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Neutron scattering, magnetization, and Mössbauer measurements on $EuPd_2Si_2$ with enriched ^{153}Eu isotopes

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We report the measurement of the dynamic magnetic susceptibility of an intermediate-valence Eu compound in inelastic neutron scattering experiments, namely, on a sample of $EuPd_2Si_2$ with enriched ^{153}Eu. The most remarkable feature is an increase of the quasielastic linewidth with decreasing temperature, which is apparently a consequence of the well-known temperature-driven valence change. Moreover, at low temperatures a strong inelastic line is observed, which is interpreted as a multiplet transition within the Eu^{3+} configuration ($J=0\rightarrow J=1$). To check the quality of the sample, additional Mössbauer and magnetization measurements were performed. From these we conclude a fraction of approximately 6% of the so-called "satellite" phase in our sample, which is ferromagnetic at low temperatures and whose effects can be separated consistently out of all of our data.

I. INTRODUCTION

Neutrons are a good probe to investigate the dynamics of the localized magnetic moment in a solid, if the relevant time scale is of the order of 10^{-13} to 10^{-10} sec. As fluctuations of typical intermediate-valence (IV) rare-earth (RE) ions run on a rather short time scale of about 10^{-12} sec, neutron scattering experiments were very successful in establishing this very fast relaxation process by detecting a quasielastic line with an anomalous large width compared to that obtained for a stable RE ion.[1] In the meantime, such experiments have been performed on many intermediate-valence Ce,[2-5] Yb,[2,6-9] and Tm systems.[10] However, to our knowledge, there are only two magnetic neutron scattering experiments on IV Sm systems, namely on $Sm_{0.75}Y_{0.25}S$ (Ref. 11) and SmS (Ref. 12), and none on any IV Eu system. The reason for this is obvious: The absorption cross section of the natural isotope mixture of Sm and Eu is so large that only samples prepared from the expensive ^{154}Sm and ^{153}Eu isotopes are suitable for neutron scattering experiments. In this paper we will present, for the first time, diffuse magnetic neutron scattering data on an IV Eu compound, namely $EuPd_2Si_2$.

We have chosen this compound because it shows a strong valence change from $\nu\cong 2.3$ at about $T=170$ K to $\nu\cong 2.75$ at about $T=130$ K. This valence change can be observed by static measurements like lattice parameters[13] or susceptibility[13-15] as well as by spectroscopic methods like x-ray absorption (L_{III} edge) (Ref. 16) or Mössbauer experiments.[13-15,17] As in all IV Eu compounds with $ThCr_2Si_2$ structure an undesired so called "satellite" phase exists also in $EuPd_2Si_2$. This phase is due to certain irregular Eu ions caused by Pd-Si disorder in the same crystal lattice and is therefore not distinguishable from the main IV phase by x-ray diffraction measurements. However it can be detected clearly in the Mössbauer spectra, where a satellite line exists besides the main Mössbauer line. The temperature dependence of the isomer shift extracted from the main line reflects the valence change around $T=150$ K, whereas the isomer shift due to the satellite line is nearly temperature independent and approximately the same as expected for Eu^{2+}. Below $T=80$ K the width of the satellite line increases with decreasing temperature and at $T=4$ K a splitting of that line into several lines is clearly visible,[18] which is interpreted as hyperfine splitting due to magnetic order of the Eu ions in the satellite phase. Obviously, one has to take into consideration the effects of this second magnetic phase if interpreting any measurement on $EuPd_2Si_2$, especially magnetic measurements.

The most important point which we will address in this work is the relaxation behavior of the magnetic moments of the Eu ions in the intermediate-valence main phase as detected in the diffuse inelastic neutron cross section. We have prepared a sample with ^{153}Eu isotopes to perform such a neutron scattering experiment. In order to obtain information about the "satellite" phase in this individual

sample we have also performed lattice parameter, static susceptibility, magnetization, and Mössbauer measurements. On the basis of these data we believe that one can separate the features due to the "satellite" phase from those due to the IV main phase. The discussion of that separation will be a second important point in this paper. It gives a justification for studying such samples, in spite of considerable problems with the sample quality.

A first prediction of the temperature dependence of the quasielastic linewidth came from model calculations using the known susceptibility and valence data and assuming only one fluctuation rate.[19] The result is shown in Fig. 10 by the dashed line and was already shown in Ref. 20. Below $T=80$ K a reliable prediction was not possible, since the low-temperature behavior of the static susceptibility is erratic, i.e., depends strongly on the sample, presumably because of the uncontrollable properties of the "satellite" phase. The prediction of the increase of the width below $T=170$ K was interesting enough to perform diffuse magnetic neutron scattering experiments on just this system. Furthermore, the neutron spectra at low temperatures were expected to give valuable information about the nature of the strange low-temperature behavior of the static susceptibility. Note that the neutron scattering experiment measures directly the dynamic susceptibility $\chi''(\hbar\omega,T)$, which is related to the static susceptibility.[2,20]

II. EXPERIMENTAL DETAILS AND RESULTS

A. Sample preparation

The sample was prepared from the elements Pd, Si (purity 99.9% and 99.9999%, respectively), and from isotopically enriched ^{153}Eu (enrichment: 98.76%) in an argon arc furnace. After melting, the sample was annealed for two weeks at 800° C in an argon atmosphere. X-ray powder patterns do not show any indication of a second crystallographic phase besides the $ThCr_2Si_2$ structure type.

B. Mössbauer spectroscopy

Mössbauer spectroscopy is a powerful method for studying mixed-valence Eu compounds because Eu^{2+} and Eu^{3+} resonances are clearly resolved, and satellite lines can be identified unambiguously. Although in our sample the concentration of ^{151}Eu is only 1.24% compared to a natural abundance of 47.77%, it is possible to record Mössbauer spectra with the 21.6-keV transition of ^{151}Eu. Concerning the spectral resolution (linewidth and isomer shift calibration constant) the 103.1-keV transition of ^{153}Eu could be used for Mössbauer spectroscopy as well. However due to the much higher transition energy the recoil free fraction is so small that the resonance can only be detected in the liquid-He temperature range.

The Mössbauer spectroscopy experiment was performed with a $^{151}SmF_3$ source and the sample was used as absorber. Both, sample and source, were held at the same temperature. Two resulting spectra recorded at 300 and 80 K are shown in Fig. 1. The main resonance moves from an isomer shift of $S=-7.77\pm0.05$ mm/s at 300 K to $S=-0.81\pm0.01$ mm/s at 80 K, demonstrating the valence transition from Eu^{2+} to Eu^{3+} with decreasing temperature in good quantitative agreement with earlier work.[17] At 80 K the above-mentioned satellite line is observed with $S=-8.9\pm0.02$ mm/s and the relative fraction of areas (satellite line—main line) is $r=6\pm2\%$. Assuming equal recoil free fractions for the main resonance and the satellite line[21] the fraction r gives the relative abundance of the (nearly) divalent Eu component. A correction for absorption (saturation effects) is not necessary, because the concentration of the absorbing ^{151}Eu is very low (0.19 mg ^{151}Eu per cm^2. We mention that the fraction of only 6% of the "satellite" phase is the lowest quoted in the literature up to now for $EuPd_2Si_2$.

C. Magnetization and static susceptibility

It is very useful to know the static susceptibility of a sample before investigating it by magnetic neutron scattering. In the case of $EuPd_2Si_2$, this is especially important because the static susceptibility at low temperatures varies from sample to sample. We have therefore measured the field dependence of the magnetization at several temperatures, and the temperature dependence of the static susceptibility for several different pieces of our single $^{153}EuPd_2Si_2$ charge, identified by sample 2 to sample 4 in the figures.

Figure 2 shows several magnetization curves obtained from sample 3. From room temperature down to 100 K the magnetization curves are linear in H, nearly temperature independent and show no spontaneous magnetization for $H=0$, i.e., they behave as they do for paramagnetic

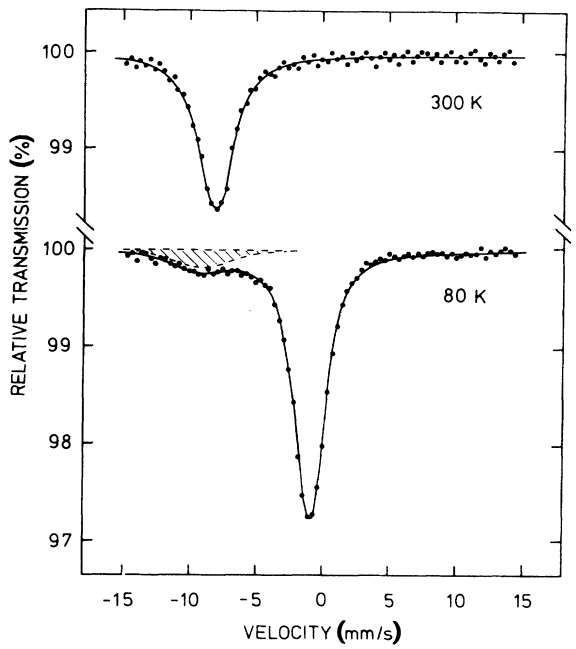

FIG. 1. Mössbauer spectra of $EuPd_2Si_2$ with enriched ^{153}Eu isotopes at $T=300$ and 80 K, repsectively, using the 21.6-keV transition of ^{151}Eu.

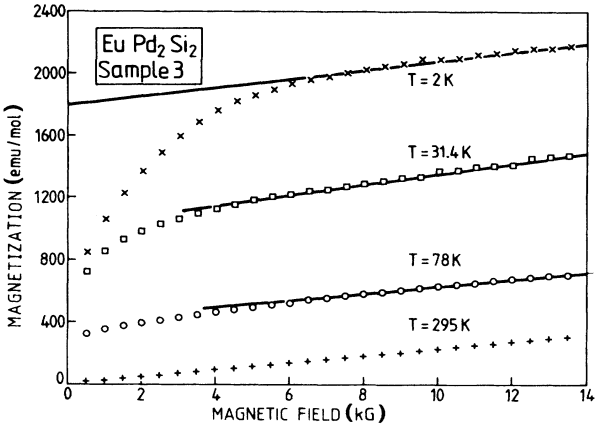

FIG. 2. Field dependence of the magnetization of $EuPd_2Si_2$ for different temperatures.

materials. Below $T=100$ K spontaneous magnetization exists at $H=0$. The static susceptibility shown in Fig. 3 is given by the ratio M/H with a magnetic field $H=3.5$ kG. Thus the observed spontaneous magnetization causes the low-temperature behavior of the static susceptibility which looks like a tail as demonstrated in Fig. 3 for two pieces of our $^{153}EuPd_2Si_2$. This observed tail shows two bumps: one at about $T=80$ K and one at about $T=30$ K. This clearly points out that the tail cannot be due to some paramagnetic impurities, but must be due to some spontaneous magnetization effects. The high-temperature susceptibility ($T>100$ K) behaves in a manner as known from earlier measurements;[13–15] it reflects the valence change around $T=150$ K.

Returning to Fig. 2, one observes for sufficiently large magnetic fields that the low-temperature magnetization again becomes linear in field with nearly the same slope as obtained for high temperatures. We therefore believe that the low-temperature magnetization curve can be separated into a linear part, which reflects the properties of the IV main phase, and into a strongly H-field dependent part, which shows saturation effects and should reflect the properties of the satellite phase. This saturation effect is in agreement with the magnetic order found in the satellite phase by the Mössbauer hyperfine splitting.[18] In other words, the high field slope gives the static susceptibility of the IV main phase, which is shown in Fig. 3 by the open circles and by the dotted-dashed curve as a guide to the eyes, the extrapolation of the linear high field behavior to $H=0$ which gives the saturation moment of the Eu ions in the satellite phase. From the magnetization curve obtained at $T=2$ K (Fig. 2) one can extract a saturation moment of 0.32 μ_B; this is 4.6% of 7 μ_B, the saturation moment of Eu^{2+}.

In order to find a value for the ordering temperature, we measured the static susceptibility at a relatively low magnetic field of $H=0.5$ kG below $T=120$ K. The result is shown in Fig. 4. Below $T=100$ K the static susceptibility obtained with $H=0.5$ kG is much more emphasized than that obtained with $H=3.5$ kG. From the differences between both, one can extract two critical temperatures: one at about $T=30$ K and the other at about $T=100$ K. The structure of the bump around $T=80$ K does not change, whereas that of the bump around $T=30$ K changes with magnetic field. From that one can speculate that below $T=100$ K some ferromagnetic order arises in the satellite phase, while the critical temperature at $T=30$ K seems to be better interpreted by an antiferromagnetic ordering in the satellite phase.

At the end of this section we will mention a remarkable observation. Although the fraction of the satellite line extracted from Mössbauer experiments in our sample is the lowest compared to those published in the literature, the low-temperature tail is the strongest. This can only be understood if one assumes that the magnetization behavior in the satellite phase differs strongly from sample to sample, independently of the amount of this phase. Obviously in our sample the magnetic moment of the satellite phase

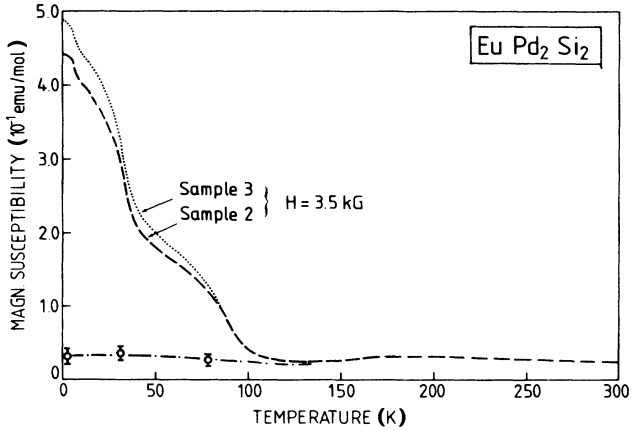

FIG. 3. Static susceptibility of $EuPd_2Si_2$ in dependence of temperature. The open circles are extracted from the slopes of the high field magnetization (solid line in Fig. 2). The dotted-dashed curve is a guide to the eyes representing the static susceptibility of the IV main phase.

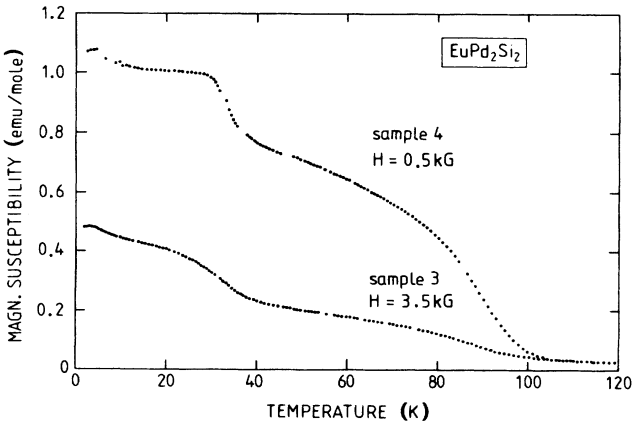

FIG. 4. The static susceptibility of $EuPd_2Si_2$ for $T<120$ K measured with a rather small magneitc field of 0.5 kG and with a "normal" field of 3.5 kG.

can be magnetized more easily than in the samples studied earlier (e.g., Refs. 13 and 15).

D. Neutron scattering

It is well known that the magnetic response in a neutron scattering experiment with energy analysis is the dynamic susceptibility $\chi''(Q,\hbar\omega,T)$. The paramagnetic scattering law for unpolarized neutrons is given by

$$S(Q,\hbar\omega,T)=\frac{1}{2\pi}\left[\frac{g_N r_e}{\mu_B}\right]^2\frac{1}{1-\exp(-\beta\hbar\omega)}\chi''(Q,\hbar\omega,T)$$
$$=\frac{k_0}{k_1}\frac{d^2\sigma_{\rm mag}}{d\Omega d(\hbar\omega)} . \quad (1)$$

Here S is the scattering amplitude per magnetic ion, $d^2\sigma/d\Omega d(\hbar\omega)$ the double differential cross section, $g_n=-1.91$, $r_e=2.8\times10^{-13}$ cm the classical electron radius, $\mu_B=e\hbar/mc$ the Bohr magneton, $\beta=(k_BT)^{-1}$, and $\hbar\omega=E_0-E_1$. E_0 is the energy of the incident and E_1 the energy of the scattered neutrons (for neutron energy gain $\hbar\omega$ is negative). The dynamic susceptibility is correlated to the static susceptibility by

$$\chi''(Q,\hbar\omega,T)=\chi'(Q,0,T)\hbar\omega P(Q,\hbar\omega,T) . \quad (2)$$

Here $P(Q,\hbar\omega,T)$ is the spectral function which must fulfill the relation

$$\int_{-\infty}^{\infty}P(Q,\hbar\omega,T)d(\hbar\omega)=1 \quad (3)$$

and $\chi'(Q,0,T)$ is related to the static bulk susceptibility by a magnetic form factor so that

$$\chi'(Q,0,T)=F^2(Q)\chi_{\rm bulk}(0,0,T) . \quad (4)$$

Our data analysis is based on expressions (1) and (2) using a spectral function of Lorentzian type and the local magnetic form factor of Eu^{2+} (see below).[22] In addition, we have included in our fits also inelastic phonon peaks and the elastic nuclear scattering. The resulting fits are shown by the solid lines in Figs. 5,6,8, and 9. For more details

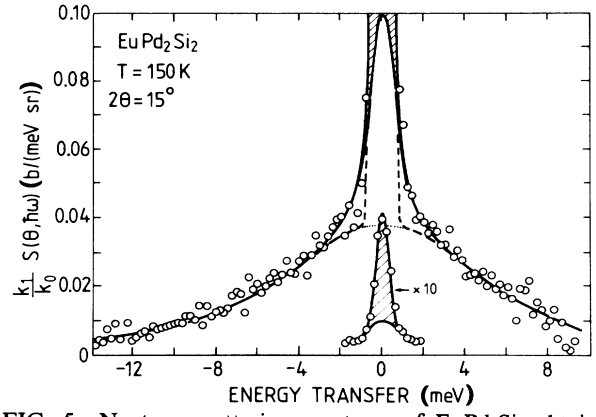

FIG. 5. Neutron scattering spectrum of $EuPd_2Si_2$ obtained with $E_0=12.7$ meV demonstrating the existence of two quasielastic linewidths. The hatched area is due to the real incoherent nuclear scattering and the dashed curve reflects a fit based only on one quasielastic line and the elastic nuclear scattering.

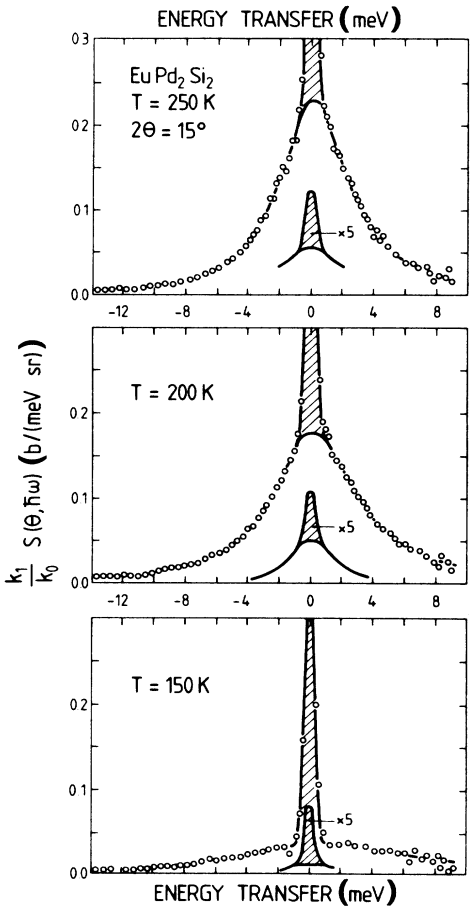

FIG. 6. Neutron scattering spectra of $EuPd_2Si_2$ obtained with $E_0=12.7$ meV for three different temperatures. The second smaller quasielastic line is subtracted in these plots. The hatched areas are due to incoherent nuclear scattering.

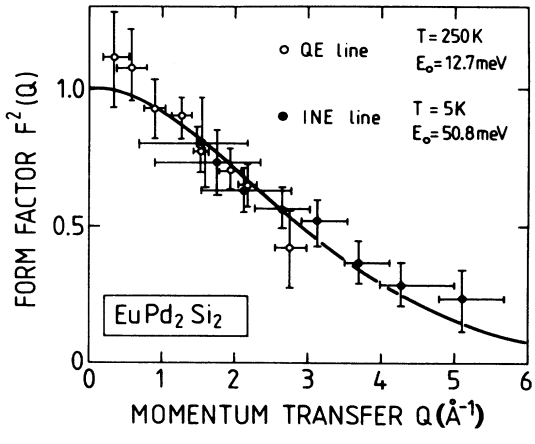

FIG. 7. Local magnetic form factor of Eu in $EuPd_2Si_2$ extracted from the quasielastic line at high temperatures and from the inelastic line at low temperatures. The solid line is the theoretical Eu^{2+} form factor taken from Ref. 22. The horizontal error bars indicate the Q window of which the intensities are added.

concerning the data analysis see Refs. 2 and 23.

All magnetic intensities given in this paper are directly related to the local magnetic moment and not to the local magnetic susceptibility. This value cannot simply be extracted from the neutron scattering data in the case of a broad quasielastic line. In Refs. 2 and 20 a procedure is described which results in an approximate value of the total magnetic cross section (compare also Sec. III).

As mentioned above the two mixing Eu configurations in $EuPd_2Si_2$ are the divalent and the trivalent configurations. The Hund's rule ground state of the Eu^{2+} configuration has a magnetic cross section of about 38 b and is a pure spin state with $S=J=\frac{7}{2}$, without crystal field (CF) splittings. In contrast to this the magnetic cross section of the $J=0$ Hund's rule ground state of the Eu^{3+} configuration is zero. However, with increasing temperature the first excited state ($J=1$), which is 46.5 meV above the ground state in the free ion,[24] is partly populated. Its full magnetic cross section has a value of 2.72 b. Moreover, the transition between $J=0$ and $J=1$ should be detectable by a neutron scattering experiment; this multiplet transition has an expected intensity of 7.3 b.

The neutron scattering experiment was performed on the time-of-flight (TOF) spectrometer IN4 at the high-flux reactor of the Institute Laue-Langevin in Grenoble. Using the double monochromator in the mode of two rotating graphite crystals we chose an energy of incident neutrons of about 12.7 meV (first order) or of about 50.8 meV (second order). The powdered sample of a weight of 7.5 g was measured in an aluminum box, which has a plane cross section of 20×80 mm^2. This set-up leads to an effective sample thickness of 0.6 mm and to a neutron transmission rate of 63% using $E_0=12.7$ meV. All energy spectra presented in this paper show the background and neutron absorption corrected double differential cross section. Figure 5 shows such a spectrum obtained at $T=150$ K with $E_0=12.7$ meV. Here it is demonstrated that also in neutron scattering spectra the features due to the IV main phase can be clearly separated from those of the satellite phase. There are two quasielastic lines in the spectra with different widths. The main line is rather broad, while the second line has a width of only 0.6 meV at $T=150$ K increasing to a value of 1 meV at $T=250$ K. The intensity of the dominating line is 16 b, 42% of the full Eu^{2+} value, and the other has an intensity of 2.3 b (see Fig. 10), only 6% of the full Eu^{2+} value. Therefore, the broad line can unambiguously be associated with the IV main phase, while the more narrow line should be due to the satellite phase. Thus the fraction of the satellite phase extracted from both the neutron scattering experiment and from the magnetization measurement are in very good agreement with the results of Mössbauer spectroscopy. This gives us the confidence to interpret the following neutron scattering results as a real property of the IV main phase. The second quasielastic line could not be resolved in spectra taken with $E_0=50.8$ meV, since at this incident energy the resolution is worse than for $E_0=12.7$ meV.

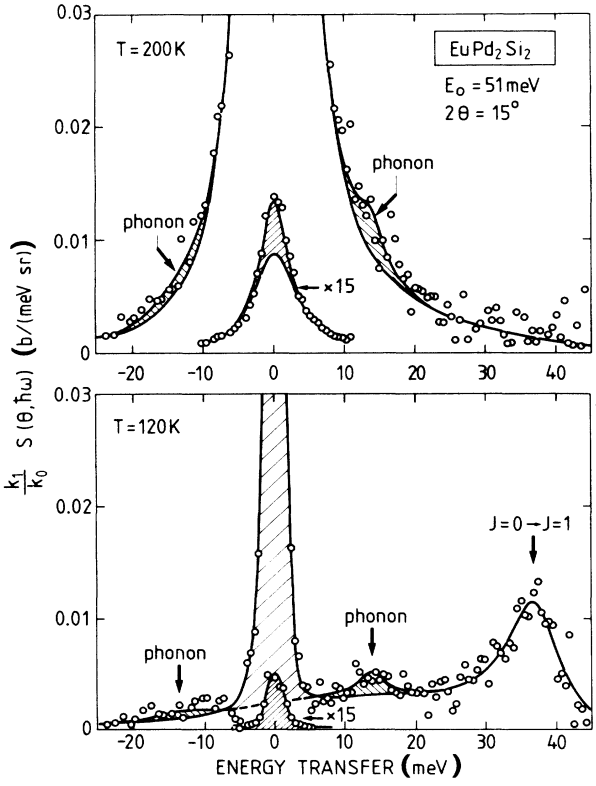

FIG. 8. Two neutron scattering spectra of $EuPd_2Si_2$ obtained with $E_0=50.8$ meV: one at a temperature above and the other below the temperature of valence change.

In Fig. 6 more spectra obtained with $E_0=12.7$ meV are shown for several temperatures above the valence change. To show only the behavior of the main IV phase the second, rather narrow, quasielastic line is subtracted in these spectra. As well as in Fig. 5 the hatched areas are due to the elastic incoherent nuclear scattering. The quasielastic intensity has magnetic character because its Q dependence agrees quite well with the local magnetic form factor[22] as demonstrated in Fig. 7. However, the temperature dependence of the quasielastic linewidth behaves abnormally, even for an intermediate-valence system. Due to the valence change from a nearly divalent magnetic state at high temperatures to a nearly trivalent nonmagnetic state at low temperatures, this width increases with decreasing temperature. This is best demonstrated in Fig. 8 by two spectra taken with $E_0=50.8$ meV: one of these spectra was obtained at $T=200$ K, i.e., above the temperature of valence change $T\cong150$ K; the other at $T=120$ K, i.e., below that temperature. With this incident energy, contributions due to phonon scattering also become important. The inelastic nuclear scattering is marked by the hatched areas as well as incoherent elastic scattering. The magnetic contributions of both spectra look quite different. The upper one at $T=200$ K shows again a quasielastic spectrum of a width of about 4 meV. As the energy resolution for $E_0=50.8$ meV is worse by a factor of 4, the quasielastic line is not so well separated from the elastic line as in Fig. 6 using $E_0=12.7$ meV for the same temperature. The quasielastic contribution in the lower spectrum at $T=120$ K is very broad; its width is approximately $\Gamma/2\cong22$ meV, i.e., much larger than at

$T=200$ K. The asymmetry, which is visible for the quasielastic line at $T=120$ K, is due to the so-called Bose-factor $\hbar\omega/[1-\exp(-\beta\hbar\omega)]$ [see Eq. (1) and Ref. 25]. The dominant feature in this lower spectrum is an inelastic excitation line at about $\Delta\cong 38$ meV. Its intensity again agrees with the local magnetic form factor as again shown in Fig. 7. Therefore we interpret this line as a transition from the Hund's rule ground state ($J=0$) to the first excited Hund's rule state ($J=1$) of the Eu^{3+} configuration. As there is a large correction due to neutron absorption on the energy loss side of the neutrons, the absolute extracted intensity of this excitation is rather uncertain. Nevertheless, the value of about 8 b extracted from the experimental data is near to 7.3 b expected theoretically for this excitation within the Eu^{3+} configuration. This inelastic line is not visible in the upper spectrum at $T=200$ K.

Finally, Fig. 9 shows two spectra at $T=5$ K taken with $E_0=12.7$ meV (upper part) and with $E_0=50.8$ meV (lower part). Again, the hatched areas are due to nuclear scattering. The above-mentioned difference in the energy resolution due to E_0 is clearly demonstrated in this figure. With $E_0=50.8$ meV the inelastic excitation line at $\Delta=38$ meV is again observable. In addition, a very weak inelastic line at about 7 meV is visible. As this line could not be detected at higher temperatures, one may interpret it as due to magnons in the satellite phase. However there is no evidence for a quasielastic line from those spectra. To obtain more information we assume that a quasielastic line may exist and that the valence may be 2.85. This value for the valence is an upper limit obtained by different experimental methods, i.e., this valence leads to a lower limit of the magnetic cross section of about 5.5 b for the intermediate-valence Eu ion. With these assumptions we calculated quasielastic spectra using different linewidths. The results are also shown in Fig. 9. If a quasielastic line with $\Gamma/2<3$ meV exists, one cannot resolve it with $E_0=50.8$ meV. However, such a narrow line was also not visible with the better energy resolution at $E_0=12.7$ meV. Moreover the elastic cross section of about 3 b obtained at $T=5$ K with $E_0=12.7$ meV is the same as found for higher temperatures. Therefore one can even exclude the existence of a quasielastic line, which would not be resolved with $E_0=12.7$ meV. Thus a quasielastic line with a relatively small linewidth ($\Gamma/2<5$ meV) does not exist at all. Moreover from the spectrum taken with $E_0=50.8$ meV it becomes obvious that the width of a quasielastic line should be larger than 25 meV if such a line exists. In other words, the assumption of a quasielastic line and of an upper limit of 2.85 for the Eu valence leads to a lower limit of about 25 meV for a quasielastic linewidth $\Gamma/2$.

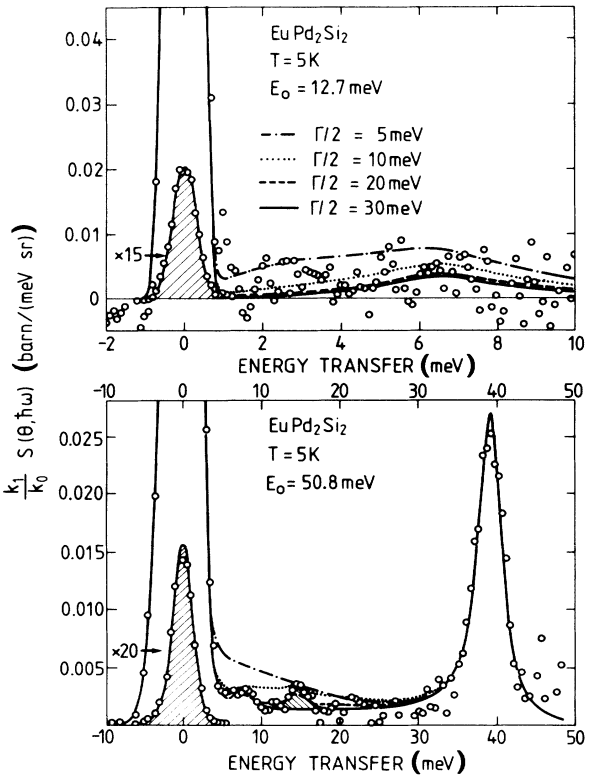

FIG. 9. Neutron scattering spectra of $EuPd_2Si_2$ obtained with $E_0=12.7$ meV and $E_0=50.8$ meV at $T=5$ K. The curves are calculations of the spectrum with a quasielastic line of different widths assuming a quasielastic magnetic cross section which is correlated with a valence of 2.85.

III. DISCUSSION

The physically relevant data extracted from the neutron scattering spectra, the linewidth, and the intensities, are summarized in Fig. 10. The temperature dependence of the quasielastic linewidth, as well as that of the quasielastic intensity, reflect the valence change around $T=150$ K. The quasielastic linewidth increases rapidly at that temperature from about 4 meV at $T=200$ K to 22 meV at $T=120$ K. This can be interpreted by a shorter relaxation time of the Eu^{2+} configuration, which seems to be a direct consequence of the valence change to a value which is close to the Eu^{3+} configuration. This behavior was roughly predicted by Wittershagen[19] as mentioned above (dashed line). More detailed model calculations allowing different linewidths for the $J=\frac{7}{2}$, $J=0$, and $J=1$ levels lead to good agreement with the neutron data,[26] i.e., a good agreement with the quasielastic and inelastic linewidths. In Fig. 10 the result for the $J=\frac{7}{2}$ level is given by the solid line. The dotted curve is a guide to the eyes. A similar relaxation behavior due to the valence change was also predicted by Kuramoto and Müller-Hartmann.[27] The low-temperature behavior of the magnetic relaxation will be discussed in context with other experimental methods at the end of this paper.

Although the magnetic scattering intensity is strongly influenced by the valence, one cannot directly extract the valence from the neutron scattering spectra. In accordance with expressions (1) and (2) the intensity factor extracted from the neutron data can be described very well by the static susceptibility. The valence and/or the local magnetic moment, which in general cannot be taken easily from neutron spectra, is given by the total magnetic cross

section. This can be obtained by solving the integral $\int_{-\infty}^{\infty} S(\hbar\omega)d(\hbar\omega)$, which can be done easily only if the linewidths are small compared to the thermal energy (see Refs. 2 and 20). In the case of $EuPd_2Si_2$ the quasielastic linewidths are larger, or at least of the same order of magnitude as the thermal energy. Thus the total magnetic cross section must be calculated by a numeric integration over the double differential cross section. As the spectra obtained by neutron scattering only show a finite-energy window of the complete response function, some assumptions are necessary to solve this integral, e.g., a cutoff energy E_c (for more details see Refs. 2 and 20). Performing this procedure with $E_c = 1.5$ eV one obtains the values given in Fig. 10, from which one can roughly extract a valence change from 2.3 at $T = 200$ K to 2.75 at $T = 120$ K. The same procedure was also used to extract the correct calculated scattering intensities in Fig. 9.

The nature of the inelastic line at $\Delta = 38$ meV observed below the temperature of valence change is not completely clear. An additional neutron scattering experiment at $T = 5$ K with $E_0 = 80$ meV shows clearly that there does not exist any further inelastic line up to an energy transfer of 70 meV. Thus from neutron scattering alone there is an evidence that the inelastic line at $\Delta = 38$ meV is due to the multiplet transition $J = 0 \rightarrow J = 1$ of the Eu^{3+} configuration, because the Q dependence of this scattering intensity behaves like a magnetic form factor and the absolute value of that intensity is in agreement with the value expected for this transition. However there are still some problems regarding that line. The transition energy is expected to be 46.5 meV for the free atomic state. Here a much lower value of 38 meV was found. Moreover this value does not agree with the value which one extracts by following the interpretation of the Raman data given in Ref. 28. They found a value of about 48.8 meV.

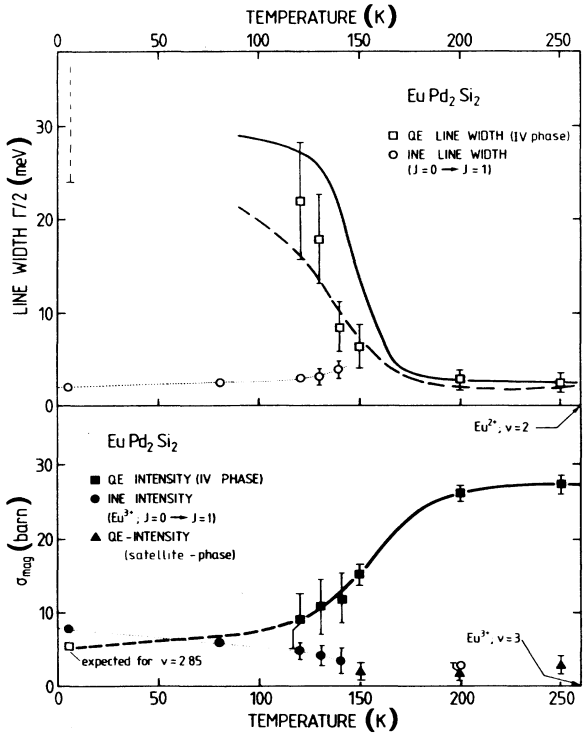

FIG. 10. Temperature dependence of the width and of the intensity of both the quasielastic and the inelastic lines. The expected magnetic intensities for the $J = \frac{7}{2}$ (Eu^{2+} configuration) and the $J = 0$ (Eu^{3+} configuration) are also given in the lower part. For detailed explanation see text.

Let us now turn to the fact that this inelastic line vanishes above the temperature of the valence change. Of course the intensity of this line is expected to be depressed above the valence change, as there the trivalent component becomes smaller compared to the low-temperature region. however, this alone cannot explain the complete vanishing of this inelastic line. In principle, two different additional processes may explain this fact. Firstly, the excitation energy may increase to a value which is close to the free atomic value of 46.5 meV, which is just out of our experimental energy window ($E_0 = 50.8$ meV). Secondly, the width of the transition line may increase with the valence change, so that a detection of this line will no longer be possible.

There are two experimental observations, which strongly support the second explanation: the transition energy is slightly decreasing from 38 meV at $T = 5$ K to 36 meV at $T = 140$ K and the width of the transition line is increasing from 2 meV at $T = 5$ K to 4 meV at $T = 140$ K (see Fig. 10). The shift of this inelastic line is a consequence of the increasing linewidth as for instance described for crystal-field transitions by Becker, Fulde, Keller.[29]

Thus we believe that the width of the inelastic line increases the more the valence shifts to the magnetic Eu^{2+} configuration. This is also supported by similar observations on IV Sm systems. In $Sm_{0.75}Y_{0.25}S$ the valence changes only slightly from 2.3 at $T = 77$ K to 2.44 at room temperature.[30] Thus, even at room temperature the valence is closer to the nonmagnetic Sm^{2+} configuration than to the magnetic Sm^{3+} configuration. Therefore the increase of the inelastic linewidth is rather smaller and the multiplet transition line will survive.[31] On the other hand, in SmS at atmospheric pressure, i.e., for integral valent Sm^{2+} ions, this multiplet transition line was also found, while this line had vanished at $p = 0.6$ GPa,[12] i.e., for Sm-ions with a valence of about 2.6. In the same sense one can understand the results of SmB_6 There the valence is again 2.6, i.e., closer to the magnetic Sm^{3+} configuration, and no clear indications for a multiplet transition line were found in the inelastic neutron scattering spectra.[32] Note that in the case of a free Sm ion the first excited Hund's rule state is expected only 36 meV above the ground state.[24] Thus in contrast to Eu the energy window chosen in the neutron scattering experiment with $E_0 = 50.8$ meV was clearly sufficiently large to detect this line.

From this point of view we believe that the missing multiplet line is a consequence of broadening effects, which are forced by the shift of the valence close to the magnetic configuration (Eu^{2+} or Sm^{3+}). Thus the temperature dependence of the inelastic linewidth behaves just inverse to that of the quasielastic one. The fact is completely in agreement with the idea of a selection rule by Wohlleben and Wittershagen.[26]

Finally we will discuss the low-temperature behavior of the ground state. Model calculations[26] done on the basis of the static susceptibility *including the low temperature tail* lead to rather small fluctuation rates: $T_{SF} < 100$ K at $T = 5$ K. If interpreting the linewidths in Raman data as a fluctuation temperature Zirngiebl *et al.*[28] indeed found $T_{SF} = 100$ K at $T = 5$ K. Both results contradict that which one finds when interpreting the quasielastic linewidth extracted from neutron scattering data as a fluctuation temperature, which is then $T_{SF} > 300$ K.

The discrepancy between the model calculations and the neutron scattering result can easily be solved. In our interpretation of the static susceptibility (see section magnetization and static susceptibility) the susceptibility of the IV main phase becomes flat for $T \rightarrow 0$ (see also Fig. 3). On the basis of this, model calculations on a flat susceptibility will result in rather large fluctuation temperatures in agreement with the results of the neutron scattering data.

There remains a contradiction to the interpretation of the Raman data.[28] There the authors pointed out that they can observe both ladders of transitions starting from $J = \frac{7}{2}$ to $J = 0, 1, \ldots, 6$ and starting from $J = 0$ to $J = 1, 2, \ldots, 6$. The intensity for the first one is expected to be larger than for the second one; exact numbers for the matrix elements cannot be given. Assuming now that *only* the first ladder with the starting level $J = \frac{7}{2}$ will be detectable by Raman scattering, another interpretation of the Raman spectra may be possible, if the Eu ions of the "satellite" phase are also intermediate valence. In analogy to the Mössbauer spectra, there will be no separation of both phases in the Raman data at high temperature, i.e., the excitation energy $E_x = E_{7/2} - E_0$ is nearly the same in both phases. Decreasing the temperature, two ladders of transitions are separated due to the fact that the excitation energy E_{ex} is increasing for the IV main phase, while E_{ex} is nearly constant for the satellite phase. This separation is best visible at $T = 145$ K: Here the peaks due to the IV main phase are slightly broadened and those due to the satellite phase are rather sharp (see Fig. 1 in Ref. 28). This broadening effect is in agreement with the broadening of the $J = \frac{7}{2}$ level as observed in the neutron scattering spectra. Assuming a further broadening of the $J = \frac{7}{2}$ level in the majority phase with decreasing temperatures, this ladder will no longer be detectable due to the very broad widths at low temperatures. Thus the surviving rather sharp peaks observed in the Raman spectrum at $T = 5$ K may be due to the "satellite" phase. In contrast to Ref. 28, this interpretation of the Raman data also takes into account the satellite phase, but it is based only on the ladder with the starting level $J = \frac{7}{2}$. In this way one obtains an agreement with the fact that the neutron scattering spectra at $T = 5$ K cannot be fitted by a quasielastic line with a width smaller than 25 meV, which is due to the $J = \frac{7}{2}$ state of the main IV phase. At that temperature the magnetic moments of the Eu ion in the "satellite" phase are ordered.[18] Thus this phase is reflected by the very weak inelastic line in the neutron data (compare discussion of Fig. 9).

Following this idea the neutron scattering and the Raman scattering method are detecting two quite different inelastic processes. The neutrons observe certainly the $J = 0 \rightarrow J = 1$ transition, while the Raman scattering process in this picture observes (mainly) the indirect process $J = \frac{7}{2} \rightarrow J = 1, 2, \ldots, 6$. Consequently, it follows that the transition energies observed in both methods may be different. Moreover, it is even reasonable that the transition energy observed by Raman scattering is larger than that by neutron scattering: In the new interpretation given above, the Raman spectrum at $T = 5$ K was interpreted as a property of the satellite phase, which should be nearly divalent; thus it is credible that the $J = \frac{7}{2}$ level is lower than the $J = 0$ level, i.e., $E_{ex} < 0$, indicating a larger transition energy for $J = \frac{7}{2} \rightarrow J = 1$ (Raman) than for $J = 0 \rightarrow J = 1$ (neutron).

We will finish the discussion with a critical remark concerning the low-temperature neutron scattering spectra of $EuPd_2Si_2$. The spectra do not show any direct evidence of a quasielastic line. Therefore one may also interpret this spectrum in another way. At low temperatures the valence fluctuation becomes time coherent, i.e., a localized coherent fluctuation exists as observed for $Tm_xY_{1-x}Se$ by an inelastic line at $\Delta \cong 12$ meV.[10] In the diluted Tm case the coherent fluctuation should be influenced by CF effects. In the case of $EuPd_2Si_2$ this coherent fluctuation should be forced by the multiplet transition $J = 0 \rightarrow J = 1$. The quasielastic scattering may then be vanishing. This interpretation also leads to a flat susceptibility of the real IV phase (Van-Vleck susceptibility). Perhaps this idea should be discussed in more detail in the future.

IV. CONCLUSION

There are two main results coming out of this work for $EuPd_2Si_2$. At first the behavior of the magnetic relaxation reflects the drastic valence change around $T = 150$ K in just a way as expected by theory[27] and as predicted by model calculations:[26] the quasielastic linewidth increases with decreasing temperature. As a second important result we emphasize that a separation of the features due to the IV main phase from those due to the satellite phase is possible in many experiments by careful analysis. Thus it can be claimed that the tail in the static susceptibility at low temperatures is due to ordering effects in the so-called "satellite" phase. Nevertheless the low-temperature relaxation behavior in the IV main phase is not yet completely understood, especially as a discrepancy between the interpretation of the neutron scattering data and the Raman data still exists.

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