Unusual magnetic response of intermediate-valent YbPd and Yb_3Pd_4 as studied by inelastic neutron scattering

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We report on some novel features of the magnetic response of intermediate-valence Yb compounds as seen by inelastic magnetic neutron scattering. We firstly confirm the existence of magnetic phase transitions in intermediate-valent YbPd and Yb_3Pd_4 by observing magnon excitations below and additional Gaussian quasielastic lines above the ordering temperatures. We then show that it is the very small magnetic fluctuation rate at helium temperatures which enables these systems to order magnetically. On the other hand, the very large quasielastic linewidth observed at higher temperatures ensures that YbPd is indeed in an intermediate-valent state. We also find for the first time two different quasielastic linewidths in these systems, which differ strongly in their temperature dependence. Distinct inelastic excitations can be interpreted in terms of crystal-field theory. The crystal-field ground states have nonvanishing quadrupole moments, whose interactions enhance the magnetic ordering temperatures in both systems.

INTRODUCTION

In this paper we report the results of quasielastic (QE) and inelastic (IN) neutron scattering in YbPd and Yb_3Pd_4. Both compounds are intermediate valent ($v=2.79-2.83$ for YbPd and $v=2.81-3.0$ for Yb_3Pd_4) and belong to a new class of intermediate-valence Yb compounds, whose common signature is the occurrence of magnetic ordering. At the present time this class consists of six members: $YbBe_{13}$,[1-3] YbPd,[4,5] Yb_3Pd_4,[6] $YbIr_2$,[7] YbPt,[8] and Yb_3Pt_4.[8] The discovery of this class was quite unexpected, because until recently *all* intermetallic compounds with Yb had been found to remain paramagnetic to the lowest temperatures measured. When Yb intermediate-valence compounds were divalent, they showed of course only a temperature-independent Pauli spin susceptibility. If, on the other hand, they showed Curie-Weiss behavior with an effective moment close to trivalent Yb, this type of high-temperature behavior was invariably followed by a temperature-independent susceptibility at low temperatures, i.e., by an apparent cutoff of the divergence of the susceptibility at a temperature far above any possible ordering temperature expected via de Gennes scaling from other isostructural trivalent rare-earth (RE) compounds. This cutoff has always prevented magnetic ordering in the past.

The intention of this paper is not only to confirm the magnetic nature of the phase transition in YbPd and Yb_3Pd_4, previously observed by specific-heat, resistivity, static-susceptibility, and thermal-expansion data, but also to show that it is a very novel behavior of the magnetic fluctuation rate, reflected by the temperature dependence of the quasielastic linewidth and the support of quadrupole interaction, which actually enables these systems to order magnetically, in contrast to the normal behavior of intermediate-valence Yb compounds mentioned above.

EXPERIMENTAL AND RESULTS

The rare earths with $R=$Dy, Ho, Er, Tm, Yb, Lu crystalline in the cubic RPd ($Pm3m$, O_h^1) CsCl-type structure. All R_3Pd_4 compounds crystallize in the trigonal $R\bar{3}$ (C_{3i}^2) structure of Pb_3Pd_4 type. Here Yb occupies sites with triclinic point symmetry (Yb: $18f$ 1, $x=0.045$, $y=0.211$, $z=0.237$) and the Pd atoms both triclinic (Pd: $18f$ 1, $x=0.273$, $y=0.218$, $z=0.278$) and trigonal (Pd: 3 b 3 and 3 a 3) crystal sites.

We have prepared 40 g of YbPd and 47 g of Yb_3Pd_4 in a Ta crucible by induction heating. In agreement with the findings of Iandelli *et al.*,[5] starting with Yb and Pd of the same batch, one obtains different sample qualities both magnetically and micrographically, depending only on the kind of container used; the quality of the sample is best with a Ta container. The samples show lattice constants in the range of $a_0=3.442-3.447$ Å, an effective moment of $\mu_{\text{eff}}=3.82\mu_B$ and a Curie temperature of $\Theta=-92$ K above room temperature. X-ray diffraction patterns of our YbPd and LuPd samples revealed broad Bragg lines in both cases but no indications of any other phase. Our lattice parameter turned out to be $a_0=3.440\pm0.004$ Å ($a_0=3.422\pm0.006$ Å) for YbPd (LuPd) and thus is within the range of good quality samples. The Yb_3Pd_4 sample

came out to be of lower quality. In contrast to Lu_3Pd_4, which showed no indication of any second phase ($a_0 = 12.880 \pm 0.008$ Å, $c_0 = 5.660 \pm 0.005$ Å), Yb_3Pd_4 exhibits some lines in the range of $2\Theta = 31°-42°$, which could not be attributed to the Yb_3Pd_4 or YbPd phase. Since the phase diagram of Yb_xPd_{1-x} is extremely complicated above $x = 3/7$ (Yb_3Pd_4), we suppose that there are small contributions from these Yb-enriched phases. We point out that such contamination was also detected in the sample of Politt *et al.*[6] Neglecting these extra lines, we determined the lattice parameters of our Yb_3Pd_4 sample to be $a_0 = 12.917 \pm 0.005$ Å and $c_0 = 5.664 \pm 0.003$ Å.

The samples and their nonmagnetic reference systems were measured at the time-of-flight (TOF) spectrometer IN6 at the high-flux reactor of the Institute Laue Langevin, Grenoble, with cold neutrons ($E_0 = 3.15$ meV). Altogether, 12 (16) spectra were taken from YbPd (Yb_3Pd_4) in the temperature range of $T = 1.3-300$ K with emphasis on the low-temperature range ($T = 1.3-4$ K). In order to determine the phonon contributions, LuPd and Lu_3Pd_4 were measured at $T = 135$ K. We took the transition energies of the phonon excitations, their line widths and their relative intensities, to determine the phonon contributions of YbPd and Yb_3Pd_4 at low Q, which, however, turned out to be negligible at those small scattering angles.

An analytical estimation of multiple scattering in our spectra showed that its contribution does not exceed 2% of the total inelastic scattering over the entire energy-transfer region. This low value, which is due to the almost absent Bragg scattering of the sample and the high absorption of Ytterbium, can be neglected compared to the statistical error of our spectra.

In the following we will focus only on the temperature and energy dependence of the quasielastic and inelastic scattering. It is well known that only a rough $|\mathbf{Q}|$ dependence can be obtained when using polycrystalline specimen on a TOF spectrometer. Due to the cold neutrons, however, the accessible Q range for quasielastic scattering in YbPd/Yb_3Pd_4 turns out to be limited to $|\mathbf{Q}| \leq 0.8$ Å^{-1} in the most interesting temperature region $T \leq 100$ K. Within this Q range we could not observe any significant Q dependence. This is in agreement with several theoretical calculations, predicting no or only a very weak Q dependence of the quasielastic linewidth in intermediate-valence compounds.

YbPd

Figure 1 gives the phonon spectrum of the reference compound LuPd at high scattering angles (high Q). In Fig. 2 we show four representative spectra of YbPd between 29 and 205 K, where the left column covers the range of quasielastic scattering and the right column the more extended region of inelastic scattering. For convenience we plot the scattering function $S(Q,\hbar\omega)$ corrected for the Bose factor and $\hbar\omega/k_BT$ in order to display directly the symmetric representation of the line shapes. This representation, however, deviates strongly from the TOF spectra as measured. In the TOF representation the property of spectrum integration of the first time channels, which cover a very broad range of energy transfer, enables one to identify very broad QE lines by a huge asymmetric contribution to the spectrum. This is in contrast to the representation of Fig. 2, where the broader of the two QE lines no longer contributes significantly to the spectrum at $T = 205$ K.

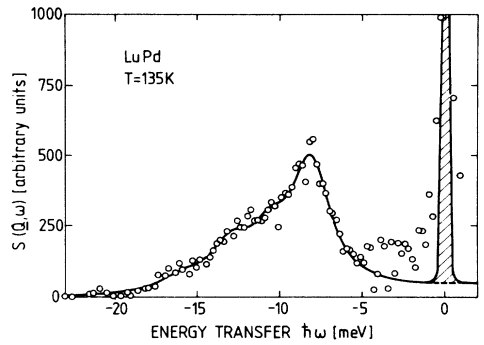

FIG. 1. The phonon spectrum of the reference sample LuPd at large scattering angles (high Q). The solid line is a fit to the spectrum.

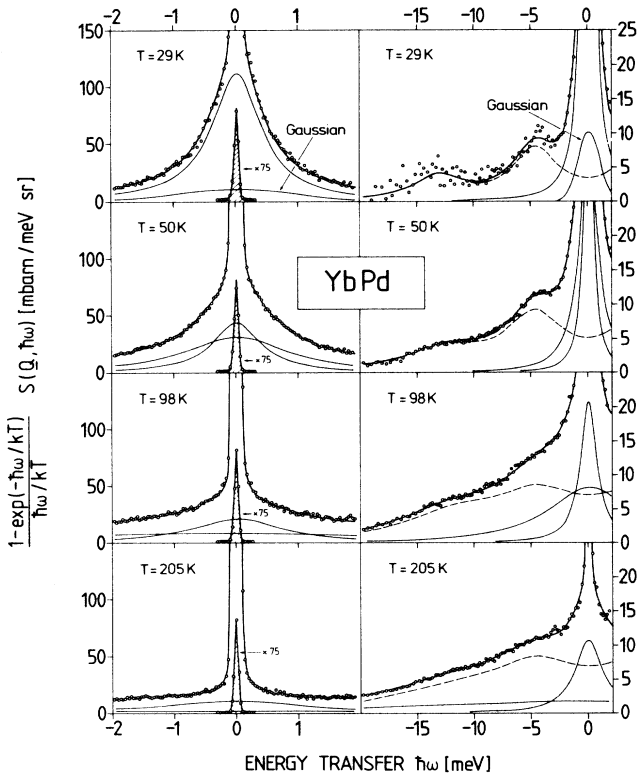

FIG. 2. The magnetic spectrum of YbPd between 29 and 205 K at small scattering angles (low Q) in the quasielastic (left column) and the inelastic (right column) energy region. The solid line is a fit to the spectra assuming the CF scheme of Fig. 3. It includes quasielastic contributions (solid lines) and inelastic contributions (dashed line). The scattering function $S(Q,\hbar\omega)$ has been modified with regard to symmetric line shapes.

From the spectra one can extract two inelastic transition lines at 4.75 and 12.3 meV. This is in agreement with CF theory, which predicts only two inelastic CF transitions for trivalent Yb in cubic symmetry. We used the CF parameters x and W as direct fit parameters. Taking the special temperature dependence of the QE and IN lines into account, there exists only one set of CF parameters, namely,

$$x = -0.365 \pm 0.01 ,$$

$$W = -0.451 \pm 0.03 \text{ meV} ,$$

which describe the spectra satisfactorily over the entire temperature range of $T = 1.3$—300 K (solid lines through the data points in Fig. 2). The corresponding CF scheme is given in Fig. 3. From the temperature dependence of the IN transitions and the measured QE intensity for $T \rightarrow 0$, which is about twice as much as that of a Γ_6 or Γ_7 CF state, it follows that Γ_8 is the ground state in YbPd, which is somewhat unusual. The most striking new feature observed is, however, the unequivocal existence of *two* QE lines in this system. The narrower line, having nearly the same line width as stable trivalent RE impurities and also as that of Yb in YPd_3,[9] shows only a weak temperature dependence (See Figs. 2 and 4), whereas the broad line changes its width between helium and room temperature by more than two orders of magnitude to 21.8 and 34 meV at 205 and 300 K (see upper-right hand corner of Fig. 4). At temperatures below 30 K these two QE lines merge together into one QE line. This dependence of the QE spectrum is unique and nothing like it has ever been seen in any RE compound before.

A comparison between the measured and calculated QE intensities reveals another interesting feature. The intensity of the narrow QE line coincides exactly with that of only one of the two Kramers doublets of the Γ_8 ground state. Within our results it is impossible to say which one it is, because both doublets of the Γ_8 state exhibit exactly the same QE matrix elements for unpolarized scattering (with the use of polarized neutrons they would differ strongly in an nonspinflip arrangement by a factor of $\frac{121}{9} \approx 13.4$). The intensity of the broad QE line on the other hand shows a temperature-dependent intensity, which can be identified as the sum of the two CF doublets Γ_6 and Γ_7 and the remaining part of the Γ_8 quartet. In other words, the two doublets of the Γ_8 ground state have very different QE linewidths. This may be understood if one remembers that they incorporate different $|JM\rangle$ states, namely

$$\Gamma_8: \ \tfrac{1}{2}\,|\pm\tfrac{5}{2}\rangle + (\tfrac{3}{4})^{1/2}\,|\mp\tfrac{3}{2}\rangle ,$$

$$(\tfrac{7}{12})^{1/2}\,|\pm\tfrac{7}{2}\rangle - (\tfrac{5}{12})^{1/2}\,|\mp\tfrac{1}{2}\rangle ,$$

i.e., they have different symmetries. We point out that the interpretation of the spectra given so far is mandatory in the sense that all other interpretations based on a CF-split ground state which we tested gave much lower quality fits and furthermore lead to temperature-dependent CF parameters.

Besides the two QE lines there are also two different IN lines (Fig. 4). The linewidth of the transition $\Gamma_6 \rightarrow \Gamma_8$ al-

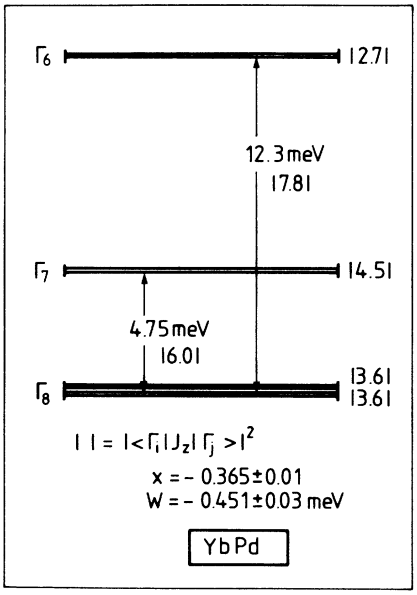

FIG. 3. The CF scheme of trivalent Yb in YbPd as deduced by inelastic neutron scattering. The transition matrix elements $|\langle \Gamma_i | J_z | \Gamma_j \rangle|^2$ are given by the $|\cdots|$ symbols.

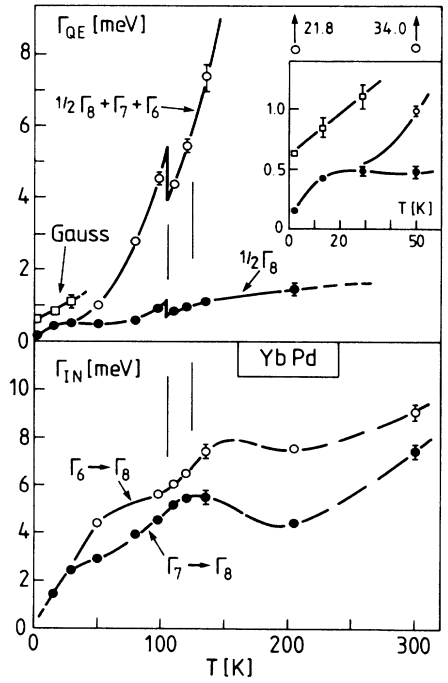

FIG. 4. The quasielastic and inelastic linewidths (HWHM) of YbPd as function of temperature. For the quasielastic line widths the filled circles correspond to the linewidth of only one Kramers doublet of the Γ_8 quartet, the circles to the linewidth of all other CF doublets (note the huge values at 205 and 300 K shown in the inset) and the open squares to the linewidth of the Gaussian critical spin fluctuation.

ways turn out to be larger than that of the $\Gamma_7 \rightarrow \Gamma_8$ transition. The difference in linewidths, however, is not as drastic as that of the QE lines.

YbPd shows two phase transitions at 105 and 205 K (vertical lines in Fig. 4),[4] which can be observed as strong anomalies in the specific-heat and the thermal-expansion data, but which are not fully understood at the present time. In order to determine the influence of these two phase transitions, we took spectra of YbPd just below ($T=98$ K), in between ($T=110$ and 120 K), and just above ($T=135$ K) these transition temperatures. Obviously only the transition at $T=105$ K has an effect on the QE linewidths. There seems to be no anomaly at $T=125$ K. The IN linewidths show no discontinuities at the phase transitions, however they show a tendency to be attracted to each other there.

On a more general level it is worth mentioning a significant difference between the behavior of the CF splitting in $YbBe_{13}$, which has a similar dependence of the QE linewidth,[2] and that of YbPd. Although in both systems the CF states have a strong overlap (linewidth comparable to line separation) above 30 K, only in $YbBe_{13}$ does this overlap lead to a decrease of the IN scattering intensity concurrent with an increase of the QE scattering; at the same time the total CF splitting shows a small reduction (motional narrowing effect[10]). None of these effects are observed in YbPd, in spite of the strong overlap of the IN CF states.

As stated above, the linewidths of the two QE lines are indistinguishable below $T=30$ K. It is just at this limiting temperature, where a new QE line starts to appear, which in contrast to the QE and IN lines discussed so far, does not have a Lorentzian but a Gaussian line shape (see Figs. 2 and 4). With decreasing temperature its intensity rapidly increases at the cost of the Lorentzian CF QE line and at $T=1.3$ K both are approximately of the same strength. Figure 5 shows these two contributions to the total magnetic scattering and illustrates the difference in shape of the Gaussian and Lorentzian QE lines at helium

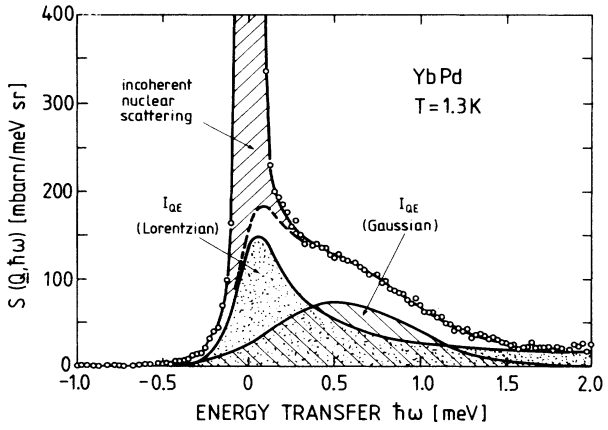

FIG. 5. Decomposition of the quasielastic magnetic scattering of YbPd at 1.3 K into the CF contribution (Lorentzian) and the critical spin fluctuation (Gaussian). Note their very different type of line shapes.

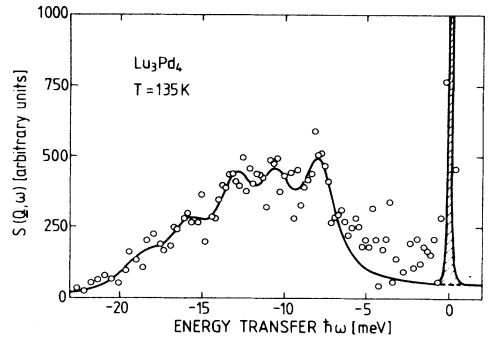

FIG. 6. The phonon spectrum of the reference sample Lu_3Pd_4 at small scattering angles (low Q). The solid line is a fit to the spectrum.

temperatures. The plot shows the scattering function, which is close to the measured spectra.

This additional Gaussian QE line is a precursor of magnetic order, as will be discussed in detail in the following section of Yb_3Pd_4.

Yb_3Pd_4

In Fig. 6 we show the phonon spectrum of the reference system Lu_3Pd_4. As one can see, there are similar phonon structures in LuPd and Lu_3Pd_4. As in YbPd, the nonmagnetic contributions in Yb_3Pd_4 turns out to be negligble at low scattering angles (low Q), where the magnetic spectra will be studied. Figure 7 gives some of these spectra at

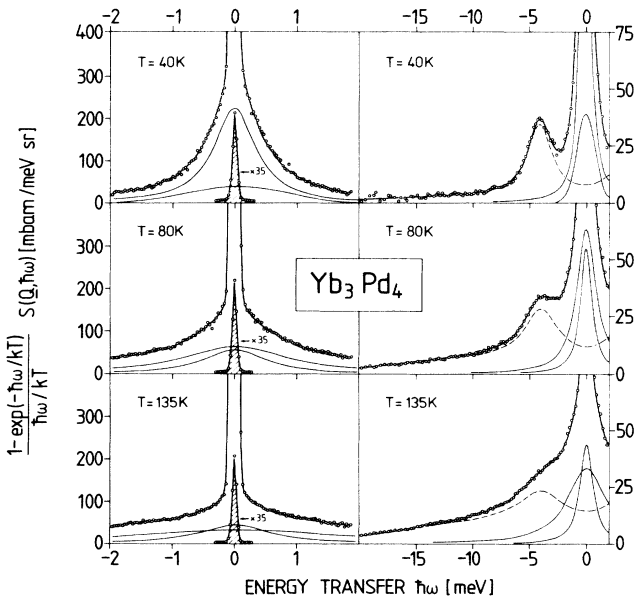

FIG. 7. The magnetic spectrum of Yb_4Pd_4 between 40 and 135 K at small scattering angles (low Q). In the quasielastic (left column) and inelastic energy region (right column). The solid line is a fit to the spectra assuming the CF scheme of Fig. 9. It includes quasielastic contributions (solid lines) and inelastic contributions (dashed line). The scattering function $S(Q,\hbar\omega)$ has been modified with regard to symmetric line shapes.

elevated temperatures using the same type of representation as that of Fig. 2. These spectra show nearly the same features as those of YbPd with the following exceptions:

(i) The first inelastic transition at $\Delta E = 4.08$ meV in Yb_3Pd_4 is shifted to lower energies by about 0.7 meV compared to that in YbPd. It is more distinct because its width is only half of that of YbPd.

(ii) There exists magnetic scattering in the energy range of -15 meV $< \Delta E < -10$ meV at all temperatures. Although one cannot recognize this scattering as a true inelastic line by eye, because the linewidth is always enormous, the integrated intensity in this energy range in fact gives the full matrix element of a $\Gamma_6 \rightarrow \Gamma_8$ transition. Moreover, this intensity is located in the same energy range where the $\Gamma_6 \rightarrow \Gamma_8$ transition is located in YbPd.

(iii) The broad QE linewidth does not reach the large value of YbPd at room temperature, it saturates at a level of about 3–4 meV (Fig. 8).

The more integral valence of Yb in Yb_3Pd_4 compared with that of YbPd manifests itself in a drastically reduced value of the high-temperature limit of this broad linewidth.

Although Yb in Yb_3Pd_4 has triclinic point symmetry and thus 26 independent CF parameters, it turns out that it is possible to interpret the measured transitions by cubic CF theory with

$$x = -0.39 \pm 0.02$$

$$W = -0.44 \pm 0.05 \text{ meV} .$$

It seems surprising to have no drastic change of the CF spectrum when the structure changes the point symmetry of Yb from cubic (YbPd) to triclinic (Yb_3Pd_4). Yet our evidence for this observation is very strong. We point out that there are also only relatively small changes in the phonon spectra (compare Figs. 1 and 6). The fit with these cubic CF parameters (the solid lines through the data points in Fig. 7) is so good that it seems appropriate to use the cubic description. The CF scheme corresponding to these CF parameters is shown in Fig. 9. The CF transition $\Gamma_{tc6} \rightarrow \Gamma_{tc7}$, in principle is not forbidden in noncubic symmetries, could not be detected. This, however, is not surprising, if it would have the same expected broad linewidth as that of the $\Gamma_{tc7} \rightarrow \Gamma_{tc8}$ transition.

Just as in YbPd we found two different QE lines. We attribute the broad QE line to the excited levels $\Gamma_{tc7}, \Gamma_{tc6}$ and to one of the Kramers doublets of the Γ_{tc8} ground state, whereas the narrower line describes the fluctuation rate of the remaining part of the Γ_{tc8} state. In contrast to YbPd, the two IN line widths behave quite differently. At low temperatures the linewidth of the $\Gamma_{tc6} \rightarrow \Gamma_{tc8}$ transition even seems to have an unusually high residual value of about 10 meV.

As mentioned earlier there are strong indications that Yb_3Pd_4 should order magnetically at $T = 3.0$ K,[6] which so far is a very rare feature in Yb compounds. In order to verify this and to study the behavior of Yb_3Pd_4 around this phase transition, we did a special run in the temperature range of $1.3 < T < 6$ K. Figures 10–12 give a detailed description of the features observed there. The additional appearance of a strong inelastic line at $\Delta E = 0.55$ meV for $T \rightarrow 0$, its decreasing intensity with increasing scattering angles (increasing Q, Fig. 10), its softening towards the phase transition at $T = 3.1$ K (Fig. 11) resulting in a temperature dependence of a second-order phase tran-

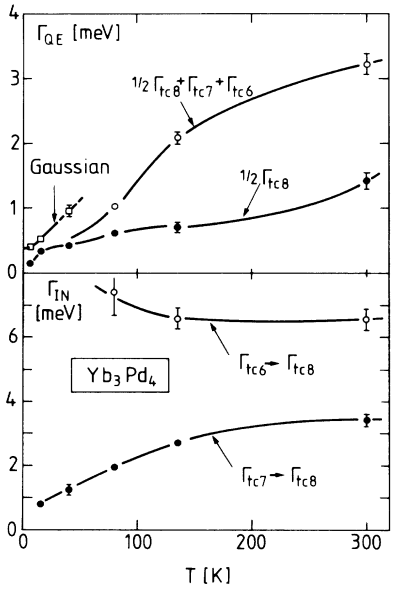

FIG. 8. The quasielastic and inelastic line widths (HWHM) of Yb_3Pb_4 as a function of temperature. For the quasielastic linewidths the filled circles correspond to the linewidth of only one Kramers doublet of the Γ_{tc8} quartet, the circles to the linewidth of the Gaussian critical spin fluctuation.

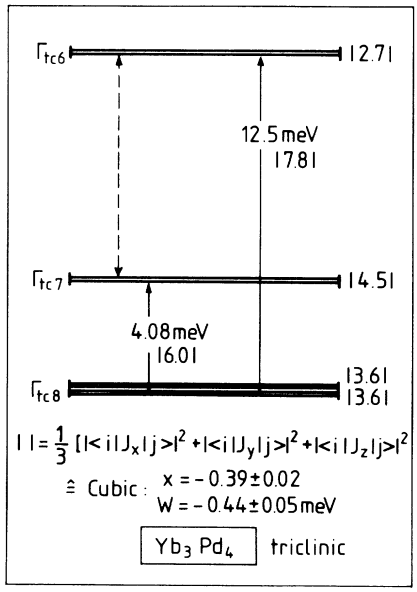

FIG. 9. The CF scheme of trivalent Yb in Yb_3Pd_4 as deduced by inelastic neutron scattering. The transition matrix elements $|\langle \Gamma_i | J_z | \Gamma_j \rangle|^2$ are given by the $|\cdots|$ symbols.

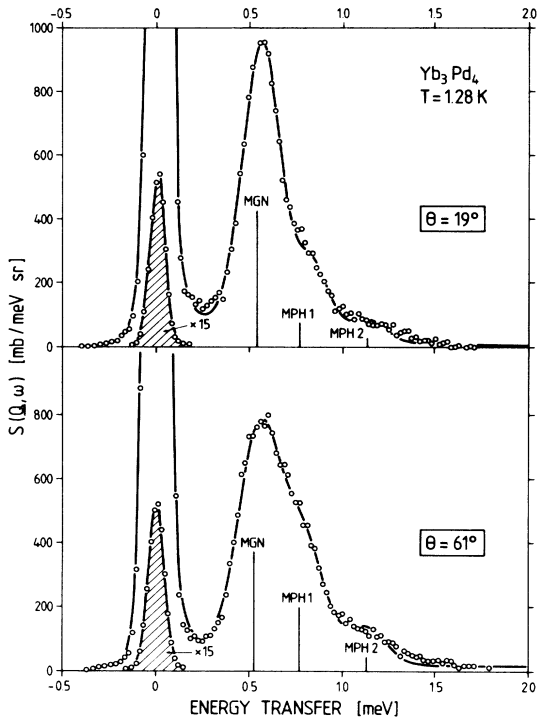

FIG. 10. The magnetic (magnon, denoted by MGN) and phonon (magnetophonon, denoted by MPH) scattering of Yb_3Pd_4 at 1.28 K compared at small (low Q) and large (high Q) scattering angles. The solid line is a fit to the spectrum taking into account the lines represented by the bars.

sition (Fig. 12), and the abrupt change of its linewidth (Fig. 12) at $T=3.1$ K proves this excitation to be a magnon in a magnetically ordered state. Moreover, a detailed analysis of the fine structure of this magnon reveals that the occurrence of the magnon induces two phononlike excitations (see Figs. 10 and 12) around $\Delta E=0.78$ and 1.13 meV (whose intensity increases with increasing scattering angles). It seems likely that they can be attributed to a hybridization of the magnon with acoustical phonons; we therefore call these excitations "magnetophonons".

At least the excitations at 0.55 and 0.78 meV strongly appear to have Gaussian line shapes and show no measurable dispersion in the accessible region of momentum transfer $0.30<Q<1.9$ Å^{-1}. Starting at $T=1.3$ K all three excitations first begin to become unstable with increasing temperature leading to a breakdown of the magnon at $T=3.1$ K. While the increasing linewidths make it difficult to trace the phonon like excitations, the second excitation seems to stabilize at $\Delta E=0.6$ meV above the ordering temperature. The third transition cannot be traced above $T=2.5$ K.

Unlike the excitation energy the intensity of the magnon does not have a breakdown at $T=3.1$ K but survives the phase transition as a Gaussian line without any measurable loss. The shape of this (as we think critical) fluctuation above $T=3.1$ K seems to change slowly above $T=10$ K, from where on the intensity decreases and the linewidth becomes larger. At about $T=40$ K the Gaussian line merges with the CF QE line into one overall Lorentizan QE line. It should be mentioned that there is no measurable Lorentzian CF QE line below the phase transition. The first detectable Lorentzian appears above $T=6$ K.

DISCUSSION

Lattice constant and L_{III} x-ray measurements show YbPd and Yb_3Pd_4 to have a valency of $v=2.79$—2.83 and $v=2.81$—3.00, respectively. A rough idea of the amount of instability is also given by the anomalies of the lattice constants of YbPd and Yb_3Pd_4 as shown in Fig. 13. The trend that YbPd is stronger mixed valent than Yb_3Pd_4 is expected from the strong electronegativity of Pd: A larger concentration of Pd works against the tendency of Yb to incorporate an electron in its $4f$ shell. $YbPd_3$, with the highest Yb concentration is already fully trivalent as judged from static susceptibility and from neutron scattering in $(Yb\underline{Y})Pd_3$ alloys,[9] which shows very sharp inelastic CF transition lines of stable $J=7/2$ and by experience can be expected to behave similar to $YbPd_3$.

There is no question that the spectra of Yb_3Pd_4 in the helium temperature range show all the features associated with magnetic order above, at and below the electronic transition temperature $T_N=3.1$ K, which was detected by specific heat and other thermodynamic measurements previously.[6] In particular, the clear separation of Gaussian and Lorentzian line shapes and the development from pure Gaussian far below T_N to pure Lorentzian far above, has been seen by inelastic scattering here and in $YbBe_{13}$ (Ref. 2) for the first time in compounds, which exhibit unstable $4f$ shells and magnetic order simultaneously.

While the observation of the evolution of a magnon below the phase transition and the adjoining critical fluctuation above in Yb_3Pd_4 and $YbBe_{13}$ is generally expected, it is very surprising to see this critical fluctuation survive to temperatures more than one order of magnitude higher that the ordering temperature. If this is a general effect in such compounds, one may predict that the appearance of a QE line with Gaussian shape at a certain temperature should imply a magnetic phase transition at a temperature more than one order of magnitude below that temperature. This prediction holds, even if the phase transition can not be observed directly, because it lies below the accessible temperature region. This obviously is the case in YbPd, where just such a Gaussian QE line is detected below $T=30$ K, whose intensity increases strongly down to $T=3$ K. We therefore conclude from our neutron data that YbPd should order magnetically somewhere below $T=1.3$ K. This prediction is in nice agreement with the occurrence of a phase transition at $T=0.5$ K as seen by static susceptibility and resistivity.[4]

Before leaving the discussion of magnetic ordering we want to remark on the interrelation between the magnetic spin-spin interaction and the electric quadrupole-quadrupole interaction. It is well known that quadrupole interactions may support magnetic ordering in RE solids or may even cause quadrupolar phase transitions at temperatures higher than the magnetic transition tempera-

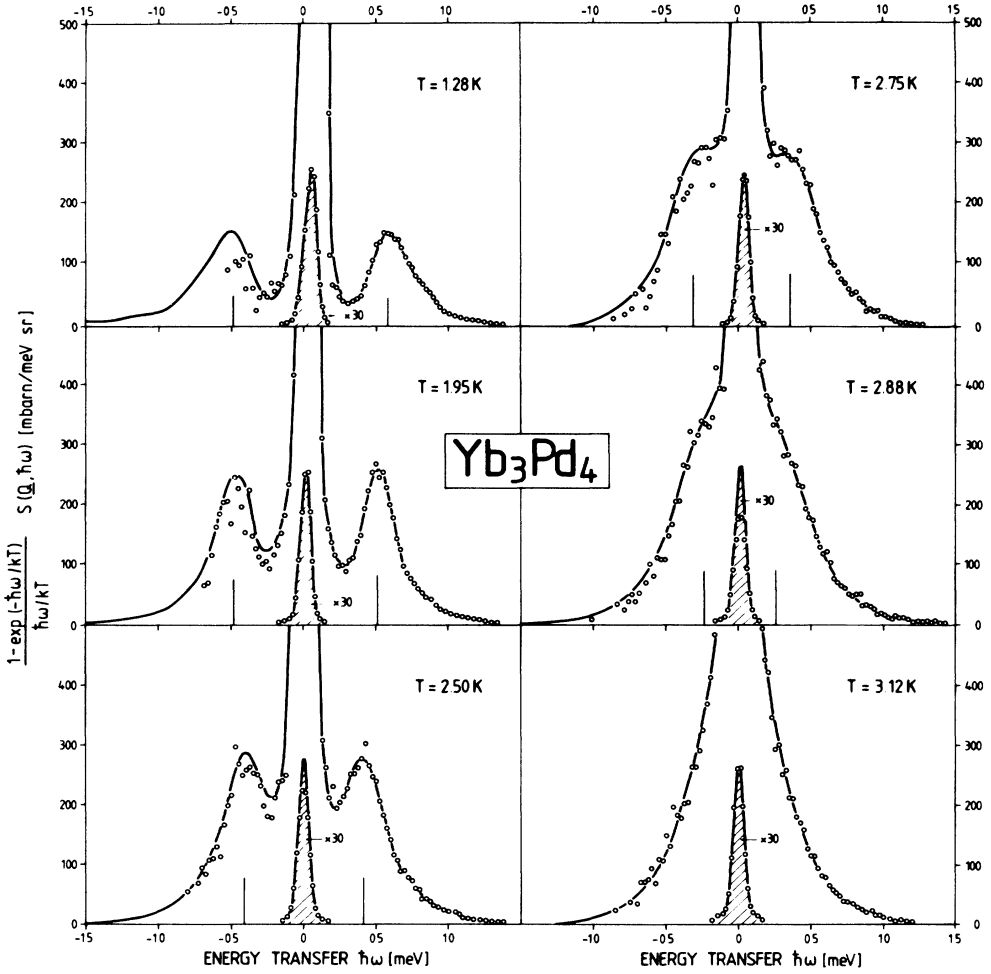

FIG. 11. The spectrum of Yb_3Pd_4 below and near the magnetic phase transition at $T_N = 3.1$ K. The solid line is a fit to the spectrum (for details see Fig. 10).

ture. The quadrupolar energies clearly are the more important the smaller the magnetic exchange integral is for a given series of isostructural RE compounds and the smaller the spin of the RE species. One therefore expects the relatively most-important quadrupole effects at the beginning and the end of the lanthanides, for Ce and Yb, which have the smallest $4f$ spin, $S = \frac{1}{2}$. Indeed there are two electronic phase transitions in YbPd at helium temperatures seen in the specific heat, and it was speculated that the one at 1.9 K is due to the quadrupolar ordering. Such speculation is now supported by the fact that we have seen a Γ_8 ground state by neutron scattering, whose two Kramers doublets exhibit opposite quadrupole moments, $\frac{1}{2}\alpha_J O_2 = \pm\frac{2}{21}$. These two doublets may of course be split by quadrupolar interactions between neighbors below 1.9 K. However, in the neutron spectra of YbPd we have not found any trace of this second-phase transition, which should be seen, for instance, by inelastic transitions between the split doublet. We therefore must say that we cannot contribute here to the elucidation of the nature of the phase transition at 1.9 K.

On one hand, quadrupole-quadrupole interactions may be the origin of the large temperature range, over which the critical fluctuations are observed above the magnetic ordering temperature, at least in YbPd and Yb_3Pd_4, which both have a Γ_8 ground state. On the other hand, in $YbBe_{13}$ such an explanation for the critical fluctuation seems unlikely, because there the Γ_8 state is 3.20 meV above the ground state.

The behavior of the QE spectra as a function of temperature observed in the helium temperature range in the magnetically ordering compounds YbPd, Yb_3Pd_4, and $YbBe_{13}$ is of course totally different from that observed in the usual Yb compounds, which do not show magnetic order. In the latter, one also observes a QE line if the high static susceptibility indicates nearly trivalent Yb by a high-temperature effective moment near $\mu_{\text{eff}} = 3.54\mu_B$. However, this QE line, whose shape is then always Lorentzian, is of order of a few times 10 K to a few 100 K and is temperature independent. On the other hand, at elevated temperatures the spectra of magnetic ordering compounds discussed here and of the usual nonordering, nearly trivalent compounds YbCuAl and $YbCu_2Si_2$ look very much alike. The distinct feature of the magnetic or-

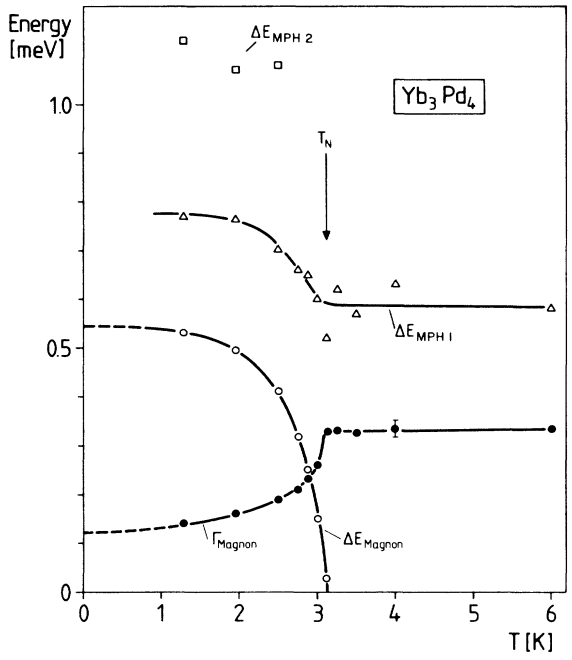

FIG. 12. The temperature dependence of the magnetic (magnon) and the phonon (magnetophonon, or MPH) excitation energies and linewidth near the magnetic phase transition $T_N = 3.1$ K.

dering compounds is therefore the dramatic decrease of the QE line width down to helium temperature, remaining at values which are always less than $k_B T$. The same dramatic drop of the QE linewidth is well known to distinguish magnetically ordering CE compounds with an unstable $4f$ shell like CeB_6 or $CeAl_2$ from nonmagnetic Ce-intermediate-valence compounds like $CePd_3$ or $CeBe_{13}$. We mention that so far the transition to a Lorentzian QE line shape at high temperatures above the magnetic ordering temperatures has not yet been observed in Ce compounds. We believe that the reason for this is that the TOF spectrometers used to study the Ce compounds in the past did not have the resolution of the IN6 spectrometer used here. It would obviously be highly interesting to have such high resolution data of magnetically ordering Ce compounds as well.

We now try to determine what the reason for the radically different temperature dependence of the QE linewidth of the magnetically ordering and nonordering intermediate-valence compounds might be. In the past, when considering Ce systems, the tendency was to answer this question by the different degrees of mixed valence. Magnetically ordering compounds have a valence very close but not exactly at integral, while nonmagnetic compounds have strongly fractional valence. In the meantime, this assumption has been disproved by a large number of independent measurements of the degree of fractional valence, most dramatically in the case of YbPd (both YbPd and $YbCu_2Si_2$ have nearly the same fractional valence of 2.8 at helium temperatures). In searching for a different reason, it was pointed out recently[11] that the matrix elements between the nonmagnetic $4f^{14}$ configuration and the various CF states of the $4f^{13}$ configuration may be very different for different CF states. In particular, a vanishing matrix element to the CF ground state and nonvanishing ones to the excited CF states obviously would lead to the desired strong temperature dependence and to the vanishing of the QE line for $T \rightarrow 0$. Although the quantitative agreement between this theory and the measured linewidths is not yet fully satisfactory, it seems that such kind of "selection rule" may be the key to the interpretation of the data. This idea is for example supported by the fact that two strongly different QE linewidths are observed in the two Kramers doublets of the Γ_8 ground state in YbPd. It should mentioned, that the reason for such a "selection rule" need not only be electronic interactions but also anomalous $4f$-phonon interactions originating from the different symmetries of the phonons.

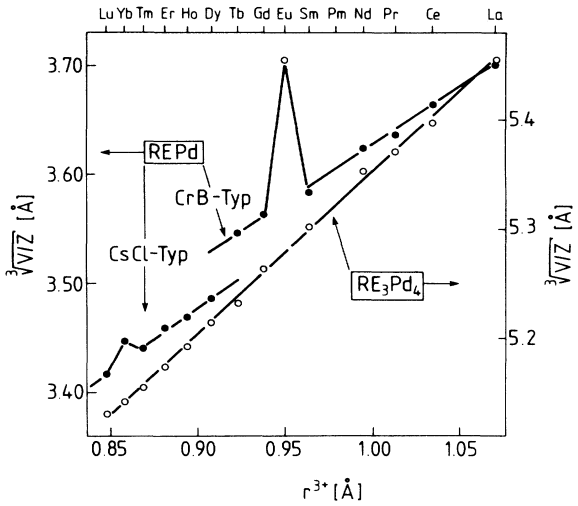

FIG. 13. Cube roots of the unit formula volume V/Z versus trivalent ionic radii for the RPd and R_3Pd_4 compounds.

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