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The elastic behaviour of Ce_3S_4 and La_3S_4

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The hydrostatic pressure and temperature dependences of the elastic stiffnesses of the cubic, Th_3P_4 structure compounds Ce_3S_4 and La_3S_4 have been measured using the ultrasonic pulse echo overlap technique. Although Ce_3S_4, unlike La_3S_4 ($T_c = 103$ K), does not undergo a phase transition when its temperature is lowered to 16 K, its elastic stiffnesses $(C_{11}-C_{12})/2$ and C_{11} soften with decreasing temperature (in a similar manner but less markedly than those of La_3S_4); this lattice instability indicates an incipient phase transition. In both compounds the elastic constants increase under pressure: the long-wavelength acoustic-mode Grüneisen parameters are all positive, and the application of pressure does not induce acoustic phonon-mode softening.

1. Introduction

A number of lanthanide chalcogenides with the cubic Th_3P_4 structure ($\bar{4}3d$ (T_d^6)) including La_3S_4 undergo structural phase transformations at low temperature. The nature of the structural instabilities in this series of compounds remains obscure and may come from diverse origins including vacancy and charge ordering [1, 2]. The structural transition temperature in La_3S_4 is sensitive to the number of vacancies, which can be formed in large concentrations without changing the crystal structure. Acoustic phonon-mode softening in La_3S_4 was first observed [3] as a reduction in the elastic stiffness: both $(C_{11}-C_{12})/2$ and C_{11} decreased as the crystal temperature was lowered into the transition region. However, the transition was not observed in the crystal on which those first studies were made. Single crystals of stoichiometric La_3S_4 have now been investigated ultrasonically and pronounced elastic softening observed as the crystal temperature is lowered to that (103 K) at which the cubic to tetragonal transformation takes place [4, 5]. The application of hydrostatic pressure can have pronounced effects on the elastic properties of crystals which undergo phonon-mode softening, and hence can provide useful information concerning lattice stability. Therefore as part of a broad study of mode-softening and its relationship to the phase stability of Th_3P_4 structure compounds, the effects of hydrostatic pressure, in addition to those of temperature, on the velocity of ultrasonic waves propagated in monocrystalline Ce_3S_4 have been measured. The central object is to compare the dependence of the elastic behaviour upon temperature and pressure of this Th_3P_4 structure compound with that in La_3S_4, which is known to undergo a structural phase transition associated with mode-softening.

2. Experimental results and discussion

Stoichiometric single crystals of La_3S_4 and Ce_3S_4 were cut and polished into specimens with pairs of flat [1 0 0] and [1 1 0] faces parallel to better than 10^{-4} radians. The elastic constants and their hydrostatic pressure and temperature dependences were measured by the ultrasonic pulse echo overlap method, using the experimental techniques and assessment of errors described previously [6].

The elastic properties of La_3S_4 and Ce_3S_4 at room temperature are compared in Table I. The elastic stiffness of the stoichiometric specimen of La_3S_4 studied here is somewhat less than that reported previously [3] for a crystal with a higher vacancy concentration. This is consistent with the finding that the stoichiometric crystal undergoes the transition to the tetragonal form at 103 K, while the crystal studied in previous work did not change structure in the temperature region above 80 K over which measurements were made. Hence at room temperature stoichiometric La_3S_4 is closer to the transition and, as acoustic-mode softening is associated with the structural change, is less stiff elastically. The larger anisotropy ratio C_{44}/C' (= 1.24) of the stoichiometric La_3S_4 crystal than that (1.07) measured earlier [3] is also in accord with this viewpoint: C' (= $(C_{11}-C_{12})/2$) softens dramatically (so that C_{44}/C' enlarges) as La_3S_4 gets nearer its transition.

An interesting feature of Ce_3S_4 at room temperature is an almost isotropic elastic behaviour (which is not retained at low temperatures). Measurements of the temperature dependences of the elastic stiffness constants of La_3S_4 and Ce_3S_4 are shown in Figs 1 and 2, respectively. In general the elastic behaviours of both crystals show certain similarities as the temperature is reduced in that (i) the shear stiffness $(C_{11}-C_{12})/2$ decreases dramatically, (ii) C_{11} shows an anomalous decrease but not so substantial as that of $(C_{11}-C_{12})/2$, and (iii) C_{44} increases in the normal way. La_3S_4 undergoes a cubic to tetragonal transformation at 103 K, where abrupt changes occur in the ultrasonic wave velocity temperature dependences. For Ce_3S_4 the anomalous decreases of C_{11} and $(C_{11}-C_{12})/2$ with

TABLE I The elastic properties of Ce_3S_4 and La_3S_4 at room temperature (291 K)

Property	Ce_3S_4	La_3S_4
Density ($kg\,m^{-3}$)	5761	5450
Elastic stiffnesses ($\times 10^{10}\,N\,m^{-2}$)		
C_{11}	11.74 ± 0.02	10.7
C_{12}	5.27 ± 0.05	5.7
C_{44}	3.14 ± 0.02	3.1
$C' = \frac{1}{2}(C_{11}-C_{12})$	3.24 ± 0.06	2.5
Elastic compliances ($\times 10^{-10}\,m^2\,N^{-1}$)		
S_{11}	0.118	0.148
S_{12}	−0.037	−0.052
S_{44}	0.318	0.322
Anisotropy ratio, C_{44}/C'	0.972	1.24
Bulk modulus, B ($\times 10^{10}\,N\,m^{-2}$)	7.43 ± 0.07	7.37
Volume compressibility ($\times 10^{-10}\,m^2\,N^{-1}$)	0.135 ± 0.002	0.136
Hydrostatic pressure derivatives of elastic stiffnesses		
$\partial C_{11}/\partial P$	12.1	9.0
$\partial C_{12}/\partial P$	4.0	5.7
$\partial C_{44}/\partial P$	2.1	3.1
$\partial C'/\partial P$	4.0	1.6
$\partial B/\partial P$	6.7	6.8
Thermodynamic pressure derivatives		
B_{11}	13.6	10.5
B_{12}	3.3	4.9
B_{44}	3.3	4.2
TOEC combinations ($\times 10^{11}\,N\,m^{-2}$)		
$C_{111}+2C_{112}$	−30.3	−23.2
$C_{144}+2C_{166}$	−7.3	−9.3
$C_{123}+2C_{112}$	−7.3	−10.8
Debye temperature, θ_D^{el}	275	
Mean acoustic-mode Grüneisen parameter $\bar{\gamma}^{el}$	3.15	2.85

reducing temperature continue down to the lowest temperature (16 K) at which measurements have been made: lattice instability develops in Ce_3S_4 as the temperature is reduced. Since La_3S_4 shows acoustic-mode softening which is associated with the onset of a phase change, and that in Ce_3S_4 is similar, it seems probable that Ce_3S_4 may undergo a transformation at an even lower temperature than has been reached. La_3S_4 has the unusual property of becoming more com- pressible as the temperature is reduced: $(\partial B^s/\partial T)_{300\,K}$ is $+5 \times 10^7\,N\,m^{-2}\,K^{-1}$. Ce_3S_4 shows the more usual increase of bulk modulus as the temperature is reduced but the effect is marginal, $(\partial B^s/\partial T)_{300\,K}$ being only $-0.7 \times 10^7\,N\,m^{-2}\,K^{-1}$.

The effect of hydrostatic pressure on the "natural" wave velocity W [7] in Ce_3S_4 is linear (Fig. 3) and the gradients for each of the modes which can be propagated along the [1 0 0] and [1 1 0] directions are positive: the acoustic modes all stiffen in the normal manner under pressure. The gradients $[\partial(\varrho_0 W^2)/\partial P]_{p=0}$ have been used to obtain the pressure derivatives $(\partial C_{ij}/\partial P)_{p=0}$ for both compounds (Table I). It is interesting that while both materials soften elastically as the temperature is reduced, they stiffen under pressure.

In general the elastic stiffnesses and their hydrostatic pressure derivatives are quite similar for Ce_3S_4 and La_3S_4. This is the usual pattern found for crystals having the same structure. A notable exception is that $\partial C'/\partial P$ is much smaller for La_3S_4 than it is for Ce_3S_4, reflecting the observation that the shear stiffness C' softens markedly in La_3S_4 as the transition is approached and is consistently smaller than that of Ce_3S_4 even at room temperature.

Knowledge of the compression $V(P)/V_0$ (the ratio of the volume $V(P)$ at a pressure P to that V_0 at zero pressure) is a pre-requisite in interpretation of the effects of hydrostatic pressure on the physical properties of materials. To evaluate this property, the Murnaghan equation of state has been used in the logarithmic form:

$$\ln\left(\frac{V_0}{V(P)}\right) = \frac{1}{B_0'^{T}} \ln\left[B_0'^{T}\left(\frac{P}{B_0^T}\right) + 1\right]$$

where $B_0'^{T}$ is the isothermal hydrostatic pressure derivative of the bulk modulus, B_0. To transform the adiabatic properties measured ultrasonically to the

TABLE II Adiabatic (S) and isothermal (T) properties at 291 K

Property	Ce_3S_4	La_3S_4
Bulk moduli ($N\,m^{-2}$)		
B_0^S	7.43×10^{10}	7.37×10^{10}
B_0^T	7.19×10^{10}	7.13×10^{10}
Temperature derivatives ($N\,m^{-2}\,K^{-1}$)		
$(\partial B_0^S/\partial T)_{P=0}$	-0.7×10^7	$+5 \times 10^7$
$(\partial B_0^T/\partial T)_{P=0}$	-0.68×10^7	$+4.8 \times 10^7$
Pressure derivatives		
$(\partial B_0^S/\partial P)_{P=0}$	6.7	6.8
$(\partial B_0^T/\partial P)_{P=0}$	6.5	5.3

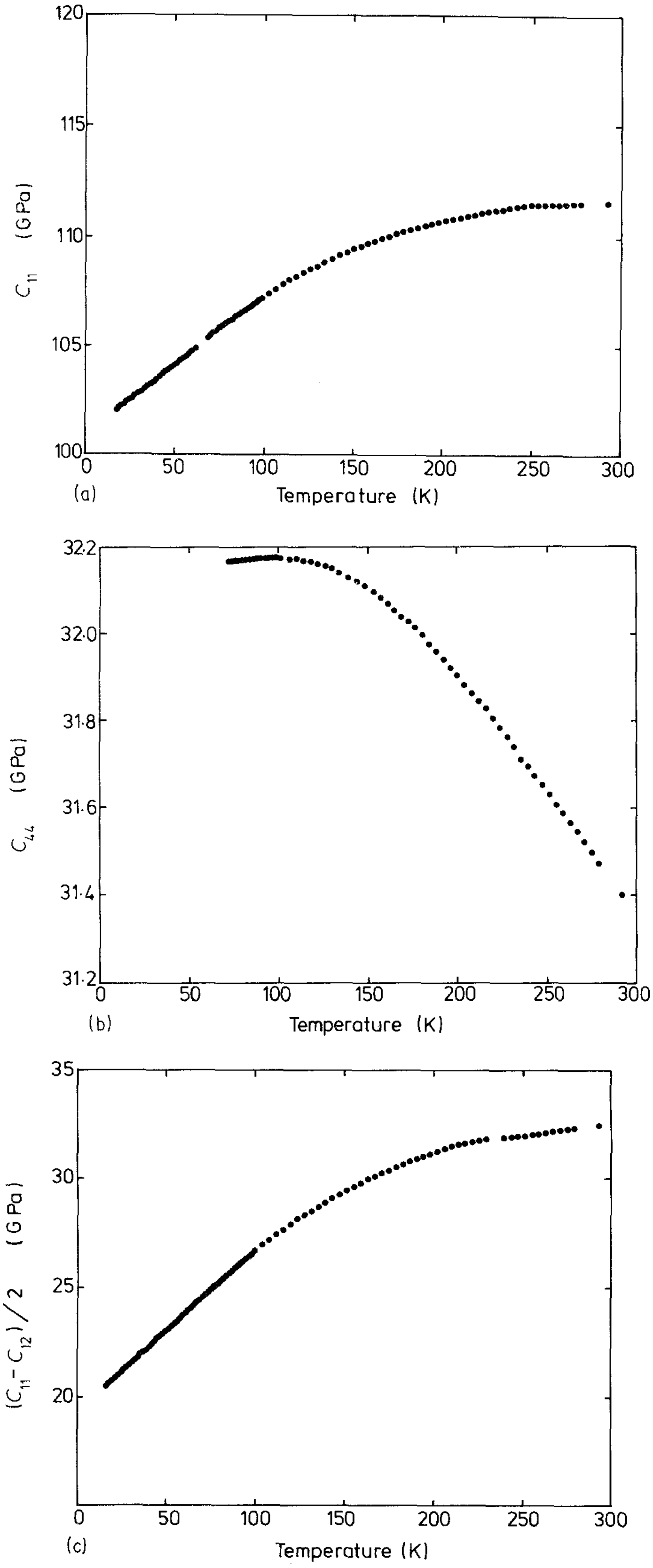

Figure 1 The temperature dependences of the elastic stiffnesses (a) C_{11}, (b) C_{44} and (c) $(C_{11}-C_{12})/2$ of Ce_3S_4.

isothermal quantities required, the following relationships have been employed:

$$B_0^{\mathrm{T}} = B_0^{\mathrm{S}}/(1 + \alpha\gamma T)$$

$$\left(\frac{\partial B_0^{\mathrm{T}}}{\partial T}\right)_{P=0} = \left(\frac{\partial B_0^{\mathrm{S}}}{\partial T}\right)_{P=0} \bigg/ (1 + \alpha\gamma T)$$

$$B_0'^{\mathrm{T}} = B_0'^{\mathrm{S}} + \alpha\gamma T\left(\frac{B_0^{\mathrm{T}}}{B_0^{\mathrm{S}}}\right) \times \left[1 - \frac{2}{\alpha B_0^{\mathrm{T}}}\left(\frac{\partial B_0^{\mathrm{T}}}{\partial T}\right) - 2B_0'^{\mathrm{S}}\right]$$

giving the quantities in Table II. Here the mean acoustic Grüneisen parameter γ^{el} has been used instead of the thermal Grüneisen parameter γ^{th}; however, since the corrections are not large, the error introduced into the compressibility is probably smaller than the experimental error. The compressions of these two isotypic crystals are found to be the same within experimental error (Table III).

The hydrostatic pressure derivatives have been used to obtain the acoustic-mode Grüneisen parameters $\gamma(p, N)$ in the long-wavelength limit as a function of

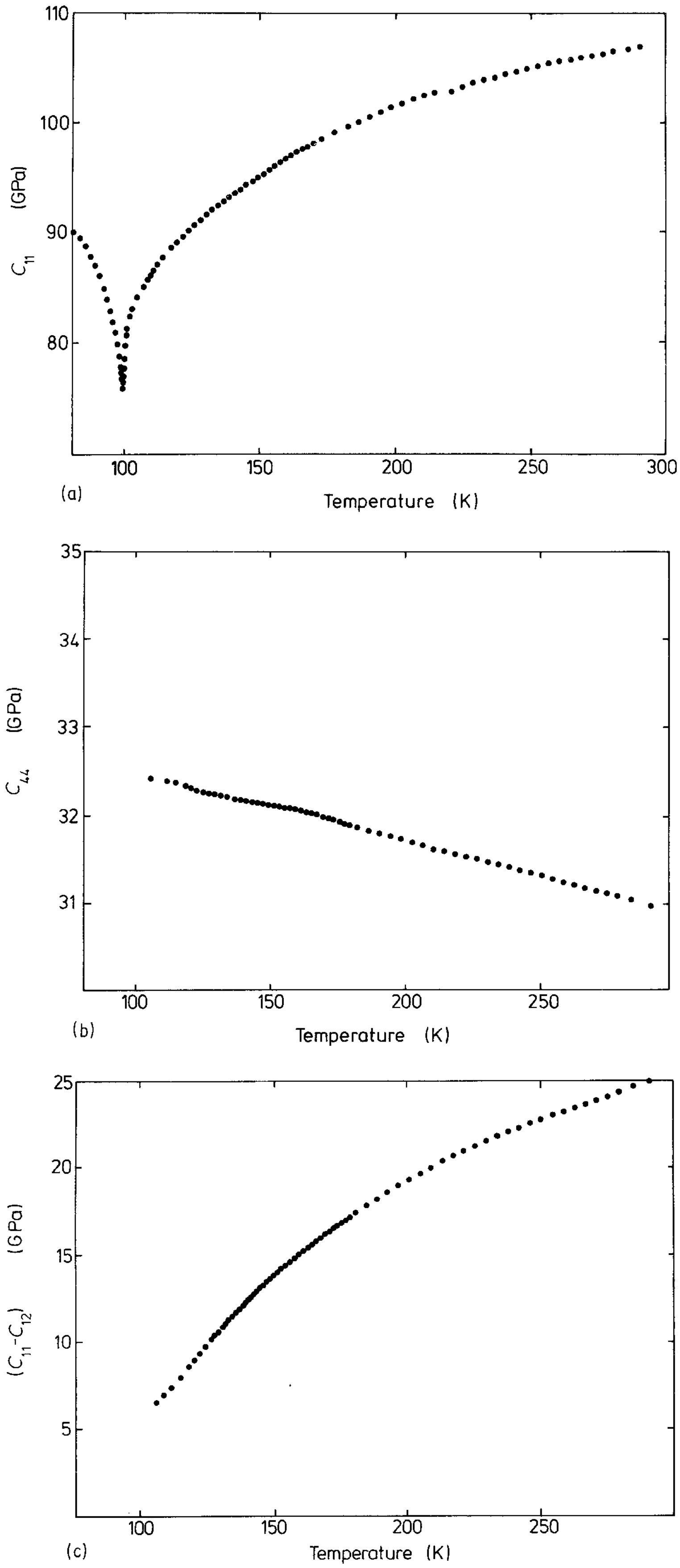

Figure 2 The temperature dependences of the elastic stiffnesses (a) C_{11}, (b) C_{44} and (c) $(C_{11}-C_{12})/2$ of La_3S_4.

the wave propagation direction for Ce_3S_4 (Fig. 4a) and for La_3S_4 (Fig. 4b) in the anisotropic continuum limit [8]. The $\gamma(p, N)$ values are positive for all modes in both crystals. Application of pressure to Ce_3S_4 (as for La_3S_4) leads to an increase in mode frequency (or energy) in the normal way: the non-linear acoustic behaviour of this crystal is normal in this sense, even though the acoustic-mode softening with temperature is so pronounced. To calculate the high-temperature mean acoustic gamma γ^{el} using

$$\bar{\gamma}^{\mathrm{el}}_{\infty} = \frac{1}{3}\int \gamma(p, N)\,\frac{\mathrm{d}\Omega}{4\pi}$$

it has been assumed that at $T \gg \theta_{\mathrm{D}}$ all modes are excited classically, so that the weighting factors become equal: the high-temperature $\bar{\gamma}^{\mathrm{el}}$ has also been calculated

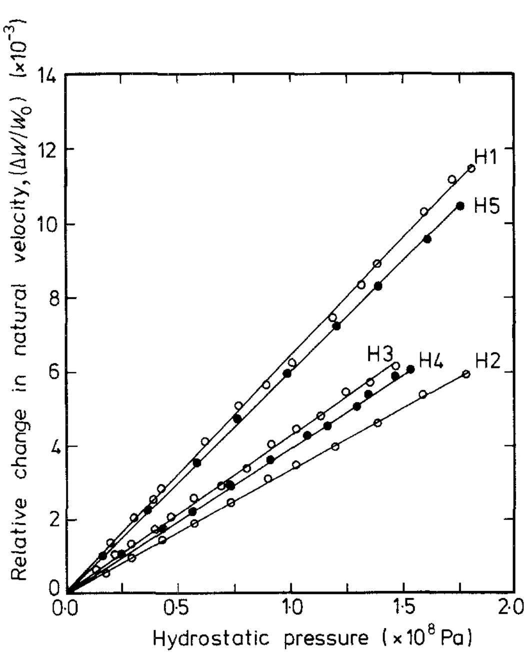

Figure 3 Relative change in natural velocity of ultrasonic waves propagated along the [0 0 1] and [1 1 0] axes in Ce_3S_4 at room temperature. The modes are H1: *N*[0 0 1] *U*[0 0 1], H2: *N*[0 0 1]*U* in (0 0 1) plane, H3: *N*[1 1 0]*U*[1 1 0], H4: *N*[1 1 0]*U*[0 0 1], H5: *N*[1 1 0]*U*[1 1 0], where *N* and *U* are the propagation and polarization vectors, respectively.

as an unweighted mean of $\gamma(p, N)$ and should be valid above the Debye temperature θ_D^{el}. The θ_D^{el} value given for Ce_3S_4 in Table I should be used with some caution as, when long-wavelength acoustic-mode softening occurs in a crystal, the soft-mode contribution to the integral over velocity space and hence to θ_D^{el} is overestimated. Since the acoustic-mode softening with temperature is considerable for La_3S_4, it is not reasonable to attempt an estimate of the elastic Debye temperature, and it is better to use the Debye temperature (224 K [2]) determined from specific heat measurements. $\bar{\gamma}^{el}$ is a measure only of the contribution of the long-wavelength acoustic modes to the vibrational anharmonicity. Optic modes are expected to play a significant role in the thermal Grüneisen parameters γ^{th} of both these crystals at room temperature, but comparison with the values of $\bar{\gamma}^{el}$ obtained here cannot be made as the thermodynamic quantities required to calculate γ^{th} are not yet available.

TABLE III The compressions $V(P)/V_0$ of Ce_3S_4 and La_3S_4 at 291 K.

Pressure (Pa)	$V(P)/V_0$	
	Ce_3S_4	La_3S_4
1×10^9	0.9868	0.9866
2×10^9	0.9748	0.9742
3×10^9	0.9638	0.9627
4×10^9	0.9536	0.9521
5×10^9	0.9442	0.9421
6×10^9	0.9355	0.9328
7×10^9	0.9273	0.9240
8×10^9	0.9197	0.9157
9×10^9	0.9125	0.9079
10×10^9	0.9057	0.9004

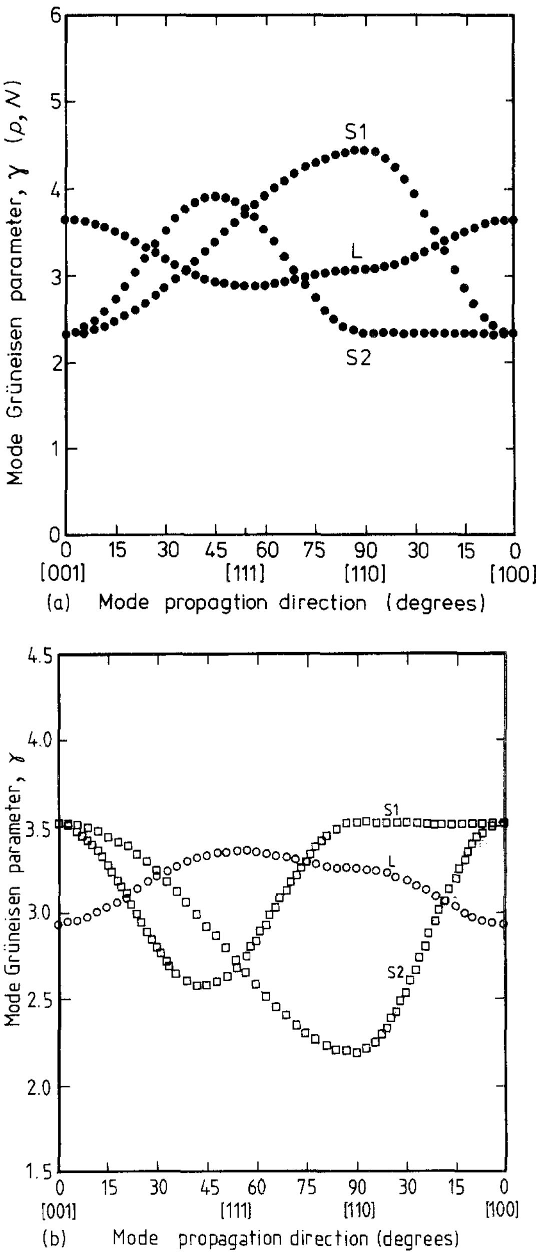

Figure 4 The orientation dependences of the acoustic-mode Grüneisen parameters $\gamma(p, N)$ in the long-wavelength limit for (a) Ce_3S_4, (b) La_3S_4.

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