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Electron-Spin-Resonance of Eu^{2+} in Ca- and Yb-Metal *

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ESR measurements of Eu^{2+} (concentration $\leqq 1\%$) in Ca- and Yb-metal in the temperature range from 5 °K to 30 °K at microwave frequencies of 35 GHz and 9.6 GHz are reported. In Ca a "bottleneck" was observed, whereas in Yb the resonance condition is determined by the "dynamical effect". By adding Ca-impurities to Yb the influence of the dynamical effect was lowered. The measurements can be adequately described by the formulas of Hasegawa, yielding an exchange integral for Eu^{2+} in Yb of $J = +0.09$ eV.

I. Introduction

The electron-spin-resonance (ESR) of S-state-ions dissolved in small concentrations in a Pauli-magnetic metal or an intermetallic compound is well suited to study the exchange interaction between the electrons of the half-filled shell of the magnetic impurity and the conduction electrons of the host lattice.

Furthermore one can get information about relaxation processes which take place between magnetic ions and conduction electrons and between conduction electrons and the lattice. Until now measurements have been done on S-state-ions of Mn^{2+} and Gd^{3+} only; a summary is given in [1]. We have measured the ESR of [2, 3] Eu^{2+}; in the present paper a comprehensive investigation of Eu^{2+} in Ca and Yb is reported. Eu^{2+} has a half-filled 4f shell and is, therefore, in an ${}^8S_{7/2}$-groundstate just as Gd^{3+}. Because divalent Eu is soluble in alkaline-earth metals, one can study the ESR in these metals as well as in the divalent rare-earth metal Yb which posesses a closed 4f shell. Yb forms solid solutions with the alkaline-earth metals, and behaves similar to these.

The exchange Hamiltonian between a spin $\mathbf{S}_n$ at lattice site $\boldsymbol{R}_n$ with the conduction electron spin density $\sigma(x)$ at the site $\boldsymbol{x}$ is commonly written as

$$\mathcal{H}_{\text{ex}} = -(1/N)\, J \cdot \mathbf{S}_{\text{n}} \cdot \sigma(\boldsymbol{x}) \cdot \delta(\mathbf{R}_{\text{n}} - \boldsymbol{x}) \qquad (1)$$

where J is the exchange integral and N the number of lattice sites per unit volume. This exchange interaction has two main effects. Firstly, it shifts the ESR-line to lower or higher magnetic fields according to the sign of the exchange integral. This shift is analogous to the Knight-shift in NMR and can be described by a change of the g-value [4]. Secondly, this interaction gives rise to a strong relaxation process, the so-called Korringa-mechanism [5]. Thus the microwave energy absorbed by the magnetic impurities relaxes to the conduction electrons. Because the relaxation rate from conduction electrons to the lattice is normally larger than the Korringa-rate by two orders of magnitude, one would expect very broad resonance-lines, corresponding to the Korringa-rate. But relaxation is complicated by the fact,

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that both the magnetic impurities and the conduction electrons have almost the same g-value of $g \cong 2$. So the conduction electrons take part in the resonance and we get an additional relaxation rate from the conduction electrons back to the magnetic impurities. This relaxation rate was first outlined by OVERHAUSER [6] and can be of the magnitude of the conduction electron lattice rate or even larger. Such a system of two coupled resonators with equal g-values was first treated theoretically by HASEGAWA [7] and later on by GIOVANNINI [8]. With the assumptions $\chi_i \gg \chi_e$ and $\lambda \cdot \chi_e \ll 1$ and neglecting the direct relaxation from the magnetic ions to the lattice which is small because of the lack of an orbital momentum, the results for the g-shift Δg and the linewidth ΔH can be written in the following form (see also DAVIDOV and SHALTIEL [9]):

$$\Delta g = \frac{x^2}{(1+x)^2 + (\gamma\,\lambda\,\chi_i\,H/\delta_{ei})^2} \cdot \Delta g_{\max} \tag{2}$$

with

$$\Delta g_{\max} = J\,\chi_e/(N\,g_e\,\mu_B{}^2)\,;$$

$$\gamma\,\Delta H = \underbrace{\frac{(1+x) + (\gamma\,\lambda\,\chi_i\,H/\delta_{ei})^2}{(1+x)^2 + (\gamma\,\lambda\,\chi_i\,H/\delta_{ei})^2}}_{\mathrm{F}} \cdot \delta_{el}\,\frac{\chi_e}{\chi_i}\,. \tag{3}$$

The "detailed balance" condition

$$\chi_e \cdot \delta_{ei} = \chi_i \cdot \delta_{ie} \tag{4}$$

holds. Here $x = \delta_{el}/\delta_{ei}$; δ_{ie}, δ_{ei}, and δ_{el} are the relaxation rates from local ions to the conduction electrons, from conduction electrons to the local ions, and from conduction electrons to the lattice. χ_i and χ_e are the susceptibilities of the magnetic ions and the conduction electrons respectively; γ is the gyromagnetic ratio; λ the molecular field constant, which is $\lambda = J/(2\,g\,\mu_B{}^2\,N)$; μ_B is the Bohr magneton and H the magnetic field.

II. Experimental

Yb, Eu and Ca mutually form continuous series of solid solutions, as was reported by SPEDDING [10], SODERQUIST and KAYSER [11], SAVITSKII et al. [12] and HÜFNER and WERNICK [13]. All the samples measured here are in the fcc-phase, as can be seen from Refs. [10–13].

Samples were prepared by arc-melting in an argon atmosphere. To ensure that the impurities were homogeneously dispersed, several master solutions were made and the concentration of the impurities was lowered step by step. Analyses of the Eu-concentration have shown that the maximal deviation from the nominal amount was about 10%. For ESR-measurements samples were rolled out to thin plates of 0.1 mm thickness, and polished under oil to have a clean metallic surface.

The measurements were performed with a standard VARIAN-spectrometer in reflection technique, working at frequencies of 9.6 GHz and 35 GHz. In order to vary temperature above liquid helium temperature, we have constructed a vaporizer cryostat of the type proposed by HAUPT [14]. Measurements were made with magnetic field parallel and perpendicular to the sample plate in order to be able to correct for demagnetization effects.

The resonance curves had the asymmetric Dysonian lineshape characteristics for ESR-measurements in metals [15]. In order to evaluate the line with more accuracy, a theoretical resonance line of Lorentzian type was fitted to the experimental curves by varying the resonance field, the linewidth, and the ratio of absorption to dispersion of the resonance line. Figure 5 shows that such a fit could be carried out with good accuracy.

III. Experimental Results and Interpretation

A) Bottleneck Effect in Calcium

The ESR of Eu^{2+} in Ca was measured in the concentration range from 0.066 to 1.0 at-% Eu. For all concentrations the g-value was found to be 1.9925 ± 0.0010 independent of temperature. If for instance we refer to the g-value of Eu^{2+} in CaF_2 ($g = 1.9926 \pm 0.0003$) given by BAKER and WILLIAMS [16] characteristic of an ionic crystal, we find that no g-shift could be observed.

The linewidth ΔH, i. e. the half-power-half-width of the absorption part of the resonance line, is given in Figure 1. There one sees that ΔH increases linearly with temperature, and the slope of linewidth versus temperature $\mathrm{d}(\Delta H)/\mathrm{d}T$ is smaller for higher Eu-concentrations. From these observations and the relatively small values of the linewidth one has to conclude that the condition $x = \delta_{el}/\delta_{ei} \ll 1$ holds, i. e. the relaxation rate from conduction electrons back to the ionic system is larger than the rate from the conduction electrons to the lattice. Such a behaviour is called a "bottleneck-effect", and was first seen by GOSSARD et al. [17] in CuMn.

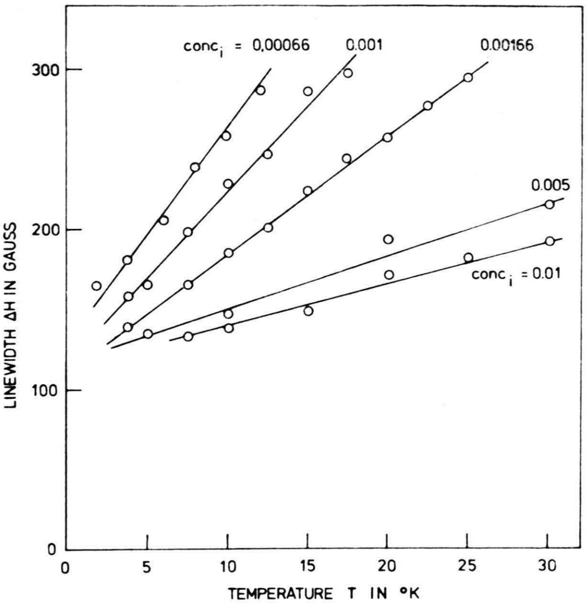

Fig. 1. Linewidth of Eu^{2+} in Ca as a function of temperature measured at 35 GHz. The Eu-concentration conc$_i$ is varied from 0.066% to 1.0%.

Neglecting x compared with 1 we get the following expression for the linewidth from Eqs. (3) and (4)

$$\Delta H = (1/\gamma) \cdot \delta_{el} \cdot \delta_{ie} / \delta_{ei} \,. \tag{5}$$

If we use the formulas given by KORRINGA[5] for the relaxation rate from the ionic system to the conduction electrons

$$\delta_{ie} = (\pi/\hbar)\, \eta^2 J^2 k\, T \tag{6}$$

and by OVERHAUSER[6] for the relaxation rate from conduction electrons to the ionic system

$$\delta_{ei} = (2\pi/3\hbar)\, \eta\, J^2 S(S+1) \cdot \mathrm{conc_i} \tag{7}$$

(here η is the density of states at the Fermi-energy per lattice site and spin orientation, k the Boltzmann factor, T the temperature, S the spin of the magnetic impurity and conc$_i$ their concentration) we get

$$\Delta H = \frac{1}{\gamma}\, \frac{3\eta}{2S(S+1)}\, \delta_{el}\, \frac{T}{\mathrm{conc_i}} \,. \tag{8}$$

The formula describes the dependence of the linewidth on temperature and concentration of the magnetic impurities. In Fig. 2 the slope of linewidth versus temperature is shown as a function of the reciprocal concentration of the Eu-ions. Because the straight line in Fig. 2 does not go through the origin we had to separate δ_{el} into two parts, one of which is independent of the Eu-concentration and gives the relaxation rate δ_{el_0} characteristic of the undisturbed host-lattice. The other is proportional to the Eu-concentration, and arises from spin-flip-scattering at the impurities due to spin-orbit-interaction [17, 18].

$$\delta_{el} = \delta_{el_0} + \left(\frac{d(\delta_{el})}{d(\mathrm{conc_i})} \right) \mathrm{conc_i} \,. \tag{9}$$

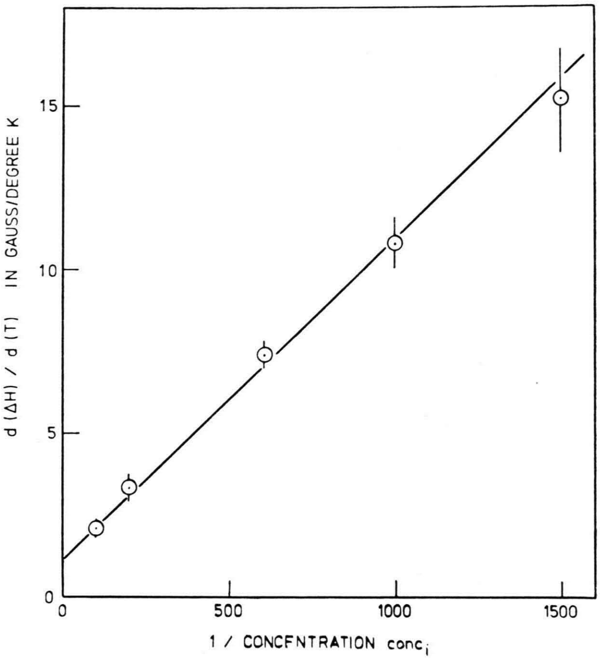

Fig. 2. Slope of linewidth versus temperature from Fig. 1 as a function of the reciprocal Eu-concentration.

From band structure calculations of VASVARI et al.[19] we get the Fermi-energy and, assuming a free electron gas, we can compute the density of states $\eta = 0.32\ \mathrm{eV}^{-1}$. With this value and the results of Fig. 2 we obtain for the relaxation rate of Ca

$$\delta_{el_0} = 6.4 \cdot 10^{10}\ \mathrm{sec}^{-1}$$

and for the spin-flip-scattering rate of Eu in Ca

$$d(\delta_{el})/d(\mathrm{conc_{Eu}}) = 8.05 \cdot 10^{10}\ \mathrm{sec}^{-1}/\%\text{-Eu}.$$

B) Dynamical Effect in Ytterbium

The experimental results of ESR-measurements in Yb-metal are given in Figure 3. A comparison with measurements in Ca shows that the linewidth is much larger reaching values of 800 Gauß for the 0.3 and 0.5% Eu samples at low temperatures. From this and the fact that the increase of linewidth with temperature is almost independent of concentration we have to conclude that the bottleneck-condition

$x \ll 1$ is *not* valid. The dependence of linewidth with temperature for Eu-concentration $\geqq 1\%$ can be seen in [2, 3]. The strong spin-flip-scattering at the Eu-impurity (see Fig. 8) is responsible for the fact that the slope of linewidth versus temperature is independent of the Eu-concentration, and not the assumption of being in the isothermal case $(x \gg 1)$ as stated in [2, 3].

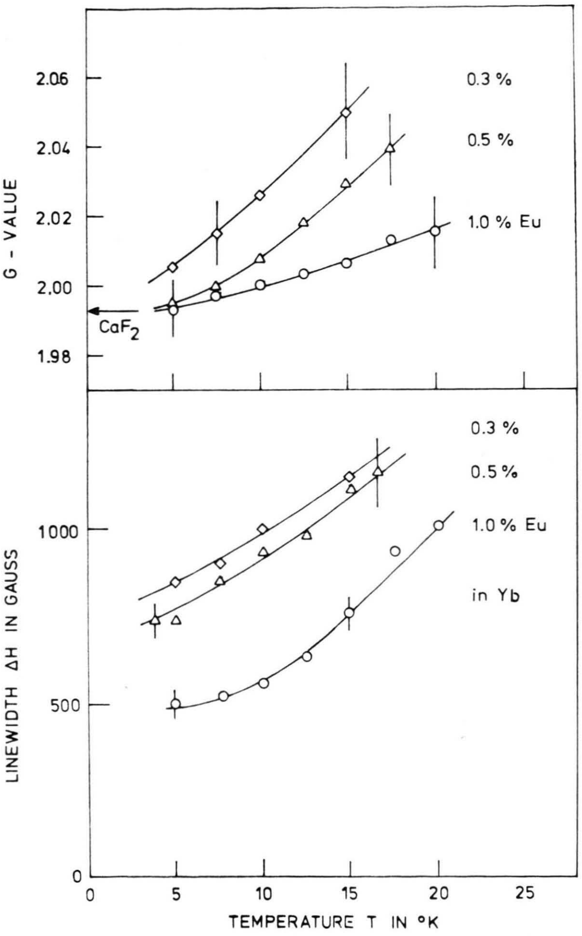

Fig. 3. The g-value and linewidth of various Eu-concentrations in Yb at 35 GHz as a function of temperature.

The g-shift being proportional to $x^2/(1+x)^2$, we would expect a change of the g-value; but as can be seen from Fig. 3, no shift was measured at low temperatures. Contrary to the measurements in Ca, where the g-value is wholly temperature-independent, we observe here a slight shift to higher g-values with increasing temperature.

This behaviour can be described by the expression for the g-shift (2), if we assume that x is in the magnitude of 1 and the condition $(\gamma \lambda \chi_\mathrm{i} H/\delta_\mathrm{ei})^2 > 1$ is valid. Then at low temperatures the susceptibility of the magnetic ions is large and the g-shift is suppressed. With increasing temperature χ_i decreases, yielding an observable shift.

The influence of the term $(\gamma \lambda \chi_\mathrm{i} H/\delta_\mathrm{ei})^2$ is called "dynamical effect" [8] and was first observed by DAVIDOV and SHALTIEL [9] in LaNi$_5$ doped with Gd^{3+} in the form of decreasing maximum g-shift at low temperatures. In Yb the effect seems to be so large, that the g-shift is almost totally cancelled.

By adding nonmagnetic impurities like Ca we have tried to increase δ_el by spin-flip-scattering and so increase x. In this way one can reduce the influence of the term $(\gamma \lambda \chi_\mathrm{i} H/\delta_\mathrm{ei})^2$ and this should yield an increase of the g-shift.

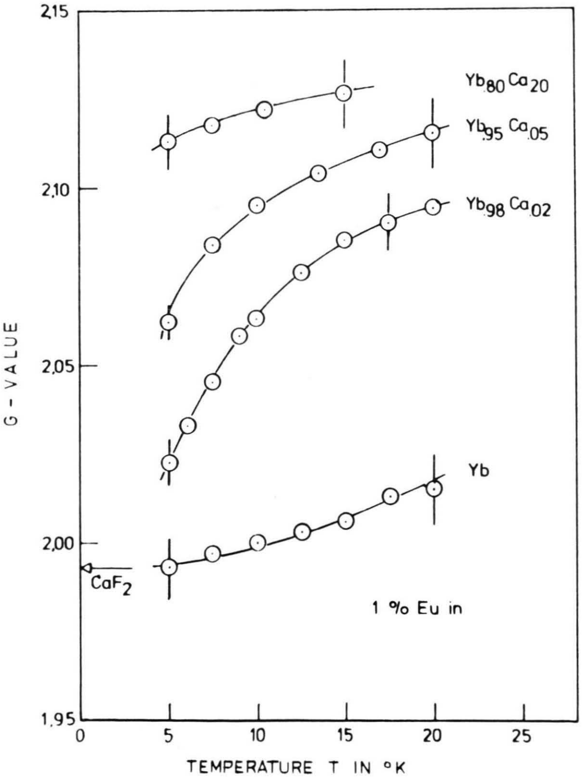

Fig. 4. The g-value of 1% Eu in various YbCa-alloys as a function of temperature measured at 35 GHz.

The result can be seen in Figure 4. We do, indeed, get an increase of the g-value. The addition of 2% Ca gives a marked temperature dependence of the g-value which, at higher Ca-concentrations, reaches a limiting value corresponding to the maximum g-shift.

To demonstrate the effect of the addition of Ca, we show two resonance lines in Fig. 5 giving the signal of 0.5% Eu^{2+} in Yb with and without Ca.

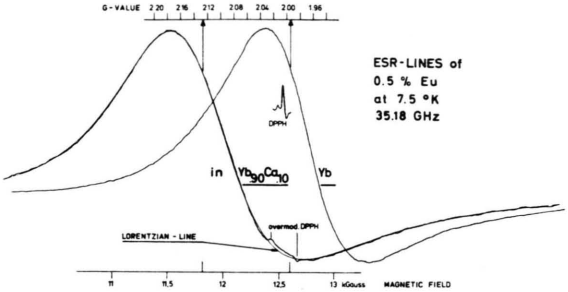

Fig. 5. Derivative of microwave-absorption of 0.5% Eu in Yb with and without 10% Ca at 7.5 °K and 35.18 GHz. To one of the resonance curves a Lorentzian-lineshape is fitted and plotted by a computer. The arrows indicate the field for resonance and the correlated g-value.

One can prove the assumption that the dynamical effect is of importance by measuring the ESR at different microwave frequencies. Because the field for resonance is lowered to a quarter by changing the microwave frequency from 35 GHz to 9.6 GHz, we should observe larger g-values at lower frequencies. This was confirmed by measurements; an example is given in Figure 6.

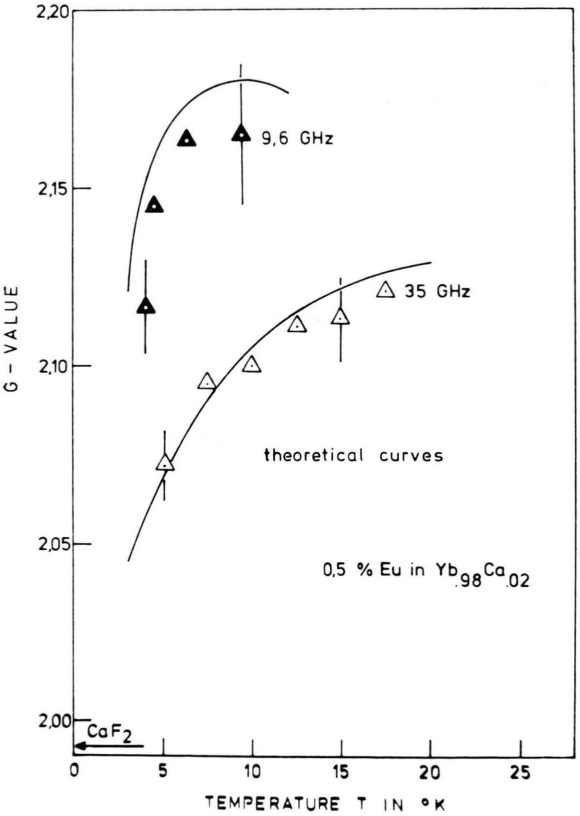

Fig. 6. The g-value of 0.5% Eu in $Yb_{.98}Ca_{.02}$ as a function of temperature measured at 35 GHz and 9.6 GHz. The curves represent the calculated g-value according to Equation (2).

We have tried to fit the formula of the g-shift to the temperature- and frequency-dependent experimental data by using Overhausers Eq. (7) for δ_{ei} and varying δ_{el}, J and η. The susceptibilities of the host-lattices with and without Eu-impurities were measured with a vibrational magnetometer. The following results were obtained: χ_{e} is only weakly influenced by adding Ca and decreases in the interesting temperature range from $2.5 \cdot 10^{-6}$ emu/g at 5 °K to $1.3 \cdot 10^{-6}$ emu/g at 30 °K. The conduction electron susceptibility of Yb can be influenced by impurities dissolved in the metal, as can be seen by comparing measurements of LOCK [20] and BUCHER et al. [21]. We have observed for example that Ba-impurities increase the susceptibility. Our measurements of the susceptibility of the Eu-ions have confirmed the results of UNTERREINER and ELSCHNER [22], who found an enhancement of the local magnetic moment of Eu in Yb. We found an effective moment of 11 Bohr magnetons per Eu-Ion, independent of the Ca-concentration up to 10%. The Curie-temperature of about 4 °K for $Eu_{.01}Yb_{.99}$ reported in [22] is lowered by the addition of Ca-impurities to zero for Ca-concentration of 10%.

As can be seen in Fig. 6, the experimental g-values could be well fitted to Eq. (2). This fit holds not only for the g-values but similarly the linewidth could be described by Equation (3). An example is given in Figure 7.

There is a striking difference between the linewidths measured at 35 GHz and those measured at 9.6 GHz, which can be explained as follows: At microwave frequencies of 35 GHz (the field for resonance is then about 12 kGauß) the term $(\gamma \, \lambda \, \chi_{\text{i}} \, H/\delta_{\text{ei}})^2$ is large. That means that the expression denoted by F in Eq. (3) becomes almost equal to 1. At 9.6 GHz (the field for resonance is now 3.2 kGauß) we can, at higher temperatures surely, neglect $(\gamma \, \lambda \, \chi_{\text{i}} \, H/\delta_{\text{ei}})^2$; so we get $F \cong 1/(1+x)$. Because $x \cong 2$ (see Fig. 8) the linewidth measured at 9.6 GHz is only about a third of that measured at 35 GHz.

The results of fitting the formulas for the g-shift and the linewidth to the experimental values can be summarized: The measurements can be adequately described by an exchange integral of $J = 0.09$ eV

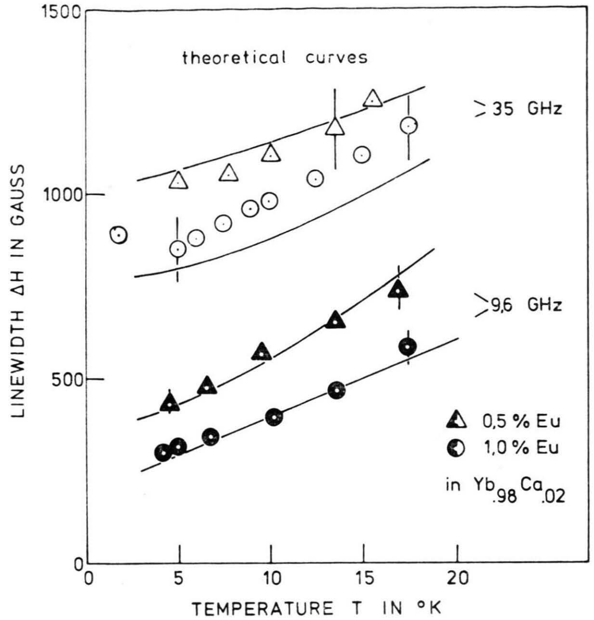

Fig. 7. Linewidth of 0.5 and 1.0% Eu in $Yb_{.98}Ca_{.02}$ as a function of temperature meakured at 35 GHz and 9.6 GHz. The curves represent the calculated linewidth according to Equation (3).

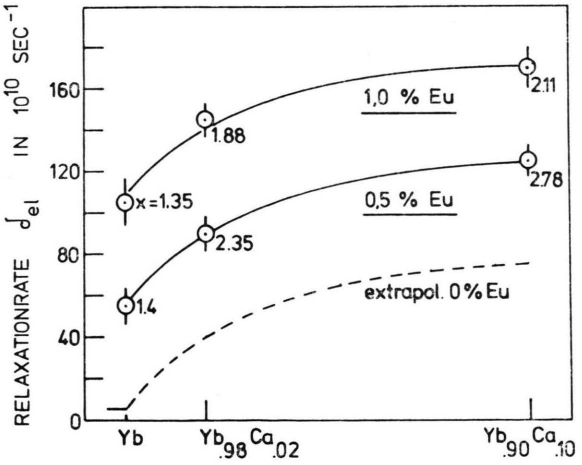

Fig. 8. Relaxations rate δ_{el} from conduction electrons to the lattice for various Ca- and Eu-concentrations in Yb. The values of $x = \delta_{el}/\delta_{ei}$ are given by the numbers attached to the circles representing the data.

and a density of states of $\eta = 0.2$ eV^{-1}, both these values are independent of Ca-concentration. The values for the conduction electron lattice relaxation rate δ_{el} which depend on Eu- and Ca-concentrations are given in Figure 8. There are two essential facts; firstly, δ_{el} increases with increasing Ca-concentration. This verifies our primary intention to increase δ_{el} by spin-flip-scattering at the Ca-impurities. Secondly, we see that there is an additional spin-flip-scattering at the Eu-impurities, which is even bigger than that at Ca. If we extrapolate to zero concentration of Eu and Ca, we get that part of the relaxation rate caused by the undisturbed Yb-lattice. It is about $5 \cdot 10^{-1}$ sec^{-1} and is of the same magnitude as the value which was found for Ca-metal. The spin-flip-scattering at the Eu-impurities in Yb is responsible for not being in the bottleneck region as in Ca. From Fig. 8 we get the following spin-flip-scattering-rate for Eu

$$d(\delta_{el})/d(\mathrm{conc}_{Eu}) = 100 \cdot 10^{10}\ \mathrm{sec}^{-1}/\%\text{-Eu}$$

and for low Ca-concentrations

$$d(\delta_{el})/d(\mathrm{conc}_{Ca}) = 20 \cdot 10^{10}\ \mathrm{sec}^{-1}/\%\text{-Ca}.$$

IV. Conclusion

Alloys of Yb:Ca doped with Eu^{2+} are a suitable system to study the dynamical effect. The measurements can be well explained with the formulas given by Hasegawa. The analysis of the experimental data has shown that one cannot presume any of the extreme cases for relaxation; neither the bottleneck-condition $x \ll 1$ nor the isothermal-condition $x \gg 1$ is fulfilled as can be seen from Figure 8.

The exchange integral evaluated above as $J = +0.09$ eV is somewhat larger than the values given for Gd^{3+} (see for instance [1]). This is compatible with x-ray-photoemission studies of HEDÉN et al. [23], which show that in Eu the 4f states are less separated from the Fermi-energy than in Gd.

HÜFNER [24] has measured with Mössbauer-measurements the contribution to the hyperfine-field of the Eu-nucleus which is a result of the positive polarizaton of the s-electrons by its own 4f spin. From the positive sign of the exchange integral, outlined here, we had to conclude that direct exchange interaction with s-electrons is the predominant effect.

The large value for the spin-flip-scattering rate of Eu in Yb compared with that in Ca is surprising. There is no evident explanation. Resistivity measurements of GEYER [25] seem to confirm our result. On adding Eu-impurities to Ca he found an increase of the residual resistance of $\Delta\varrho_{Ca} = 2.3\ \mu\Omega$ cm/%-Eu, whereas in Yb he measured $\Delta\varrho_{Yb} = 10.7\ \mu\Omega$ cm/%-Eu.

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