Crystal-field splitting and magnetic relaxation in $CeCu_{2\pm0.2}Si_2$

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We present the results of two types of inelastic neutron scattering experiments on the heavy-fermion system $CeCu_{2\pm0.2}Si_2$ to investigate the quasielastic scattering (low-energy response) and the crystal-field (CF) excitations (high-energy response). A characteristic energy width of about 0.7 meV is found for the magnetic low-energy response at low temperatures, and the CF scheme given earlier for $CeCu_2Si_2$ is roughly confirmed. The inelastic spectrum of $CeCu_{2.2}Si_2$ gives some indications for a coexistence of γ-cerium and α-cerium. The scattering intensities are compared with static susceptibility measurements.

I. INTRODUCTION

One of the most prominent members in the group of heavy-fermion systems is $CeCu_2Si_2$, which has been studied intensively since 1973 (e.g., Refs. 1 and 2). In 1979 superconductivity was found below $T_c < 1$ K (Ref. 3). The superconducting state is sensitive to the copper concentration: copper-deficient samples do not exhibit superconductivity whereas copper-excess samples become superconducting.[4,5] In the nominally stoichiometric samples the appearance of superconductivity depends sensitively on sample history like annealing temperature, cooling rate, cooling conditions, etc. Due to the tetragonal structure ($CrTh_2Si_2$, $I4/mmm$) many properties of $CeCu_2Si_2$ are strongly anisotropic. Good reviews of the present knowledge of this heavy-fermion system are given in Refs. 6 and 7.

In order to look for differences in the magnetic properties [magnetic relaxation and crystal-field (CF) splitting effects] between normal and superconducting $CeCu_2Si_2$ we have investigated both $CeCu_{1.8}Si_2$ (nonsuperconducting) and $CeCu_{2.2}Si_2$ (superconducting) by inelastic neutron scattering. Preliminary experiments were done on a "stoichiometric" sample several years ago in the temperature range of 5–300 K, i.e., above T_c (Ref. 8). A broad quasielastic (QE) line was observed at room temperature ($\Gamma/2 \approx 10$ meV), which narrows with decreasing temperature following a $(a + b\sqrt{T})$-law resulting in $\Gamma/2 \approx 1$ meV for $T \rightarrow 0$. This temperature dependence is typical for heavy-fermion or Kondo-like Ce systems.[9,10] Furthermore a CF splitting into three doublets was observed as expected for a $J = \frac{5}{2}$ state in tetragonal symmetry. A total energy splitting of about 31 meV was observed with the first excited level at about 12 meV.

In the past, doubts concerning the energy of the first excited level have been raised. On one hand, the analysis of specific heat data favors a CF scheme with a first excited state at a much higher energy.[7,11] The high-temperature anomaly in the specific heat data, derived by subtraction a $LaCu_2Si_2$ reference compound under the assumption of an identical phonon spectrum, is well described by a doublet ground state and a quartet excited state at 31 meV assuming δ-function levels and neglecting many-body effects and interactions. Discrepancies between fit and experimental data remain in the temperature region around 100 K (Refs. 7 and 11). On the other hand, the magnetic excitation line in the neutron scattering data at about 12 meV was obscured by phonon scattering. This led Rietschel[12] to interpret the additional scattering in $CeCu_2Si_2$ as paramagneto-vibrational scattering. Therefore, besides the comparison between normal and superconducting materials, our new experiments should confirm or reject the CF level at about 12 meV. The measurement of the quasielastic response above and below the superconducting critical temperature $T_c \approx 0.6$ K is one additional part of our present investigation.

II. EXPERIMENT

Since a large amount of sample (50 g) was needed for this measurement, each specimen was composed of three individually melted ingots. The appropriate amounts of Ce, Cu, and Si were arc melted in a water-cooled Cu hearth. The samples were flipped and remelted six to seven times to ensure a good homogeneity. After melting, the samples were annealed under high vacuum ($p < 10^{-6}$ mbar) in an Al_2O_3 crucible at 1000 °C for four days. In the case of $CeCu_{2.2}Si_2$ a certain amount of elementary copper sublimated at cold parts of the crucible during the annealing procedure. X-ray powder diffraction patterns were taken on both samples. For $CeCu_{2.2}Si_2$ no impurity phases were detected, whereas in $CeCu_{1.8}Si_2$ small amounts of an impurity phase (presumably $CeSi_{2-x}$) were found. Before mixing the three separately melted samples, each was checked for its superconducting properties by measuring the ac susceptibility. The three samples of $CeCu_{2.2}Si_2$ showed T_c values between 0.6 and 0.64 K; the three $CeCu_{1.8}Si_2$ samples did not become superconducting down to $T \approx 30$ mK.

We have performed two different types of inelastic magnetic neutron scattering experiments. The first one was using cold neutrons to secure high-energy resolution for investigating the low-energy response (QE range). The second experiment used thermal neutrons to provide a larger observable energy window which also allowed the investigation of CF excitations at low temperatures.

A. QE spectra (low-energy response)

The high-energy resolution experiments were performed on two different time of flight (TOF) spectrometers operating at the high flux reactor of the ILL in Grenoble. Spectra in the temperature range of 1.5 to 50 K, provided by a conventional ^{4}He cryostat, were taken on the IN6 spectrometer with $E_0 \approx 3.1$ meV (E_0: energy of incident neutrons) corresponding to an energy resolution of about 45 μeV (all resolution values refer to the HWHM of the elastic peak). To study the magnetic low-energy response below T_c we used a ^{3}He/^{4}He dilution refrigerator on the IN5 spectrometer (for details see Ref. 13). In order to improve the energy resolution we chose a lower incident neutron energy, namely $E_0 \approx 2$ meV, resulting in an energy resolution of about 35 μeV. This experiment was performed at temperatures between 60 mK and 1.5 K.

In cooling a powdered sample of about 50 g down to temperatures in the mK range problems of thermalization might arise. On one hand we did not want to obscure our data with irreproducible scattering from the use of exchange gas. On the other hand, the Al walls of the container are superconducting at those low temperatures prohibiting good thermal contact. Therefore, we used three thin ($d < 100$ μm) foils of copper, which were pulled through the sample holder from top to bottom. For details see Fig. 1. This minimized the travel path for the heat within the sample to less than 1.5 mm (compared to 6 mm without the foils). A preliminary test in our home laboratory verified the usefulness of this method of thermalization.

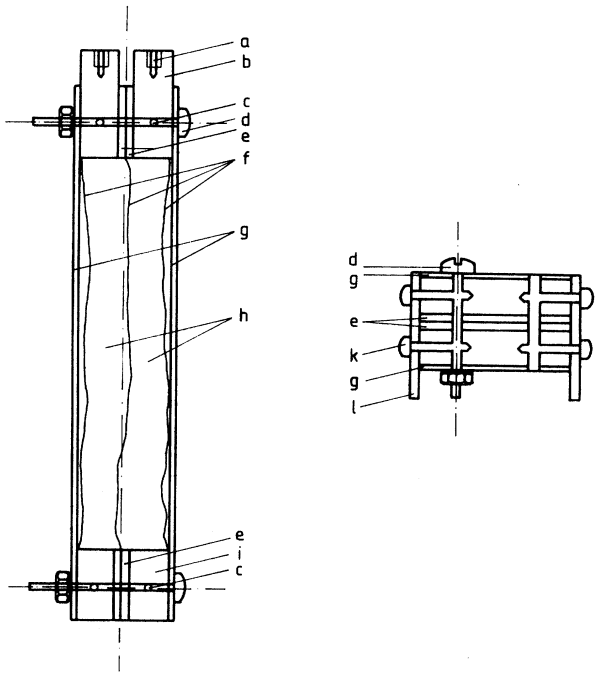

FIG. 1. Sample holder used in the ^{3}He/^{4}He-dilution refrigerator: side view on the left and view from the top on the right. (a) M2 threads to attach to cryostat (not shown in the view from top), (b) Cu block with threads and holes, (c) M2 threads to hold part 1, (d) M2 screws, (e) distance Cu block to fit different sample volume, (f) Cu foil (100 μm thin), (g) Al plates (0.5 mm thin), (h) sample volume, (i) same as (b) without parts *a*, (k) M2 screws to hold part 1, (l) Al plates (1 mm thin).

B. CF spectra (high-energy response)

The high-energy response at low temperatures was measured using thermal neutrons on two different types of spectrometers: the H7 triple axis spectrometer (TAS) at the high flux reactor in Brookhaven and the TOF spectrometer IN4 at the ILL in Grenoble. The TAS was operating in a constant final-energy mode ($E_f = 30.5$ meV) with an energy resolution of about 0.9 meV. On the IN4 the incident energy was $E_0 = 50.8$ meV resulting in an energy resolution of about 1.5 meV.

III. DATA ANALYSIS

For the background correction the empty sample holder was measured in the sample position on all instruments. In addition a cadmium plate as a strongly absorbing sample was used on the TOF spectrometers to improve the background correction by taking into account the transmission of the sample. Furthermore the TOF data were calibrated to differences in the detector

efficiency and to an absolute intensity scale by measuring a vanadium standard. Finally the TOF data have been corrected for energy and angle dependent absorption. To improve this absorption correction we used in contrast to Ref. 14 an integral method. This method takes into account the exact shape of the sample, instead of using the approximation of a plate with infinite width [Eq. (26) in Ref. 14]. The statistical error of the energy spectra obtained by the TOF method can be taken from the scatter of the data points; for the TAS data they are indicated explicitly to the spectra.

We will present briefly the paramagnetic scattering law which was used to fit our spectra (for detailed description see Ref. 14):

$$S(Q,\hbar\omega,T)=\frac{1}{2}\left[\frac{g_N r_e}{\mu_B}\right]^2 F^2(Q,T)\chi_{\text{bulk}}(T) \times P(Q,\hbar\omega,T)\hbar\omega\frac{1}{1-e^{-\beta\hbar\omega}} . \quad (1)$$

$P(Q,\hbar\omega,T)$ is the spectral function which fulfills the normalization condition $\int_{-\infty}^{\infty} P(Q,\hbar\omega,T)d\hbar\omega=1$. In Eq. (1) the scattering intensity is proportional to the static (local) susceptibility $\chi_{\text{loc}}(Q,T)=F^2(Q,T)\chi_{\text{bulk}}(T)$, which can be determined rather precisely from the neutron scattering data. Another convenient intensity parameter is the (local) magnetic moment, which is given by the total magnetic cross section obtained by integration:

$$\sigma_{\text{mag}}(Q,T)=\int_{-\infty}^{\infty} S(Q,\hbar\omega,T)d\hbar\omega = A\mu_{\text{loc}}^2 F^2(Q,T) . \quad (2)$$

If the linewidth is small compared to the thermal energy ($\Gamma/2 \ll k_B T$), a δ-function is a good approximation to $P(\hbar\omega)$. Then the integral in Eq. (2) can be solved easily. Standard CF theory furnishes magnetic moments (σ_{mag}) and the magnetic neutron scattering intensity the susceptibility. Thus this CF theory can only be applied to the magnetic neutron cross section in the limit $\Gamma/2 \ll k_B T$, i.e., when the Curie law gives a simple relation between the magnetic moment and the susceptibility: $\chi \propto \mu_{\text{loc}}^2/T$. This simple relation is a result of the integration in Eq. (2) assuming a δ-function. Generally, this limit is valid for stable rare earth (R) ions diluted in a nonmagnetic matrix, e.g., $R_x Y_{1-x} Pd_3$ (Ref. 15) (for more details, e.g., inelastic lines, see again Ref. 14). However, in our case $\Gamma/2$ becomes larger than the thermal energy ($\Gamma/2 \geq k_B T$; see below) and the above integration over $S(\hbar\omega)$ can only be performed numerically. As this integral diverges, a relation between the magnetic moment and the susceptibility can only be found by introducing a cutoff energy. This cutoff energy is somewhat arbitrary and therefore the obtained values for the cross section σ_{mag} are fairly uncertain (for more details see Ref. 16). An exact solution of the integral is only possible, if the *exact* shape of $P(\hbar\omega)$, especially for $\hbar\omega \to \infty$, is known. Nevertheless, we have used this method in order to apply the CF formalism directly to the $CeCu_2Si_2$ problem using $E_{\text{cut}}=1.5$ eV, which roughly reflects the $4f$ bandwidth.

IV. RESULTS

A. QE spectra

Figure 2 shows IN6 spectra of the copper-excess and the copper-deficient sample at $T=25$ K. Both spectra are fitted well using a QE Lorentzian, but the respective widths differ. The width of the QE line for the superconducting sample is about twice as large as the one for the normal conducting sample at this temperature (see Fig. 3, upper part). The QE linewidths decrease with decreasing temperature for both samples. At $T=1.5$ K the magnitude of both widths is roughly the same, but a much larger intensity is observed for $CeCu_{1.8}Si_2$ than for $CeCu_{2.2}Si_2$ at this temperature [see lower part of Fig. 3(b) and discussion]. Besides this dominant response we find a much smaller QE line of less intensity ($\Gamma/2 \approx 0.08$ meV and $\sigma \approx 0.03$ b) which is an artifact of the experimental setup and is associated with double Bragg reflections from the sample and cryostat walls. This very narrow line is represented in Fig. 2 by the area between the solid line and the hatched area. A similar QE scattering is also observed in the low-temperature IN5-spectra. There the spurious character of this scattering becomes obvious, since this QE line could only be fitted assuming a temperature of about 1.5 K, which is a little higher than the sample temperature. This scattering is already subtracted out from the data shown in Fig. 4 for both samples. Due to the high-energy resolution, the neutron flux at the sample was rather low (10^4 sec^{-1}). Thus the quality of these spectra is worse than that of the IN6 spectra shown in Fig. 2. Fits to the data with a QE line are not satisfactory and worsen with decreasing temperature, since the spectra resemble rather an inelastic excitation as demonstrated in Fig. 4 by fits with an inelastic line at 0.4 and

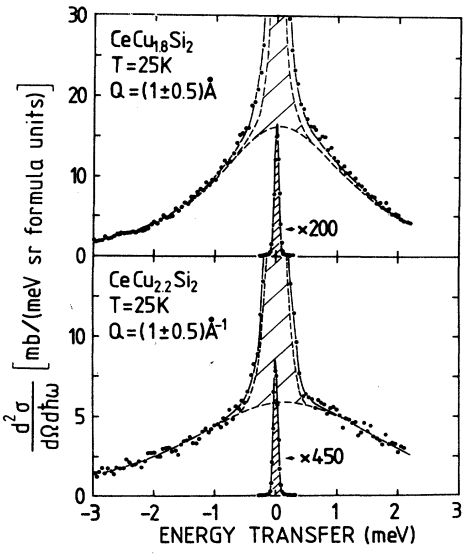

FIG. 2. Background and absorption corrected energy spectra of $CeCu_{2\pm0.2}Si_2$ as obtained at the IN6 TOF spectrometer with $E_0=3.1$ meV. The hatched areas mark the elastic nuclear peaks.

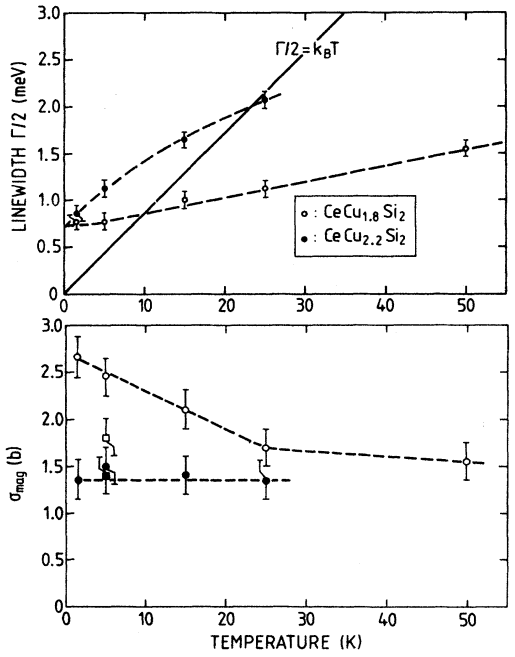

FIG. 3. QE linewidth (upper part) and total QE intensity (lower part) as a function of temperature from the IN6 spectra. The triangles of the QE intensities extracted from the CF analysis.

0.8 meV for the copper-deficient and the copper-excess sample, respectively (solid lines). From Ref. 8 and from our CF analysis (see below) we know the positions of the CF excitations ($\Delta > 10$ meV), i.e., we can exclude that the inelastic excitation at about 1 meV is due to a CF transition. However, from the theory of Kuramoto and Müller-Hartmann such a behavior is expected. Therefore we tried to fit our spectra also with an analytic function given in Ref. 17 (K-MH function). These fits do not differ much from those with an inelastic Lorentzian (see dotted curve in Fig. 4). All fits show some deviations from the data points near 1.1 meV. As such an additional scattering is not observed in the IN6-spectra at $T = 1.5$ K, this effect should be due to some uncertainties in the background correction of the IN5 data.

A summary of the results with respect to the low-energy part of the magnetic response is given by the temperature dependence of $\Gamma/2$ (circles) in the upper part of Fig. 3 for the IN6 data and of the inelastic linewidth (triangles) and of T_K (squares) in Fig. 5 for the IN5 data. In addition, the corresponding magnetic cross sections σ_{mag} are plotted as a function of temperature in the lower part of Fig. 3. The relevant result is the temperature dependence of the QE linewidth yielding a value at low temperatures which is equal to the inelastic linewidth as well as to the Kondo temperature deduced from the K-MH-function fit to the spectra at very low temperatures ($T \leq 770$ mK). This is demonstrated in Fig. 5 showing the QE linewidth (circles) at $T = 1.5$ K as obtained from the IN6 data. We want to note the particular behavior of the spectrum of $CeCu_{1.8}Si_2$ at $T = 60$ mK. The inelastic linewidth and the obtained T_K are smaller than expected by comparison with the other temperature points. This

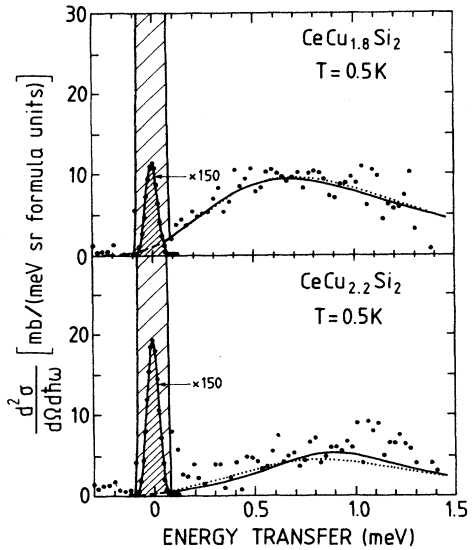

FIG. 4. Background and absorption corrected energy spectra of $CeCu_{2\pm0.2}Si_2$ as obtained at the IN5 TOF spectrometer with $E_0 = 2$ meV and using a $^3He/^4He$ refrigerator. The hatched areas indicate the elastic nuclear peaks. The solid line represents a fit with an inelastic Lorentzian, while the dotted curve is the result of a fit with the analytic K-MH function.

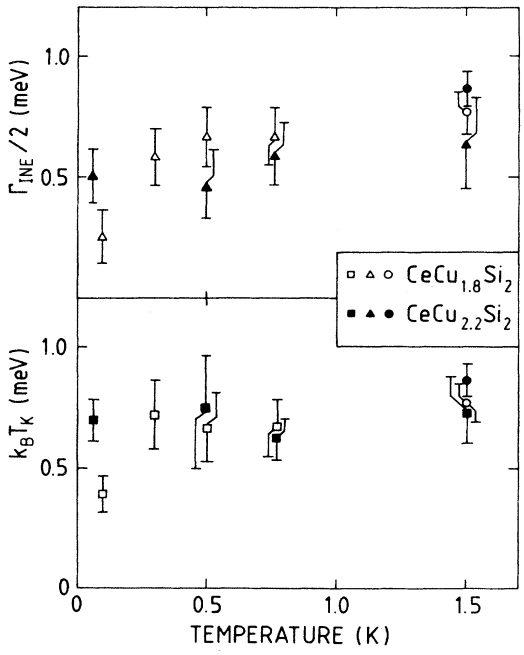

FIG. 5. Values for the inelastic linewidth (upper part) and for the Kondo temperature (lower part) as a function of temperature as obtained from the IN5 spectra. The values for T_K result from fits using the K-MH function. The circles represent the corresponding QE linewidths as obtained from the IN6 spectra at $T = 1.5$ K (see Fig. 3).

spectrum shows also a Q dependence which was not observed in any other spectrum. Thus we take this as an indication for magnetic order in the main $CeCu_2Si_2$ phase below $T \approx 300$ mK.

The second parameter obtained by fits with the K-MH function is the degeneracy of the $4f$ ground state. This value can be determined rather inaccurately from our data. We found roughly a value of 6, which is in contrast to the expected value of 2 for a doublet CF ground state and $n_f \approx 1$. $CeRu_2Si_2$ behaves quite similar. Here $k_B T_K$ was found to be 1.4 meV from spectra of much better quality.[18]

B. CF spectra

The magnetic cross section of 1.3 and 2.6 barn observed for the QE scattering of the two samples at low temperatures (see Fig. 3, lower part) are smaller than the expected value for the full Ce moment (3.92 b). However, since the full Ce^{3+} moment has been derived from static susceptibility measurements for $T > 50$ K, it is obvious that strong inelastic components like CF excitations are present. Indeed, our earlier experiment[8] showed a total CF splitting of about 31 meV. Now we were able to confirm this result by comparing the inelastic excitation spectra of our copper-deficient and copper-excess samples. The spectra at $T = 5$ K are shown in Fig. 6 for large scattering angles. Due to the magnetic form factor and the phonon structure factors, the phonon scattering (hatched area) dominates over the magnetic scattering at these angles. Qualitatively both spectra look similar. Only a slight difference in the intensity is observed, which is due to the higher copper concentration per formula unit in the superconducting sample. Figure 7 shows the same spectra at low scattering angles. Here the magnetic scattering dominates the phonon contribution (hatched area). A qualitative difference between the two spectra of Fig. 7 is observed. The vallye at about 23 meV is deeper in the superconducting sample and the intensity ratio of the two peaks at 13 and 19 meV is different. Since the phonon spectra look the same for both samples (see Fig. 6), one can unambiguously conclude that the differences between the spectra at low-scattering angles are due to *differences in the magnetic excitation spectra.* Therefore we attribute these differences to a magnetic excitation hidden underneath the phonon spectra and moving from 20 meV in $CeCu_{1.8}Si_2$ to 17 meV in $CeCu_{2.2}Si_2$. This is a confirmation of our earlier result[8] (see discussion), which contradicts the analysis of the specific heat data.[11]

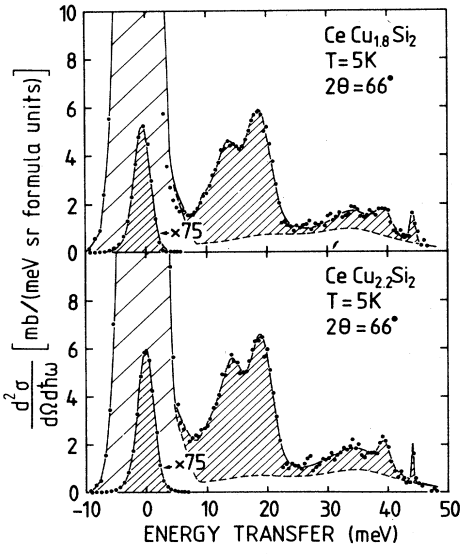

FIG. 6. Background and absorption corrected high angle energy spectra of $CeCu_{2\pm0.2}Si_2$ obtained at the IN4 TOF spectrometer with $E_0 = 50.8$ meV. The hatched areas indicate the elastic nuclear peak and the nuclear phonon scattering.

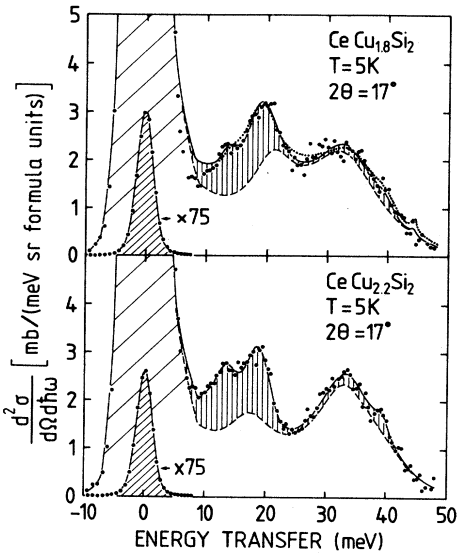

FIG. 7. Background and absorption corrected low angle energy spectra of $CeCu_{2\pm0.2}Si_2$ obtained at the IN4 TOF spectrometer with $E_0 = 50.8$ meV. The hatched areas indicate the elastic nuclear peak and the nuclear phonon scattering.

The magnetic character of the dominant scattering around 16 meV also becomes evident from Fig. 8. There the scattering intensity obtained between 8 and 23 meV at $T = 5$ K is plotted as a function of momentum transfer in a double logarithmic scale for $CeCu_{1.8}Si_2$ as well as for the reference compound $LaCu_2Si_2$. The latter data are taken from an earlier experiment using the same experimental set up.[14] In order to reduce the noise the counts of maximal four detectors were added. The horizontal error bars give the momentum transfer range of the spectra points taken into account for the summation. We chose the unit counts per 12 h and per N_L formula units (N_L: Loschmidt's number). That allows us to compare both systems directly.

The Q dependence of the scattering intensity shown in Fig. 8 exhibits two different behaviors. At high Q it is roughly linear with a slope of 2, corresponding to $I(Q) \propto Q^2$ as is expected as an average for phonon scattering on a polycrystal. At low Q we find a smaller

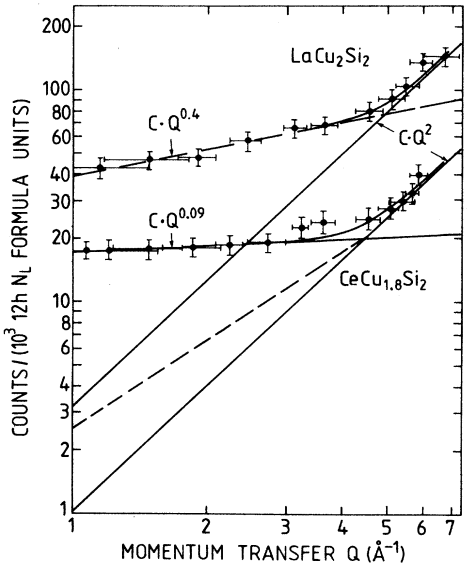

FIG. 8. Double logarithmic plot of the integrated intensity in the energy window of 8–23 meV vs momentum transfer. The horizontal error bars reflect the lowest and highest Q value for this energy window. For details, see text.

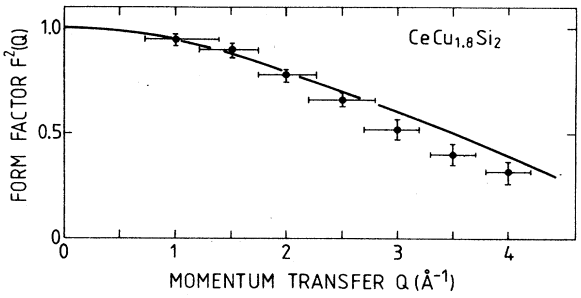

FIG. 9. Q dependence of the observed magnetic scattering as extracted from Fig. 8 (difference between data points and dashed line); the solid line indicates the behavior of the magnetic $4f^1$ form factor.

slope for the cerium system and also for the lanthanum reference compound. This anomalous slope at low Q in the reference compound can be explained by a double scattering process: elastic Bragg scattering and inelastic phonon scattering. This type of double scattering yields roughly the same spectral distribution at low angles as observed mainly by a single scattering process at high angles. This explanation is strongly supported by calculations of Ch. Ziegler.[19]

The important question is now whether the small slope for $CeCu_{1.8}Si_2$ results only from this double scattering process or if magnetic scattering is dominant. To decide between the two possibilities we recall that the scattering rate of this double scattering process can be roughly described by the counts $\mathcal{C}$

$$\mathcal{C}=C(\sigma^{\mathrm{nuc}}N)^2 , \tag{3}$$

where N is the number of scatters, σ^{nuc} the nuclear cross section and C a sample-independent proportionality factor. The weights of the samples give us the value $N_{\mathrm{Ce}}/N_{\mathrm{La}}=0.436$ and from the straight solid lines in Fig. 8, i.e., from the high Q values one can derive $\sigma^{\mathrm{nuc}}_{\mathrm{Ce}}/\sigma^{\mathrm{nuc}}_{\mathrm{La}}=0.324$. Thus one can conclude, using Eq. (3), that the cross section of the double scattering process should be about 50 times smaller in $CeCu_{1.8}Si_2$ than in $LaCu_2Si_2$. The expected behavior inferred from this comparison with the reference compound is depicted roughly by the dashed line in Fig. 8 which lies much lower than the experimental points. Subtracting the dashed line from the experimental points yields the points shown in Fig. 9, which are consistent with a local magnetic Ce^{3+} form factor. A similar result is found for the copper-excess sample. In other words, these considerations also lead to the conclusion that between 8 and 23 meV the dominant contribution to the scattering at low angles is of magnetic origin in both samples.

Constant $|Q|$ measurements at $|Q|=2.0$ Å^{-1} and 5.3 Å^{-1} performed on the H7 TAS spectrometer in Brookhaven confirm the upper results. In Fig. 10 the energy spectra at $|Q|=2$ Å^{-1} are shown for both samples, corresponding to the same monitor rate but slightly different sample weights. Due to the constant E_f mode the resulting spectra are directly proportional to $S(Q,\hbar\omega,T)$, i.e., to $(k_0/k_1)d^2\sigma/d\Omega d\hbar\omega$. This explains the difference to Fig. 7. Q scans taken for both samples in the valley at $\hbar\omega=23$ meV show the magnetic origin of

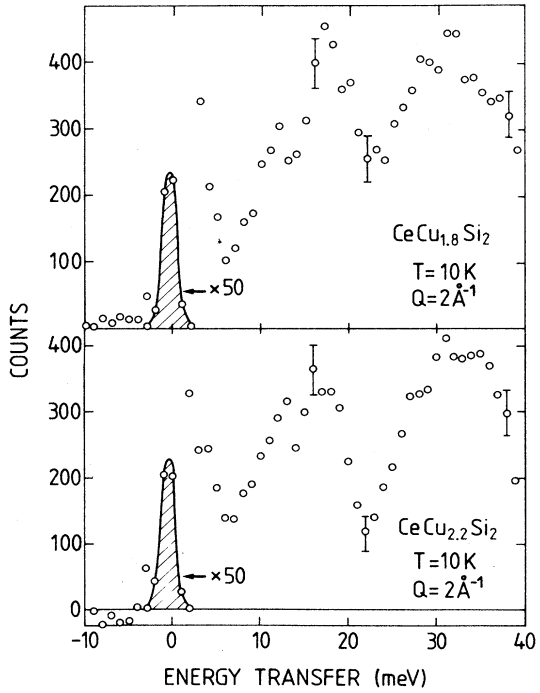

FIG. 10. Background corrected energy spectra as obtained at the H7 TAS spectrometer using a constant final-energy mode with $E_f=30.5$ meV.

the enhanced scattering intensity in $CeCu_{1.8}Si_2$. The difference of these constant-E scans is consistent with the local magnetic form factor of Ce^{3+}.

In the past the paramagneto-vibrational scattering process[12] has been suggested to be the cause of magneticlike contributions. In the case of $CeCu_2Si_2$ recent quantitative calculations show that this contribution is negligible,[20] in agreement with our qualitative considerations.

As the TOF spectra have a much better quality than the TAS data we have concentrated our analysis on these data. In order to perform a quantitative CF analysis it is necessary to separate magnetic from phonon scattering. That is generally the major source of uncertainties from the experimental point of view. The best way to accomplish this separation is certainly the use of polarized neutrons such as in Refs. 21 and 22. Unfortunately, the statistical error of such data is rather large due to the low flux of polarized neutrons. For the same reason such experiments are usually operating with a worse energy resolution than standard unpolarized neutron scattering experiments. Therefore it is not in contradiction to our results that the authors of Refs. 21 and 22 do not find evidence for a CF line at about 17 meV. Their data do not exclude an excitation at 17 meV, hence their data and our published magnetic spectrum of $CeCu_2Si_2$ (Ref. 8) are in agreement within experimental error. The disadvantage of the unpolarized neutron scattering technique, i.e., the uncertainty of the phonon corrections is very often more than compensated by the better statistical quality of the spectra due to the considerable higher neutron flux and by the better energy resolution.

In our analysis the phonon scattering has been taken into account in the following way. First we fitted the phonon spectrum at high angles. Since the phonon contribution at low angles is mainly due to the above described double scattering process (i.e., the phonon scattering observed at low angles has to be associated with a *high* scattering angle), we claim that the energy distribution of the phonon scattering at low angle detectors looks approximately the same as at high angle detectors. This assumption is not in complete agreement with the result of the calculations of Ch. Ziegler, but we did not use these quantitative calculations for our fits, since the agreement between calculated and experimental spectra is not yet satisfactory even for $LaCu_2Si_2$ (Ref. 19). Therefore we took the same peak positions and linewidths known from the high angle spectra to describe the phonon scattering contribution at low angles. Furthermore, we used the same relative intensities as found for high angles. This means that we fitted the phonon contributions using only one intensity parameter, which scales the phonon spectrum observed at high angles to the low angle spectra. Although this procedure is only an approximation, it is the best we can do at the moment. The magnetic contribution of the spectra were fitted within the CF theory. The CF splitting of Ce in tetragonal symmetry ($I4/mmm$) can be described by three CF parameters B_2^0, B_4^0, and B_4^4. For convenience we have used the parameters W, x_4^0, and x_4^4 (Ref. 23) defined in analogy to the cubic case discussed by Lea, Leask, and Wolf.[24]

V. DISCUSSION

First we discuss the CF fits of the IN4 spectra and then compare the results with our QE IN6 experiment and with static susceptibility measurements on the same samples.

A. CF analysis

Using the procedure described above, the CF fits on the $CeCu_{1.8}Si_2$ spectrum unambiguously yielded CF parameters and the corresponding CF scheme shown in Fig. 11(b). According to these fits we found that the ground state is mainly of $|\pm\frac{5}{2}\rangle$ character. Investigating the possibilities of other ground states we performed fits enforcing a ground state of mainly $|\pm\frac{1}{2}\rangle$ or $|\pm\frac{3}{2}\rangle$ character. However, these attempts produce inelastic intensities which are too large corresponding to larger CF-transition matrix elements. In order to counteract this effect, the fits produce large linewidths, resulting in poorer fits to the experimental data points. The dotted curve in the upper part of Fig. 7 exemplifies this behavior for a ground state of mainly $|\pm\frac{3}{2}\rangle$ character. The $|\pm\frac{1}{2}\rangle$ ground state behaves even worse. Therefore we can exclude these two possibilities.

The situation in the copper-excess system is more complex. From the above discussion of Fig. 7 it is clear that one has to expect some changes of the CF parameters due to the shift of the lower lying excitation from about 20 meV in $CeCu_{1.8}Si_2$ to lower energy in $CeCu_{2.2}Si_2$. All our attempts to fit the spectrum by a pure CF ansatz (including phonons), however, were not successful. The linewidth of the lower excitation as well as the phonon intensity were not feasible. Therefore we have assumed in our next step that only a portion of Ce ions shows the normal CF splitting and that the other Ce ions show a single broad excitation line around 40 meV. Under these assumptions a good fit with reasonable CF linewidths and phonon intensities (solid line in the lower part of Fig. 7) is obtained taking about 80% of the Ce ions to show a normal CF splitting. The additional excitation line at about 40 meV has a width $\Gamma/2\approx 10$ meV and an intensity $\sigma_{\text{mag}}\approx 0.4$ b. The total magnetic intensity of 3.6 b, given by $0.8\cdot 3.98\text{ b}+0.4$ b, is slightly less than expected for a Ce^{3+} ion (3.98 b). The resulting CF parameters and the corresponding CF level scheme are shown in Fig. 11(c). Comparing the CF parameters obtained from our new analysis with those of Ref. 8 for $CeCu_2Si_2$ [Fig. 11(a)] we find a change in the sign of the B_4^0 parameter. However, since this parameter is nearly zero, this change does not influence the CF scheme drastically. Thus the level sequence (see also the wave functions) which we found in our analysis does not differ much from that published in Ref. 8. This is not surprising considering the work of H. F. Braun and J. L. Jorda[25] and a recent neutron diffraction result of Neumann, Capellmann, and Ziebeck:[26] Even in the nonstoichiometric samples $CeCu_{2\pm 0.2}Si_2$, the main phase is the tetragonal $CeCu_2Si_2$ with a nearly stoichiometric composition. In their analysis the difference in the Cu concentration is at least partly balanced by impurity phases. However, the

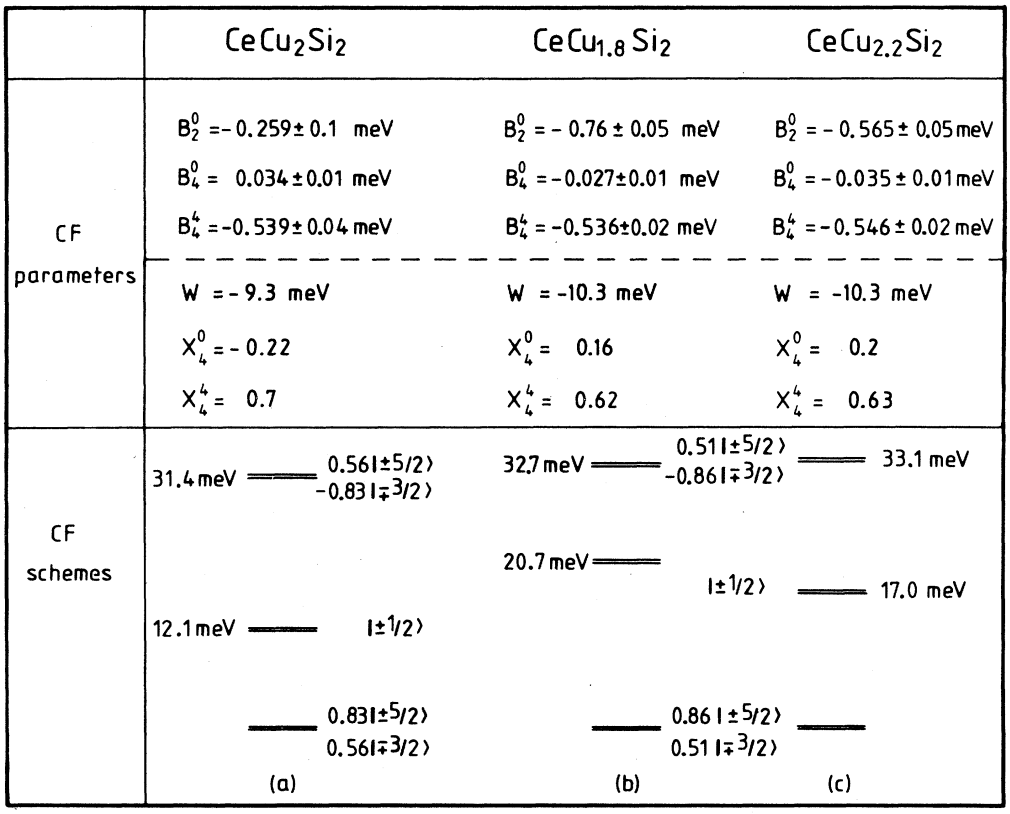

FIG. 11. CF parameters and corresponding CF schemes. For $CeCu_2Si_2$ the values are taken from Ref. 8.

volume of the unit cell is smaller in $CeCu_{2.2}Si_2$ than in $CeCu_{1.8}Si_2$ in agreement with lattice parameters found by earlier x ray diffraction experiments on single crystals.[27] This volume difference might cause the total CF splitting in the copper-excess sample to be slightly larger than in the copper-deficient sample. We note that the neutron diffraction work of Neumann, Capellmann, and Ziebeck was performed on the same samples and at nearly the same time as our inelastic neutron scattering experiment. Thus a direct comparison is admissible.

Now we want to discuss the more important question how one can understand, that only a portion of Ce ions shows a CF splitting, while the others behave in quite a different manner. Applying pressure on a nominal stoichiometric $CeCu_2Si_2$ sample a γ-α phase transition was observed at 35 kbar measuring the valence by L_{III} edges.[28,29] The valence of cerium in a $CeCu_{2.26}Si_2$ single crystal (the same crystal as in Ref. 27) was found to be between the values of γ- and α-type cerium in $CeCu_2Si_2$ (Refs. 28 and 29). Within a thermodynamic model, Wittershagen and Wohlleben[30] have calculated the Gibb's enthalpy as a function of valence and pressure. From that a coexistence of γ-Ce and α-Ce should be expected near the phase transition. γ-type cerium should show normal CF splitting effects, while α-type cerium should behave strongly intermediate valent like $CePd_3$, which shows a broad QE magnetic spectrum at high temperatures,[31] but a broad inelastic excitation at low temperatures.[32] Thus a possible explanation of the low-temperature spectrum ($T=5$ K) of the copper-excess sample may be the coexistence of γ- and α-cerium: the additional excitation line at about 40 meV is then associated to a α- cerium phase, while the remaining CF structure is due to the main γ-cerium phase. This interpretation is supported by the fact that the reduced magnetic CF intensity is not completely restored by the inelastic excitation at about 40 meV. Thus the missing intensity can be taken as an indication for the existence of some intermediate valent α-Ce. EXAFS measured on Cu-excess and Cu-deficient samples look different, but they were not yet analyzed in detail.[33]

The above interpretation of the inelastic neutron scattering spectra obtained for the copper-excess sample is one possibility. We want to mention that the pressure extracted from the bulk moduli and from the difference in the unit cell volume is only few kbar.[27,29] This is in contrast to the pressure of 35 kbar found for the phase transition in $CeCu_2Si_2$. The assumption of only one kind of Ce ion with still unknown magnetic properties cannot be excluded.

B. Comparison of CF result with QE result

We now want to verify the consistency of our QE and inelastic (CF) results. The QE intensity, which is not resolved in the IN4 spectra for reasons of energy resolution, should originate from the ground state only for temperatures small compared to the CF excitation energies. Therefore we present the QE intensities calculated from the CF parameters (including reduction for $CeCu_{2.2}Si_2$) by the triangles in the lower part of Fig. 3. The results of both experiments are in excellent agreement for the copper-excess sample, while for the copper-deficient sample the CF value is only in good agreement with the QE intensity for $T \geq 25$ K. The increase of the QE intensity with decreasing temperature in the copper-deficient sample (which does not appear in the copper-excess sample) reflects the disagreement between the values calculated from the CF parameters and the measured QE intensities in that system.

C. Comparison of neutron scattering intensities with static bulk susceptibilities

In order to clarify this discrepancy in $CeCu_{1.8}Si_2$ at low temperatures we have calculated the static magnetic bulk susceptibility from our fit parameters in accordance with Eq. (1) and assuming the local $4f^1$ form factor. In Fig. 12 we give a comparison of these values with the bulk susceptibility measured on a part of the same sample using a Faraday balance method. The IN6 values (closed squares) are in rather good agreement with the bulk measurements for the copper-excess sample but, again, there is a disagreement for the copper-deficient sample, which shows a strong tail in the static bulk susceptibility below $T \approx 15$ K. The IN6 points do not contain the Van-Vleck terms due to the CF excitations, hence these values become smaller than the bulk values with increasing temperature. As expected from Fig. 3 (lower part), the CF value (open triangle in Fig. 12) agrees quite well with the bulk data of the copper-excess sample, while there is again a discrepancy for the copper-deficient sample (open triangle in Fig. 12). The clue for solving this discrepancy in $CeCu_{1.8}Si_2$ can be taken from a magnetization measurement on $CeCu_{1.8}Si_2$ at $T = 1.8$ K (see Fig. 13). In addition to the normal slope due to the main phase $CeCu_2Si_2$ saturation behavior with a nominal magnetic moment of about 0.045 μ_B per Ce ion is observed. This effect does not occur in the magnetization curve of $CeCu_{2.2}Si_2$. Thus the strong tail in the susceptibility of $CeCu_{1.8}Si_2$ originates from magnetic ordering in this sample. Magnetization measurements on this sample were performed for several temperatures. Calculating the static susceptibility from the high field slopes (see, e.g., Fig. 13) one obtains values as given by the open circles in Fig. 12. This susceptibility is still larger than that of $CeCu_{2.2}Si_2$, but now our CF value at $T = 5$ K is in excellent agreement with the bulk value. Furthermore, the IN6 values (closed squares) are in much better agreement with these susceptibility values.

Therefore we believe that the IN6 results at low temperature reflect the presence of a mixture of the dominant

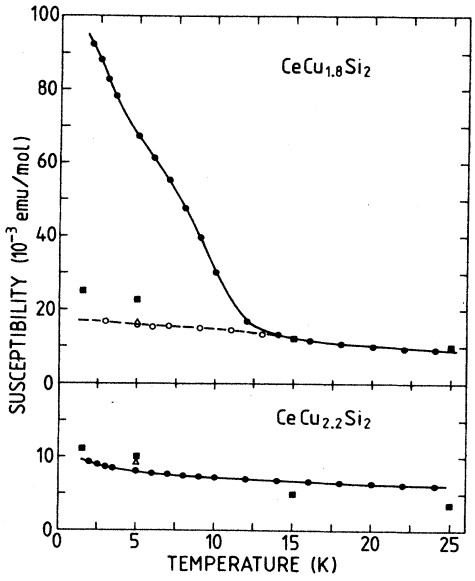

FIG. 12. Static bulk susceptibility as a function of temperature (closed circles), the corrected susceptibility for $CeCu_{1.8}Si_2$ using the slopes shown in Fig. 13 for $T = 1.5$ K (open circles), static susceptibility values as extracted from the intensity of the QE line in the IN6 spectra (closed squares) and static susceptibility values as obtained from the CF analysis (open triangle).

$CeCu_2Si_2$ phase and at least one impurity phase containing Ce. Since $CeSi_{1.8}$ orders magnetically at about $T_N = 8$ K (Ref. 34) and since Ce_xSi_{2-x} was found as an impurity phase by Neumann, Capellmann, and Ziebeck,[26] it is possible that this additional magnetism in the copper-deficient sample could be associated with $CeSi_{1.8}$. This phase could also be responsible for the difference between the IN6-susceptibility values (solid squares in Fig. 12) and the susceptibility of the main $CeCu_2Si_2$ phase (open circles in Fig. 12). In contrast to the copper-deficient sample, the impurity phases in the copper-excess sample are

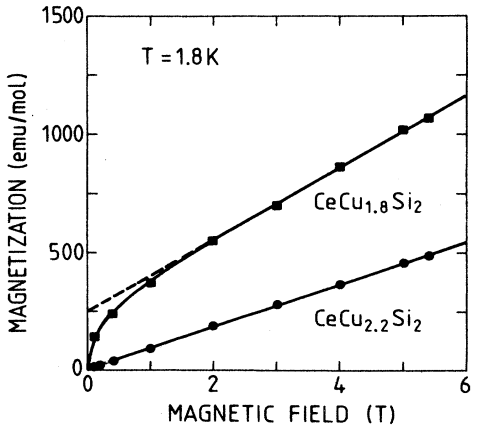

FIG. 13. Magnetization as a function of magnetic field at low temperature.

Cu-rich and do not contain Ce, as, e.g., Cu_xSi_{1-x} and Cu_5Si (Ref. 26). Thus the observed magnetic behavior in $CeCu_{2.2}Si_2$ should reflect that of the dominant $CeCu_2Si_2$ phase. There remains a difference to the magnetic behavior of the dominant $CeCu_2Si_2$ phase in $CeCu_{1.8}Si_2$ (e.g., a factor of about 2 in the static susceptibility, see Fig. 12). This is due to the different unit cell volumes, which might cause the differences in the magnetic neutron scattering spectra of both samples: quasielastic intensity and additional high-energy response in the copper-excess sample.

VI. CONCLUSION

We have performed two types of inelastic neutron scattering experiments: using cold neutrons and a high resolution in energy (IN6,IN5) we studied the QE behavior and using thermal neutrons (IN4,H7) we investigated the CF splitting of $CeCu_2Si_2$. We have presented a consistent interpretation, in which the static bulk susceptibility and the neutron diffraction work of Neumann, Capellmann, and Ziebeck[26] has been taken into account. The $CeCu_{1.8}Si_2$ spectra can be explained by pure CF splitting of the dominant $CeCu_2Si_2$ phase and a second crystallographic phase containing magnetically ordering Ce ions. A magnetic ordering of the $CeCu_2Si_2$ phase may be possible below $T=300$ mK. The $CeCu_{2.2}Si_2$ spectra can be understood, if two different kinds of Ce ions are assumed to be present in the main $CeCu_2Si_2$ phase. The α-cerium phase may be responsible for the superconductivity. In both systems the CF analysis leads to a ground state of mainly $|\pm\frac{5}{2}\rangle$ character for the dominant $CeCu_2Si_2$ phase. Thus this level scheme matches well to the CeM_2Si_2 series with $M=$Au, Ag, Pd (Ref. 35). The low-temperature spectra at $T<1$ K have inelastic character. No change in the magnetic scattering is observed when lowering the temperature below the superconducting transition.

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