = \frac{1}{2}$, $2S + 2s = 8$ transitions. Plefka¹⁶ and Barnes¹³ calculated the dynamic transverse susceptibility including Zeeman interaction, exchange coupling, and crystal-field effects. More recently a new interpretation of local-moment resonances in metals has been demonstrated for the system Ag:Gd.¹⁷ This system shows two resonance lines which are interpreted in terms of a high- and low-wave-vector mode; unfortunately a resolved fine structure is missing. We therefore use the theory and computer program of Barnes.¹³

The *single-ion spectrum* was calculated using the following parameters. All the experimental results show no evidence for bottleneck properties; we choose the electron lattice rate $\delta_{eL} = 10^{12} \text{ sec}^{-1}$. For this value the Overhauser rate δ_{ei} is always small compared to δ_{eL} . The ionic and conduction-electron g factors were chosen to be $g_i = 1.993$, $g_e = 2.11$.¹⁸ The thermal broadening $b = 9.8 \text{ G/K}$ yields a coupling strength $\rho J_2(\text{linewidth}) = 0.02$. The center of gravity for the angular-dependent resonance transition yields a g shift $\Delta g = \rho J_1 = 0.04$. We assumed b_6 to be neglectable. The best fit for all spectra gave the crystal-field splitting $b_4 = +30.5 \pm 1 \text{ G}$. It can be seen from the computer-simulated spectra in Figs. 4 and 5 that the line shape of the individual transitions deviates strongly from a simple Dysonian one. It is therefore difficult with the poor signal-to-noise ratio of the low-concentration sample to fit the line shape in detail very accurately. We used a residual linewidth $a = 28 \text{ G}$. This set of parameters yield our best fit for both microwave frequencies and different tem-

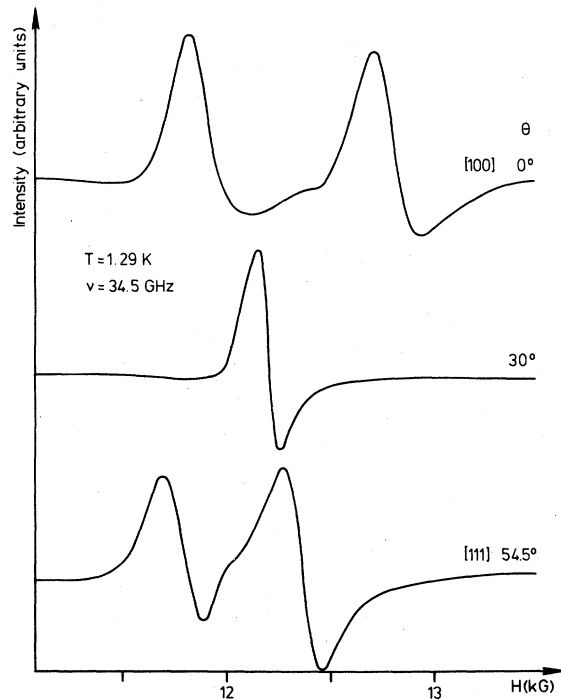


FIG. 4. Theoretical spectrum (Ref. 13) for the 20 ppm sample corresponding to Fig. 1. The parameters are given in Sec. III.

peratures between 1 and 2.0 K. Figures 4 and 5 show the nonappearance of the central $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, which is in agreement with experiment. Similar effects have been observed and explained in other systems (e.g., Pd,^{3(b),12} or⁵ LaAl₂:Eu).

After successful simulation of the single-ion spectrum of the 20 ppm Gd experiments we now introduce the effect of local-moment *spin-spin interaction* in the molecular-field approximation.¹⁴ This introduces a new parameter T_{ord} which is identified with a Curie-Weiss susceptibility function $\chi = C/(T - T_{ord})$. This method is a very rough approximation; unfortunately, more detailed theoretical calculations are missing. Figure 5 shows how the spectra are modified for increasing T_{ord} . A complete exchange-narrowed single-line spectrum appears already for $T_{ord} = 0.3 \text{ K}$, but the position of this high-intensity line still shifts with increasing ordering temperature. The best fit is given in Fig. 5(d) using $T_{ord} = 1 \text{ K}$. In this rough model the ordering temperature can be converted into field¹⁴ using $H_{ss} = (T_{ord}/T)H_0$ which gives for the 100 ppm sample $H_{ss} \cong 2 \text{ kG}$. A similar degree of narrowing would correspond to a relaxation rate $\tau_{ss} \cong 6 \times 10^{10} \text{ sec}^{-1}$.¹⁹ The dashed line in Fig. 2 is the superposition of Figs. 5(a) and 5(d), reducing Fig. 5(a) by a factor of 32 relative to Fig. 5(d). The experimental linewidth of the central line in Fig. 2 is broader than the theoretical one in Fig. 5(d). We

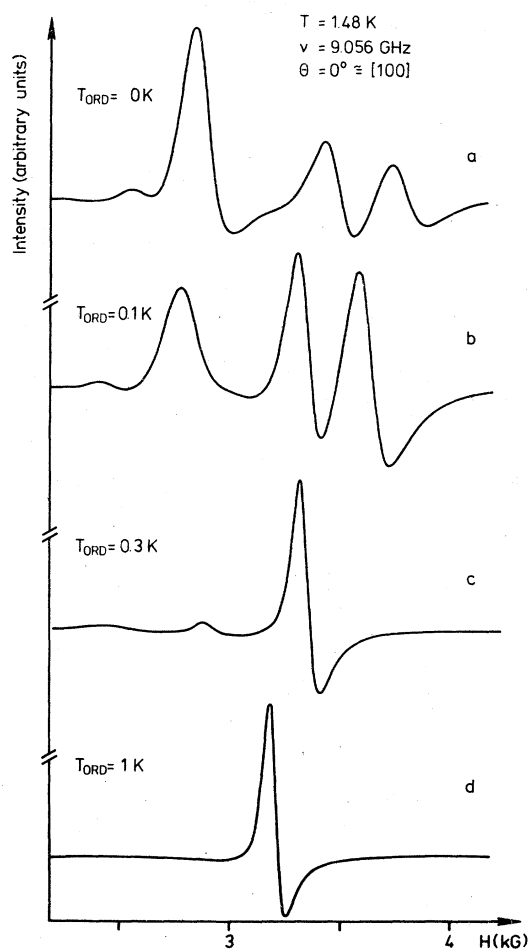


FIG. 5. Theoretical spectrum using the same parameter as in Fig. 4 but for the X-band frequency and 100 ppm. The following magnification factors were used: $d:1$; $c:20$; $b:35$; and $a:32$.

modified Fig. 5(d) by increasing the residual linewidth to about 150 G. This is equivalent to a static internal field distribution. From the relative overall intensity in Fig. 2 we conclude that approximately 50% of the 100 ppm act as individual spins and the rest show a dynamical spin-spin interaction of the order of 1 K.

Figures 5(c) and 5(d) show clearly that the position of the exchange-narrowed lines depends on the coupling strength. It is not meaningful to attribute a g factor to such a line. If we did so, the corresponding g factor of the "cluster-line" would be 2.05.

In summary, we have shown, that for a very low Gd concentration the single-ion line is obtained, yielding $b_4 = +30.5$ G. This value fits quite well into the recent susceptibility measurements;²⁰ it is in accord with a general observation of the crystal-field splitting of Gd^{3+} in elementary metals. Furthermore ESR seems to be a useful tool to detect dynamic spin-spin interactions in the low-concentration limit. This interaction should also affect the magnetic contribution to the resistivity, but would be very hard to separate in a resistivity experiment.

ACKNOWLEDGMENT

The authors are indebted to Dr. S. E. Barnes for many illuminating discussions and for introducing us to the computer program, to Dr. O. Symco for sending us his data prior to publication. We thank Dr. J. Nagel for experimental assistance. Discussions with Dr. H. Hurdequint, Dr. R. Orbach, Dr. P. Monod, and Dr. S. Schultz are acknowledged. This work is supported by the DFG, Special Research Fund Sfb 161.

¹E. P. Chock, R. Chui, D. Davidov, R. Orbach, D. Shaltiel, and L. J. Tao, *Phys. Rev. Lett.* **27**, 582 (1971).

²M. Hardiman, S. E. Barnes, and J. Pelisson, in *Crystal Field Effects in Metals*, edited by A. Furrer (Plenum, New York, 1977), p. 71.

³(a) R. A. Devine, D. Shaltiel, J. M. Moret, J. Ortelli, W. Zingg, and M. Peter, *Solid State Comm.* **11**, 525 (1972);

(b) M. Moret, R. Orbach, M. Peter, D. Shaltiel, J. T. Suss, W. Zingg, R. A. B. Devine, and P. H. Zimmermann, *Phys. Rev. B* **11**, 2002 (1975).

⁴D. Shaltiel, K. Baberschke, J. Nagel, and G. Koopmann, *Phys. Rev. B* **16**, 3262 (1977).

⁵S. Oseroff, B. L. Gehman, and S. Schultz, *Phys. Rev. B* **15**, 1291 (1977).

⁶K. Baberschke, H. J. Jenrich, and J. Nagel, in *Proceedings Second Rare Earth and Actinides Conference, Durham, England, 1977* (Institute of Physics, Bristol and London, 1978), p. 161.

⁷S. E. Barnes, K. Baberschke, and M. Hardiman, *Phys. Rev. B* **18**, 2409 (1978).

⁸P. M. Zimmermann, D. Davidov, R. Orbach, L. H. Tao, and J. Zitkova, *Phys. Rev. B* **6**, 2783 (1972).

⁹J. Nagel and K. Baberschke, in *Crystal Field Effects in Metals*, edited by A. Furrer, (Plenum, New York, 1977), p. 66; J. Nagel, thesis (FU Berlin, 1976).

¹⁰G. Weimann and B. Elschner, *Z. Phys.* **261**, 85 (1973).

¹¹K. Baberschke and N. Nagel, *Phys. Rev. B* **13**, 2793 (1976).

¹²For convenience the CEF splitting b_4 is given in Gauss. This is converted in energy units for $g = 2$:
 $1\text{G} \cong 9.337 \cdot 10^{-5} \text{cm}^{-1}$.

¹³S. E. Barnes, *Phys. Rev. B* **9**, 4789 (1974).

¹⁴Ref. 13 and S. E. Barnes, *J. Phys. F* **4**, 1535 (1974).

¹⁵See for example A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transitions Ions*, (Clarendon, Oxford, 1970), p. 150.

¹⁶T. Plefka, Phys. Status Solidi B 55, 129 (1973); thesis (TH Darmstadt, 1973).

¹⁷S. Oseroff, B. Gehman, S. Schultz, and C. Rettori, Phys. Rev. Lett. 35, 679 (1975); D. R. Fredkin and S. Schultz, Phys. Rev. Lett. 35, 682 (1975).

¹⁸P. Monod and A. Janossy, J. Low Temp. Phys. 26, 311 (1977).

¹⁹Negative and positive Curie-Weiss temperatures, T_{ord} , affect the exchange narrowing differently. Our experiments are not sensitive enough, to determine the sign of T_{ord} .

²⁰E. Jaehne and O. G. Symko (unpublished).