

Lattice and spin dynamics of γ -Ce

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Inelastic-neutron-scattering techniques have been used to study the lattice dynamics and magnetic scattering of fcc γ -Ce. The phonon dispersion curves at room temperature were determined along the [100], [110], [111], and [0 $\bar{1}$ 1] symmetry directions. Comparison of the measured dispersion curves with those of Th show that the spectrum of γ -Ce is in general softer than one would expect by taking into account the differences in mass, interatomic spacing, and melting temperatures of these elements. This relative softening of the phonon frequencies is more pronounced for the phonon branches whose slopes in the elastic limit involve the elastic constants c_{11} and c_{12} which determine the bulk modulus of the element. Thus it seems that premonitory effects of the $\gamma \rightarrow \alpha$ transition are present in the room-temperature dispersion curves of γ -Ce. The elastic constants and lattice specific heat were evaluated by a standard Born-von Kármán analysis. We find that the values of c_{11} and c_{44} are comparable, which is extraordinary for an fcc metal. As a result the shear moduli c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ differ by almost a factor of 3 which implies large anisotropy with regard to the propagation of elastic waves. Constant- Q scans performed at reciprocal-lattice points, where the one-phonon contribution to the scattering vanishes, show unambiguously that there is no well-defined low-energy crystal-field excitation in γ -Ce. The magnetic scattering follows quite well the $4f$ magnetic form factor of Ce^{3+} . Assuming a relaxational form for the imaginary part of the generalized susceptibility, the spin relaxation energy $\hbar\Gamma$ is found to be approximately 4 THz.

I. INTRODUCTION

Over the last several years there has been considerable interest¹⁻³ in cerium and some of its compounds which under certain conditions undergo a transformation to a state in which the cerium ions have a nonintegral valence. In these systems the transformation to a mixed valence state usually occurs at low temperatures but it can be induced also by an increase in pressure or by alloying. These valence transitions can be first order, second order, or continuous. They are in general isostructural but the lattice parameter of the nonintegral valence state (which is also referred to as the collapsed phase) is considerably smaller than that of the integral valence state. Although the detailed mechanism of these transitions is not well understood, it is generally believed^{1,2} that at the transition the atomiclike $4f$ level is pinned at the Fermi level. It has also been suggested,⁴ in the case of Ce, that the $\gamma \rightarrow \alpha$ transformation is a Mott type of transition involving the $4f$ electron. Clearly a detailed knowledge of the electronic structure and lattice dynamics of these materials in both phases is

essential for a fundamental understanding of these transitions.

Under various temperature and pressure conditions, cerium metal exists⁵ in five allotropic forms designated as α , β , γ , δ , and α' . Of particular interest is the face-centered cubic γ phase in which under normal conditions of temperature and pressure the cerium atom is approximately in the trippositive state. When γ -Ce is compressed to modest pressures (~ 8 kbar at 300 K) or cooled to low temperatures (≤ 100 K at 1 atm) it undergoes a transformation to the collapsed α phase (with the same fcc structure but with a 17% smaller volume) in which the cerium ions are in a mixed valence state. The study of the temperature dependence of the physical properties of γ -Ce is complicated by the $\gamma \rightarrow \beta$ transformation which occurs at approximately 260 K at 1 atm. The γ to α transition has also been observed^{3,6} with a lowering of temperature in alloys of cerium with thorium.

Since its discovery there have been numerous investigations of the properties of cerium.⁵ Unfortunately most of these studies have been performed

on polycrystalline samples which contained, depending on the thermal treatment and temperature of the sample, various amounts of two or three phases of Ce (γ -, α -, and β -Ce). Thus in most cases it has been difficult to separate experimentally the contribution of each phase to the total observed property. In the last few years substantial progress has been made in the preparation of allotropically pure α -, β -, and γ -Ce samples⁷ and this has opened the way for a systematic study of their properties. However, only recently single crystals of sufficient size for neutron scattering experiments have been prepared in the Ames Laboratory. In a previous paper⁸ we presented the results of a study of the spatial distribution and temperature dependence of the magnetization induced in γ -Ce by an externally applied magnetic field, using polarized neutron scattering techniques. In the present work inelastic neutron scattering techniques have been used to study the lattice and spin dynamics of fcc γ -Ce.

II. EXPERIMENTAL DETAILS

Two single crystals of γ -Ce were grown at the Ames Laboratory from high purity (~ 99.9 at. %) material by a combined levitation zoning-strain annealing technique.⁹ The smaller crystal was used for the polarized neutron experiments⁸ and the larger crystal (~ 3 cm³) was used for the inelastic neutron scattering experiments reported in the present paper. Standard neutron diffraction techniques were used to establish that the samples were single crystals of γ -Ce with a lattice constant of 5.16 Å. No evidence was found for the presence in the samples of any other phases of Ce (α and β). The mosaic spread of the samples has been estimated by measuring the full width at half maximum (FWHM) of the (111) reflection, using a monochromatic neutron beam obtained by reflection from the (111) planes of a perfect Ge crystals. The FWHM, measured using the smaller γ -Ce crystal, was found to be 17.5 minutes of arc. To avoid oxidation of the sample the crystal was sealed in a thin-wall aluminum container and kept under vacuum or in a helium atmosphere throughout the experiments.

Some preliminary phonon measurements were performed using two triple-axis spectrometers at the 5-MW Ames Laboratory Research Reactor. In both spectrometers pyrolytic graphite was used as monochromator and analyzer. One of the instruments was operated with a fixed incident neutron energy of 8.4 THz and the other with a fixed scattered neutron energy of 3.3 THz; in the second instrument a pyrolytic graphite filter was used in the scattered beam to attenuate higher-order contaminations. All measurements were performed in the constant- Q (where Q is the neutron scattering vector) mode of operation. A complete set of phonon and magnetic scattering

measurements was obtained using two triple-axis spectrometers at the 100 MW High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. Nearly all phonon frequencies obtained in Ames were remeasured at Oak Ridge and they were found to agree to within experimental errors. Beryllium [set to reflect from the (101) or (002) planes] was used as monochromator and both instruments were operated in the fixed scattered neutron energy mode. Pyrolytic graphite and beryllium [set to reflect from the (002) planes] were used as analyzers. All phonon measurements were performed in the constant- Q mode of operation. For intensity reasons most of the phonon measurements along the [001], [110], and [111] symmetry directions were performed with a scattered neutron energy E' of 6 THz and a pyrolytic graphite analyzer. To improve the resolution for the measurements of the low-frequency phonons an energy of $E' = 3.3$ THz was used; in these measurements a pyrolytic graphite filter was inserted in the scattered beam to attenuate higher-order contaminations. The phonon measurements along the [0 $\bar{1}$ 1] direction were obtained using $E' = 8.4$ THz and a beryllium analyzer. The energy and scattering vector dependence of the magnetic scattering was studied by performing a series of constant Q and constant energy transfer scans, respectively. A definite advantage of using a single crystal for studying the magnetic scattering is that contamination of the constant- Q scans by one phonon scattering can be avoided by performing the measurements at the reciprocal-lattice points.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The phonon dispersion curves were determined, at room temperature, along the [001], [110], [111], and [0 $\bar{1}$ 1] symmetry directions. The measured phonon frequencies are listed in Table I and the experimental dispersion curves are plotted in Fig. 1.

It would have been instructive to compare the dispersion curves of γ -Ce with those of fcc La, since the latter element has the same outer electronic structure and approximately the same mass as Ce. Unfortunately the dispersion curves of fcc La have not yet been measured. However several rather unique features of the lattice dynamics of γ -Ce can be revealed by comparing the dispersion curves with those of other fcc elements and in particular with those¹⁰ of Th which is in the same column of the Periodic Table as Ce. Comparison of the dispersion curves in Fig. 1 with those of Th shows that the spectrum of γ -Ce is in general softer than one would expect from the Lindemann homology rule¹¹ which takes in account the differences in mass, interatomic spacing, and melting temperatures of these elements. This relative softening is particularly pronounced for

the longitudinal branches as well as the T [111] and T_1 [110] branches. On the other hand the lowering of the frequencies with respect to the values obtained from the Th frequencies by application of the Lindemann rule is not as pronounced for the T [100] and T_2 [110] branches; actually the frequencies of the

TABLE I. Measured normal-mode frequencies (in THz) for the symmetry branches in γ -Ce at room temperature.

[00 ξ]L		[00 ξ]T		[$\xi\xi\xi$]L	
ξ	ν	ξ	ν	ξ	ν
0.1	0.35 $\pm$ 0.02	0.1	0.29 $\pm$ 0.01	0.1	0.84 $\pm$ 0.04
0.15	0.52 $\pm$ 0.02	0.2	0.60 $\pm$ 0.02	0.15	1.20 $\pm$ 0.05
0.2	0.76 $\pm$ 0.03	0.3	0.97 $\pm$ 0.03	0.2	1.55 $\pm$ 0.06
0.3	1.04 $\pm$ 0.06	0.4	1.27 $\pm$ 0.02	0.3	2.27 $\pm$ 0.08
0.4	1.35 $\pm$ 0.06	0.5	1.50 $\pm$ 0.04	0.4	2.66 $\pm$ 0.08
0.5	1.70 $\pm$ 0.07	0.6	1.74 $\pm$ 0.04	0.5	2.75 $\pm$ 0.07
0.6	2.04 $\pm$ 0.07	0.7	1.99 $\pm$ 0.05		
0.7	2.45 $\pm$ 0.05	0.8	2.04 $\pm$ 0.06		
0.8	2.72 $\pm$ 0.08	0.9	2.10 $\pm$ 0.09		
0.9	2.94 $\pm$ 0.08	1.0	2.05 $\pm$ 0.06		
1.0	3.04 $\pm$ 0.07				
[$\xi\xi\xi$]T		[0 $\xi\xi$]L		[0 $\xi\xi$]T ₂	
ξ	ν	ξ	ν	ξ	ν
0.1	0.43 $\pm$ 0.01	0.1	0.58 $\pm$ 0.02	0.1	0.47 $\pm$ 0.01
0.15	0.60 $\pm$ 0.01	0.2	1.28 $\pm$ 0.03	0.15	0.70 $\pm$ 0.01
0.2	0.76 $\pm$ 0.02	0.3	1.74 $\pm$ 0.03	0.2	0.95 $\pm$ 0.01
0.3	0.99 $\pm$ 0.03	0.4	2.09 $\pm$ 0.03	0.3	1.41 $\pm$ 0.02
0.4	0.83 $\pm$ 0.03	0.5	2.20 $\pm$ 0.05	0.4	1.79 $\pm$ 0.02
0.5	0.75 $\pm$ 0.03	0.6	2.20 $\pm$ 0.04	0.5	2.13 $\pm$ 0.04
		0.7	2.19 $\pm$ 0.06	0.6	2.30 $\pm$ 0.06
		0.8	2.15 $\pm$ 0.05	0.7	2.59 $\pm$ 0.07
		0.9	2.04 $\pm$ 0.06	0.8	2.82 $\pm$ 0.07
		1.0	2.05 $\pm$ 0.06	0.9	2.90 $\pm$ 0.07
				1.0	3.04 $\pm$ 0.07
[0 $\xi\xi$]T ₁		[0 ξ 1] Λ		[0 ξ 1] π	
ξ	ν	ξ	ν	ξ	ν
0.1	0.27 $\pm$ 0.01	0.05	1.87 $\pm$ 0.08	0.2	2.78 $\pm$ 0.06
0.15	0.40 $\pm$ 0.01	0.1	1.89 $\pm$ 0.06	0.4	2.54 $\pm$ 0.06
0.2	0.54 $\pm$ 0.01	0.2	1.82 $\pm$ 0.06	0.6	2.16 $\pm$ 0.06
0.3	0.83 $\pm$ 0.02	0.35	1.71 $\pm$ 0.06	0.8	1.99 $\pm$ 0.06
0.4	1.09 $\pm$ 0.03	0.50	1.75 $\pm$ 0.08	1.0	2.05 $\pm$ 0.06
0.5	1.3 $\pm$ 0.03				
0.6	1.43 $\pm$ 0.05				
0.7	1.62 $\pm$ 0.07				
0.8	1.79 $\pm$ 0.05				
0.9	1.85 $\pm$ 0.06				
1.0	2.05 $\pm$ 0.06				

T [100] branch scale quite well with those of the corresponding branch of Th. This observation is rather interesting since the T [100] and T_2 [110] are the only branches whose slopes in the elastic limit do not involve the elastic constants c_{11} and c_{12} which determine the bulk modulus B of the material [$B = \frac{1}{3}(c_{11} + 2c_{12})$]. The bulk modulus of γ -Ce at room temperature decreases with increasing pressure and exhibits a dramatic decrease at the $\gamma \rightarrow \alpha$ transition pressure.¹² Thus it seems that premonitory effects of the transition are present in the dispersion curves of γ -Ce at room temperature: the relative softening of the frequencies of γ -Ce with respect to those of Th is more pronounced for those branches which are sensitive to a volume change in the elastic limit. Finally it should be pointed out that the anomalously low frequencies of T [111] branch of γ -Ce relative to those of the corresponding branch of Th may be related to the fcc—dhcp ($\gamma \rightarrow \beta$) transformation which occurs at approximately 260 K.

Unfortunately the microscopic theory of the lattice dynamics of metals in its present form cannot be easily adapted to a numerical analysis of the experimental data. Thus to obtain information about the elastic constants of γ -Ce (which have not yet been measured) and to evaluate the lattice specific heat we fitted the data to a conventional Born—von Kármán force constant model. The fitting procedure will be described only briefly since it is similar to that used by Svensson *et al.*¹³ in their analysis of the dispersion curves of Cu. In the present analysis the experimental data were fitted to various models with up to eight-nearest-neighbor atomic force constants. It is well known¹³ that there is not sufficient orthogonal information in measurements made only along the symmetry directions to make a completely general force-constant analysis which includes interactions beyond fourth neighbors. For instance when eight neighbors are included four constraints (i.e., four axially symmetric conditions) must be imposed in order to obtain the twenty-six atomic force constants of the model.¹³ We find that an adequate fit to the measurements is not obtained until at least sixth-nearest neighbors are included. The force constants obtained by fitting the data to an eighth-nearest-neighbor model are listed in Table II. At it can be seen from Fig. 1, this model provides a satisfactory fit to the experimentally determined dispersion curves. The elastic constants evaluated using the force constants listed in Table II are also included in the same table. Note the small difference between c_{11} and c_{44} , which is quite unusual for an fcc metal. As a result the shear moduli c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ differ by almost a factor of three (see Table II) which implies that γ -Ce is very anisotropic with regard to the propagation of elastic waves. No data on the elastic constants of γ -Ce are presently available to compare with the results

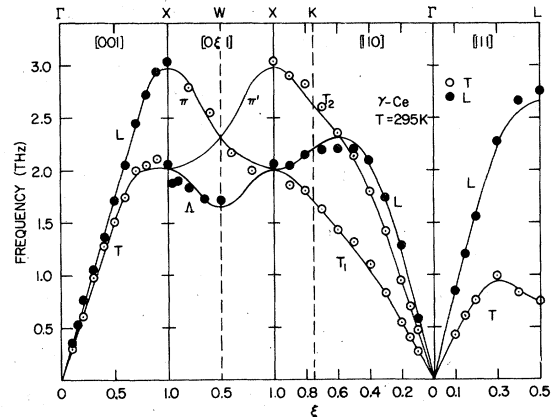


FIG. 1. Experimental dispersion curves of γ -Ce. The solid lines were obtained by fitting the data to an eighth-nearest-neighbor force-constant model.

of the present analysis. Bulk elastic moduli of polycrystalline samples, on the other hand, have been determined by several workers.^{12,14-16} Unfortunately polycrystalline elastic moduli cannot be accurately evaluated from single-crystal elastic constants by simple averaging techniques unless the crystal is nearly isotropic,¹⁷ a condition which is not valid for γ -Ce. Nevertheless values for the polycrystalline elastic moduli obtained¹⁸ by the Voigt¹⁹ and Reuss²⁰ averaging methods (from the elastic constants listed in Table II) were found to be consistent with the experimentally determined^{12,14-16} values (actually for the shear modulus there is good agreement between the calculated and measured values).

The force constants listed in Table I were used to calculate the phonon density of states $g(\nu)$ by the method of Gilat and Raubenheimer.²¹ From this density of states (Fig. 2) the lattice specific heat has been calculated as a function of temperature and the results expressed in terms of an effective Debye temperature Θ_D are plotted in Fig. 3. The 0-K value for Θ_D (135 K) obtained in the present analysis is in good agreement with the values^{12,14-16} (135–144 K) obtained by ultrasonic measurements on polycrystalline samples. Since γ -Ce transforms to the β and α phase upon cooling below room temperature no reliable data are available for the temperature dependence of the specific heat to compare with the results of the present analysis.

The first inelastic magnetic neutron scattering measurements on γ -Ce were performed on polycrystalline samples.^{22,23} In these studies relatively well-defined peaks were observed below approximately 2.5 THz. Due to the difficulty in identifying the various contributions to the scattering from polycrystalline samples, these peaks were attributed either to Ce^{3+} crystal-field excitations²³ or to one-phonon scattering.²⁴

The inelastic magnetic neutron scattering from a

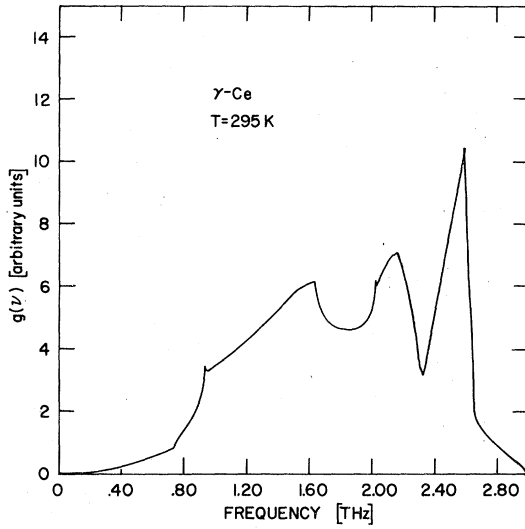


FIG. 2. Phonon density of states $g(\nu)$ evaluated using the force constants listed in Table II.

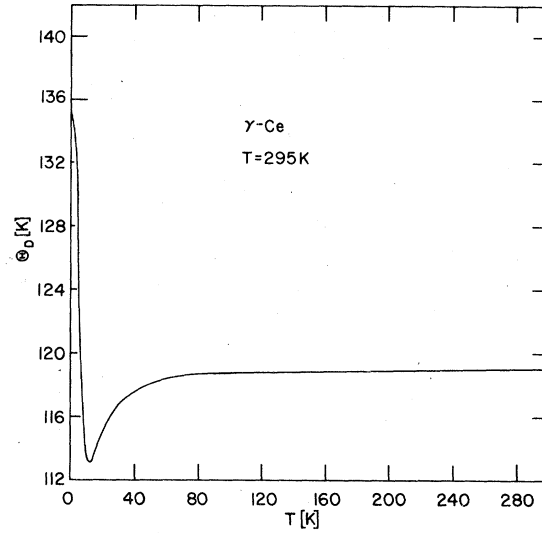


FIG. 3. Temperature dependence of the effective Debye temperature of γ -Ce, evaluated using the phonon density of states plotted in Fig. 2.

TABLE II. Atomic force constants and elastic constants obtained by fitting the data to an eighth-nearest-neighbor model. The notation is that of Ref. 13.

Atomic Force Constants [10^4 dynes/cm]		Elastic Constants [10^{12} dynes/cm ²]	
1XX	0.43726 ± 0.00749	c_{11}	0.241
1ZZ	-0.02264 ± 0.00866	c_{44}	0.194
1XY	0.45798 ± 0.01097	c_{12}	0.102
2XX	-0.23562 ± 0.01655	Constraints $8(5ZZ) = 9(5YY) - 5XX$ $3(7YZ) = 7XY$ $8(5XY) = 3(5XX) - 3(5YY)$ $2(7XZ) = 7XY$	
2YY	0.00773 ± 0.00850		
3XX	0.02058 ± 0.00559		
3YY	0.03169 ± 0.00400		
3YZ	-0.00547 ± 0.00253		
3XZ	-0.00496 ± 0.00336		
4XX	0.01231 ± 0.00497		
4ZZ	0.00114 ± 0.00737		
4XY	0.01505 ± 0.00949		
5XX	-0.00525 ± 0.00560		
5YY	-0.00992 ± 0.00416		
5ZZ	-0.01044 ± 0.00471		
5XY	0.00193 ± 0.00264		
6XX	-0.03316 ± 0.00436		
6YZ	-0.02194 ± 0.00689		
7XX	0.01057 ± 0.00355		
7YY	-0.01138 ± 0.00378		
7ZZ	0.00263 ± 0.00239		
7YZ	0.00050 ± 0.00188		
7XZ	0.00763 ± 0.00228		
7XY	-0.00068 ± 0.00184		
8XX	-0.00009 ± 0.00018		
8YY	0.02219 ± 0.00796		

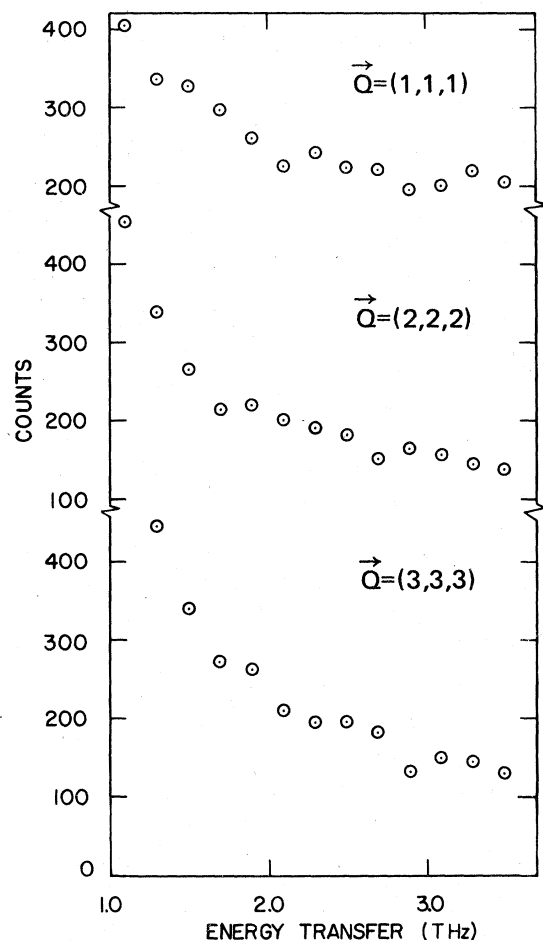


FIG. 4. Typical constant- Q scans covering the energy range in which well-defined peaks were observed in measurements on polycrystalline samples (Refs. 18–20). The average counting time per point in these scans was 15 minutes.

single crystal, however, can be isolated from the one-phonon scattering by performing constant- Q scans at reciprocal-lattice points where the phonon frequencies go to zero. Adopting this procedure we performed a systematic study of the magnetic scattering up to energy transfers of approximately 12 THz. In Fig. 4 are plotted some typical scans covering the energy range in which well-defined peaks were observed in measurements on polycrystalline samples.^{22–24} No indication was found of any discrete magnetic excitations. Thus below approximately 12 THz the energy-transfer range studied in the present experiments there are no well-defined crystal-field excitations. A similar conclusion has been reached by Shapiro *et al.*²⁵ in their systematic study of the $\text{Ce}_{1-x}\text{Th}_x$ system and by Holland-Moritz *et al.*²⁶ in

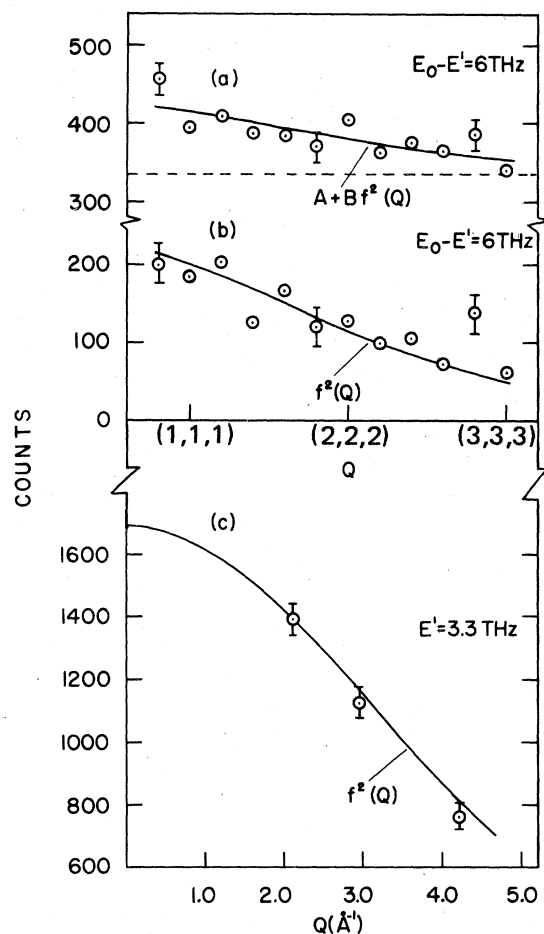


FIG. 5. (a) Constant-energy-transfer scan fitted to a function $A + Bf^2(Q)$. The dashed line indicates the background level. The background determined by this method was found to agree quite well with that obtained experimentally (see text). (b) Constant-energy-transfer scan corrected for background (see text), fitted to $Cf^2(Q)$. (c) Integrated intensity (between 1 and 7 THz) corrected for background vs Q .

their study of CePd_3 . Thus it appears that the absence of any well-defined low-energy crystal-field excitations is characteristic of systems which undergo a transition to a mixed valence state.

In order to deduce information about the spin dynamics of γ -Ce the magnetic scattering must be separated from measured spectra like those shown in Fig. 4. In the present analysis we assumed that the magnetic scattering can be obtained by simply subtracting a constant background from the measured spectra. Under the conditions of the present experiment this is a reasonable assumption since there is no one-phonon contribution to the scattering and the multiphonon component is small (the incoherent nuclear cross section of Ce is approximately 10 mb). To assess the validity of this constant background as-

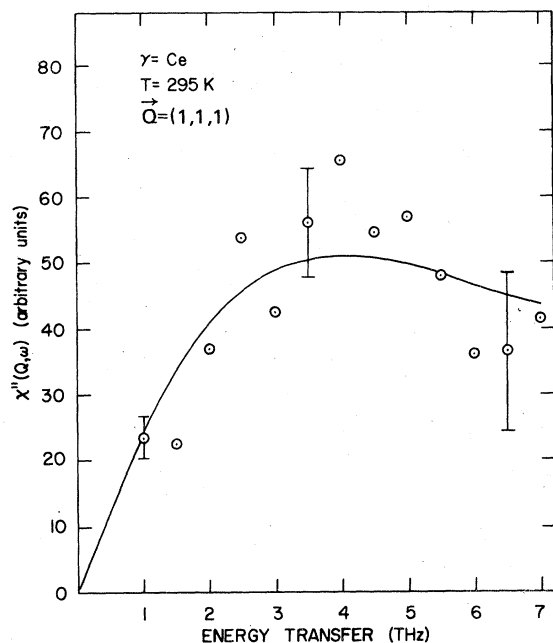


FIG. 6. Energy dependence of the imaginary part $\chi''(Q, \omega)$ of the generalized susceptibility. The solid line is a fit to the relaxational form $\omega\Gamma/(\omega^2 + \Gamma^2)$.

sumption we performed several constant-energy-transfer scans and we found [see Fig. 5(a)] that indeed the data can be adequately fitted to a function of the form $A + Bf^2(Q)$ where A, B are constants and $f(Q)$ is the calculated²⁷ magnetic form factor of Ce^{3+} . Also we estimated the background experimentally by repeating the same constant-energy-transfer scans with the analyzer set 4° off the position for elastic scattering of neutrons with energy E' . We found [see Fig. 5(b)] that the data obtained, by subtracting point by point from a constant-energy-transfer scan the corresponding scan carried out with the analyzer off the position for elastic scattering of neutrons with energy E' , can be well fitted by a function proportional to $f^2(Q)$. In addition the same experimental procedure was used to separate the background from constant Q scans. As it can be seen from Fig. 5(c) where the integrated intensity between 1 and 7 THz is plotted versus Q the data are in good agreement with the square of the calculated magnetic form factor of Ce^{3+} . We therefore conclude that the procedure adopted to separate the magnetic scattering

is adequate and that the magnetic inelastic scattering in $\gamma\text{-Ce}$ follows the $4f$ magnetic form factor of Ce^{3+} . This conclusion is in agreement with the results obtained in a direct measurement⁸ of the magnetic form factor of $\gamma\text{-Ce}$ using polarized neutrons and the results obtained in the study^{25, 28} of the $\text{Ce}_{1-x}\text{Th}_x$ system.

After correcting for the background the constant- Q energy scans provide a measure of the energy dependence of the imaginary part $\chi''(Q, \omega)$ of the generalized susceptibility. Actually the energy dependence of $\chi''(Q, \omega)$ can be obtained by simply dividing the data of a constant- Q energy scan by the population factor $[n(\omega) + 1]$. The $\chi''(Q, \omega)$ obtained from a scan at $\bar{Q} = (1, 1, 1)$ is plotted in Fig. 6. The data presented in Fig. 6 scale quite well [see Fig. 5(c)] with those taken at $\bar{Q} = (2, 2, 2)$. Thus in the range 2.11–4.22 $\text{\AA}^{-1}$ the energy dependence of the imaginary part of the generalized susceptibility is essentially independent of Q . Unfortunately because of the decrease in the signal to background ratio no reliable data were obtained at $\bar{Q} = (3, 3, 3)$. Assuming a relaxational form for the energy dependence of

$$\chi''(Q, \omega) [\chi'' \sim \omega\Gamma/(\omega^2 + \Gamma^2)]$$

a spin-relaxation energy Γ of (4.0 ± 0.5) THz was obtained by fitting (see Fig. 6) to the experimental data. This value for the relaxation energy is somewhat larger than the value (~ 2.5 THz) deduced by Rainford *et al.*²⁴ from their measurements on polycrystalline samples, but comparable to the values obtained by Shapiro *et al.*²⁵ and Holland-Moritz *et al.*²⁶ in the $\text{Ce}_x\text{Th}_{1-x}$ and CePd_3 systems, respectively. In order to obtain a more reliable value for the relaxation energy and to establish whether a relaxational form adequately describes the energy dependence of $\chi''(Q, \omega)$ the measurements should be extended to higher energies. Only limited measurements were performed out to 12 THz since at these energies prohibitively long counting times were necessary to separate the magnetic scattering from the background.

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