

Phonon dispersion curves of fcc La

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Large single crystals of fcc La were grown *in situ* and were used to study the lattice dynamics of this phase of La by coherent inelastic neutron scattering. The phonon dispersion curves have been measured along the $[\xi 00]$, $[\xi \xi 0]$, $[\xi \xi \xi]$, and $[0\xi 1]$ symmetry directions at 660 and 1100 K. The $T[\xi \xi \xi]$ branch exhibits anomalous dispersion for $\xi > 0.25$ and, in addition, close to the zone boundary, the phonon frequencies of this branch decrease with decreasing temperature. This soft-mode behavior may be related to the $\beta \rightarrow \alpha$ transformation in La, an assumption supported by recent band-theoretical calculations of the generalized susceptibility of fcc La. At X the frequencies of the $L[\xi 00]$ branch are considerably lower than those of the corresponding branch of γ -Ce; a similar but not as pronounced effect is observed for the frequencies of the $L[\xi \xi \xi]$ branch close to the point L . Since the calculated generalized susceptibility of fcc La exhibits strong peaks at X and L , these anomalies may be due to the renormalization of the phonon frequencies by virtual $f \leftrightarrow d$ transitions to the unoccupied $4f$ level in La. The data were used to evaluate the elastic constants, the phonon density of states, and the lattice specific heat at constant pressure $C_P^{(d)}$.

I. INTRODUCTION

Lanthanum metal exists in three different crystallographic modifications at atmospheric pressure: the high-temperature bcc γ phase which exists between 1191 K (the melting point) and approximately 1138 K, the fcc β phase, which is stable in the 1138–609 K temperature region, and the double hcp (dhcp) α phase, which is the stable phase of La below 609 K. The free-energy difference, however, between the α and β phases is so small that these two phases can coexist below approximately 609 K.

The physical properties of lanthanum are quite unusual and have been the subject of many investigations.^{1–7} Although La is in the same column of the Periodic Table as Y and Sc, it is a relatively high-temperature superconductor (T_c is approximately 5 and 6 K for the dhcp and metastable fcc phase, respectively) and its melting point is much lower than those of these metals. It was found that both the magnetic susceptibility¹ and Knight shift² increase with decreasing temperature and that the thermal expansion coefficient³ is negative at low temperatures. In addition, the coefficient of the electronic specific heat was found to be unusually large.⁴ The pressure dependence of the physical properties of La is also quite unusual. The superconducting transition temperature increases⁵ with

increasing pressure and saturates to a value of nearly 13 K at approximately 200 kbar. Anomalies in the measured pressure derivative of T_c were observed at 25 and 53 kbar and were attributed⁵ to isostructural (fcc \rightarrow fcc) phase transitions. These experimental observations might seem to suggest that the electronic wave functions at the Fermi level contain a significant admixture of $4f$ character, and actually it has been argued⁵ that La must be a “ $4f$ -band” metal. However, tunneling experiments^{6,7} have shown that La is a typical d -electron superconductor, and recent band-theoretical calculations⁸ indicate that the f bands lie approximately 2–2.5 eV above the Fermi level.

As demonstrated by Pickett, Freeman, and Koelling,⁸ the electronic structure of La can explain at least qualitatively the physical properties of La. In particular, it has been suggested⁹ that the low melting point and high superconducting transition temperature of La may be due to the renormalization of the phonon spectrum of La to lower frequencies arising from the virtual $d \leftrightarrow f$ transitions between the valence and the unoccupied $4f$ bands. Such a renormalization of the phonon spectrum may also arise, however, from transitions within d bands near the Fermi energy, a mechanism which was found to play an important role in determining the phonon spectra of transition metals.¹⁰ In addition, even a qualitative understanding of the properties of La

under pressure (in particular the transitions at 25 and 53 kbar) depends on the assumptions made regarding the pressure dependence of the phonon spectrum.⁵ Clearly detailed information regarding the lattice dynamics of La could help in clarifying the physical picture emerging from the theoretical and experimental investigations of the properties of La.

To our knowledge no detailed study of the dispersion curves of the various phases of La has been undertaken, probably because of the difficulty of growing single crystals of sufficient size for coherent inelastic neutron scattering experiments. Recently we were able to grow *in situ* large single crystals of fcc La and in this paper we present the results of measurements of the phonon dispersion curves of this phase of La.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of high-purity La were prepared by arc melting and were encapsulated under helium in thin-wall tantalum crucibles. The tantalum crucibles were mounted on the sample holder of a vacuum neutron-diffraction furnace which was positioned on the sample goniometer of a triple-axis neutron spectrometer. We were able to grow *in situ* large ($2-3 \text{ cm}^3$) single crystals of fcc La by cycling through the fcc \rightarrow bcc transformation temperature ($\sim 865^\circ\text{C}$). In several cases large single crystals were also grown by cycling the polycrystalline samples through the fcc \rightarrow dhcp transformation temperature ($\sim 336^\circ\text{C}$). After a single crystal of sufficient size for the experiments was grown it was oriented and maintained at the desired temperature. Throughout the crystal preparation and the data collection period the vacuum was approximately 10^{-5} Torr. Six different single crystals were used to measure the phonon dispersion curves at 660 and 1100 K. The frequencies of a selected number of phonons were measured on all six crystals used in the experiment and were found to agree to within experimental precision.

The experiments were performed with the use of a triple-axis spectrometer at the 30 MW Oak Ridge Research Reactor (ORR) of the Oak Ridge National Laboratory. Most of the data were collected with the use of the constant \vec{Q} (where \vec{Q} is the neutron scattering vector) method and a constant scattered-neutron energy E' of 3.6 THz. Pyrolytic graphite reflecting from the (002) planes was used as both monochromator and analyzer and a pyrolytic graphite filter was used in the scattered beam to at-

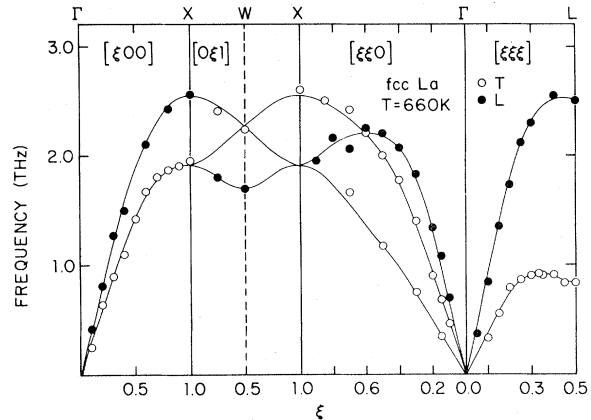


FIG. 1. Experimental dispersion curves of fcc La at 660 K. The solid lines were obtained by fitting the data to an eighth-nearest-neighbor force-constant model.

tenuate higher-order contaminations. The collimation before and after the sample was forty minutes of arc.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The phonon dispersion curves of fcc La were measured along the $[00\xi]$, $[\xi\xi0]$, $[\xi\xi\xi]$, and $[0\xi1]$ symmetry directions at 660 and 1100 K. The data are tabulated in Table I and the dispersion curves at 660 K are plotted in Fig. 1. Several interesting features of the dispersion curves of fcc La can be obtained by comparing them with those^{11,12} of γ -Ce. Lanthanum and cerium have comparable masses, lattice constants, melting points, and similar ($5d6s^2$) outer electronic configurations (of course La, unlike Ce, does not have any localized $4f$ electrons). As a result one would expect the dispersion curves of these elements to be practically identical. In fact, the dispersion curves of fcc La bear a striking resemblance to those^{11,12} of γ -Ce. In particular, note (Fig. 1) (a) the large difference in the slopes of the $T_1[\xi\xi0]$ and $T_2[\xi\xi0]$ branches, which implies that fcc La, like γ -Ce, is very anisotropic with respect to the propagation of elastic waves, and (b) the anomalous dispersion exhibited by the $T[\xi\xi\xi]$ branch for $\xi > 0.25$, which is also the most striking feature of the dispersion curves of γ -Ce.

A detailed comparison, however, reveals a rather important difference between the dispersion curves of fcc La and those of γ -Ce. The phonon frequencies of the $L[\xi00]$ (and $T_2[\xi\xi0]$) branch of fcc La close to the zone boundary (at X) are considerably lower than those of γ -Ce; a similar but not as pro-

TABLE I. Measured phonon frequencies (THz) at 660 and 1100 K of fcc La.

ξ	$T=660$ K	$T=1100$ K	ξ	$T=660$ K	$T=1100$ K
	$L[\xi 00]$			$T[\xi 00]$	
0.1	0.42±0.02		0.1	0.25±0.02	
0.2	0.81±0.02	0.78±0.02	0.2	0.64±0.01	0.58±0.01
0.3	1.27±0.04		0.3	0.89±0.04	
0.4	1.50±0.04	1.50±0.04	0.4	1.10±0.03	1.15±0.03
0.6	2.10±0.04	2.10±0.12	0.5	1.42±0.03	
0.8	2.43±0.05		0.6	1.67±0.04	1.60±0.04
1.0	2.56±0.10		0.7	1.80±0.10	
	$L[\xi\xi 0]$		0.8	1.87±0.03	1.78±0.06
0.1	0.70±0.03	0.60±0.03	0.9	1.90±0.04	
0.15	1.08±0.05		1.0	1.95±0.04	1.85±0.12
0.2	1.34±0.05	1.25±0.03		$T_2[\xi\xi 0]$	
0.3	1.83±0.04	1.80±0.04	0.1	0.46±0.02	0.42±0.01
0.4	2.07±0.03		0.15	0.68±0.03	0.64±0.03
0.5	2.20±0.07	2.15±0.04	0.2	0.90±0.03	0.84±0.02
0.6	2.25±0.06		0.3	1.40±0.03	1.26±0.03
0.7	2.06±0.08	2.00±0.08	0.4	1.78±0.03	
0.8	2.16±0.04		0.5	2.00±0.05	1.90±0.04
0.9	1.95±0.03		0.6	2.20±0.04	
	$T_1[\xi\xi 0]$		0.7	2.42±0.05	2.45±0.05
0.15	0.35±0.03	0.31±0.03	0.85	2.50±0.10	
0.3	0.75±0.03	0.65±0.03	1.0	2.60±0.08	
0.5	1.17±0.03	1.09±0.05		$T[\xi\xi\xi]$	
0.7	1.66±0.10		0.1	0.33±0.02	0.32±0.02
	$L[\xi\xi\xi]$		0.15	0.55±0.02	
0.05	0.37±0.02	0.40±0.04	0.20	0.79±0.04	0.67±0.05
0.10	0.84±0.03	0.92±0.05	0.25	0.86±0.04	
0.15	1.35±0.03	1.29±0.03	0.3	0.90±0.05	0.80±0.07
0.20	1.73±0.05	1.70±0.03	0.333	0.92±0.06	
0.25	2.12±0.05		0.35	0.90±0.04	
0.30	2.30±0.04	2.25±0.10	0.40	0.91±0.06	0.90±0.04
0.40	2.55±0.05		0.45	0.83±0.04	0.95±0.04
0.50	2.50±0.05	2.47±0.04	0.50	0.84±0.03	1.02±0.04
	$\Lambda[0\xi 1]$			$\Pi[0\xi 1]$	
0.25	1.80±0.04		0.25	2.41±0.08	
0.5	1.70±0.04	1.60±0.05	0.5	2.24±0.05	

nounced effect is observed for the frequencies of the $L[\xi\xi\xi]$ branch close to the point L . This is illustrated in Fig. 2 for the $[\xi\xi 0]$ direction. It can be seen (Fig. 2) that for ξ larger than 0.7–0.8 the frequencies of the $T_2[\xi\xi 0]$ branch of fcc La are considerably lower than those of γ -Ce. This is interesting in view of the suggestion⁵ that short-wavelength phonons may be involved in the phase transformations of fcc La at 25 and 53 kbar. Since the calculated⁸ generalized susceptibility $\chi(q)$ of fcc La exhi-

bits strong peaks at X and L , it is tempting to assume that the softening of these modes in La (relative to those of γ -Ce) is due to the renormalization of the phonon frequencies by virtual $f \leftrightarrow d$ transitions to the unoccupied $4f$ level in La. Certainly a detailed analysis of the various contributions to the generalized susceptibility of fcc La is necessary to reach a definitive conclusion.

Another interesting aspect of the dispersion curves of fcc La is the anomalous dispersion ex-

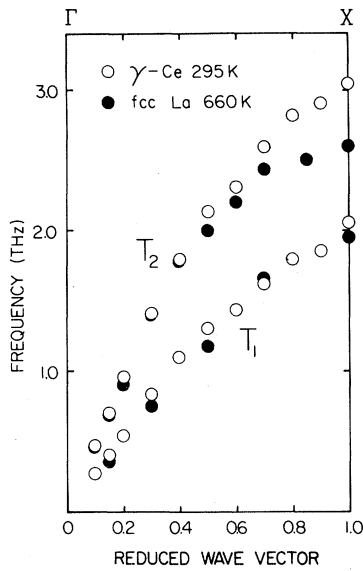


FIG. 2. Comparison of the transverse branches along the $[\xi\xi 0]$ direction of fcc La and γ -Ce. The large difference between the frequencies of the $T_2[\xi\xi 0]$ branches cannot be accounted for by the temperature dependence (Ref. 12) of the γ -Ce phonon frequencies.

hibited by the $T[\xi\xi\xi]$ branch for $\xi > 0.25$. This observation has motivated us to study the temperature dependence of the dispersion curves of fcc La. It can be seen (see Table I) that the temperature dependence of all but the $T[\xi\xi\xi]$ branch is normal in the sense that their frequencies decrease with increasing temperature. The frequencies in the vicinity of the zone boundary of the $T[\xi\xi\xi]$ branch, on the other hand, decrease with decreasing temperature (Fig. 3). The dispersion and temperature dependence exhibited by the $T[\xi\xi\xi]$ branch of fcc La bears a striking resemblance to those of the corresponding branch^{11,12} of γ -Ce. Since both fcc La and γ -Ce undergo a transformation to the dhcp phase (γ -Ce at ~ 260 K and β -La at ~ 610 K), it is natural to assume that the soft-mode behavior of the $T[\xi\xi\xi]$ branch, close to the zone boundary, is related to the fcc \rightarrow dhcp phase transformation in these metals. As a matter of fact, the calculated generalized susceptibility $\chi(q)$ along the $[111]$ direction exhibits⁸ peaks near the (reduced) wave vectors ($q = \frac{1}{4}, \frac{1}{3},$ and $\frac{1}{2}$) of the four transverse waves which are involved in the fcc \rightarrow dhcp phase transformation.

To obtain information about the elastic constants and the phonon spectrum of fcc La and to evaluate the lattice specific heat, the data were analyzed with the use of Born—von Kármán force-constant models (including up to eighth-nearest-neighbor

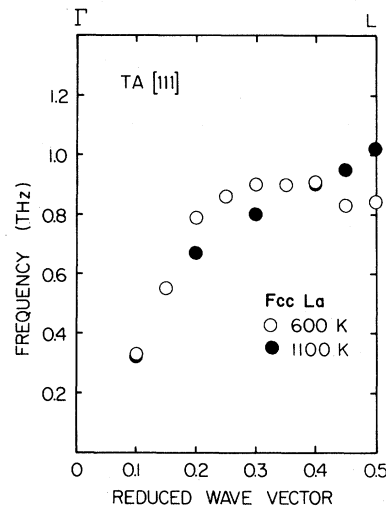


FIG. 3. Temperature dependence of the $TA[\xi\xi\xi]$ branch of fcc La.

atomic force constants). We find that an adequate fit to the experimental data cannot be obtained until at least sixth-nearest-neighbors force constants are included. The force constants obtained by fitting the data to an eighth-nearest-neighbor model are listed in Table II. It can be seen (Fig. 1) that this model provides an adequate description of the measured dispersion curves. The elastic constants evaluated with the use of this model are also includ-

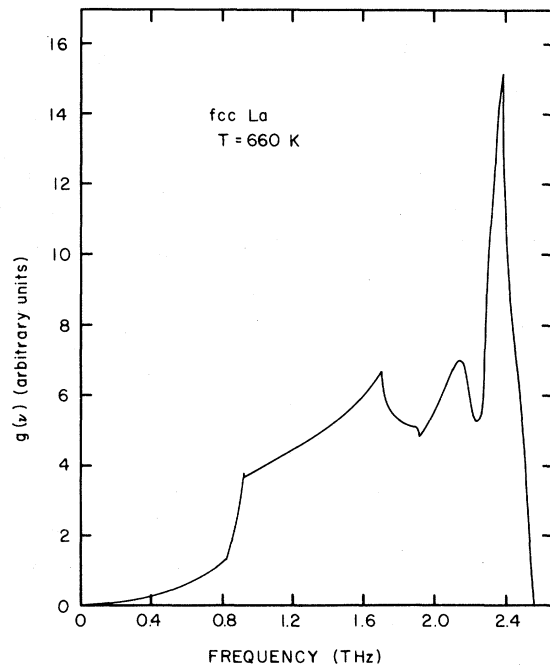


FIG. 4. Phonon density of states $g(\nu)$ of fcc La at 660 K, evaluated with the use of the force constants listed in Table II.

TABLE II. Atomic force constants and elastic constants obtained by fitting the data to an eighth-nearest-neighbor model, with four axially symmetric constraints. The notation is that of Ref. 22.

Atomic force constants (10^4 dyn/cm)		Elastic constants (10^{12} dyn/cm ²)	
1XX	0.362 69±0.020 40	c_{11}	0.2846
1ZZ	-0.016 06±0.029 24	c_{44}	0.1653
1XY	0.404 61±0.024 70	c_{12}	0.2041
2XX	-0.164 02±0.018 72	Constraints	
2YY	0.006 74±0.009 71	8(5ZZ)=9(5YY)-5YX	
3XX	0.046 85±0.025 30	3(7YZ)=7XY	
3YY	0.006 97±0.014 58	8(5XY)=3(5XX)-3(5YY)	
3YZ	-0.013 86±0.009 69	2(7XZ)=7XY	
3XZ	0.009 82±0.006 46		
4XX	0.036 43±0.005 12		
4ZZ	0.000 66±0.009 32		
4XY	0.060 28±0.023 02		
5XX	-0.002 62±0.021 00		
5YY	0.004 23±0.008 95		
5ZZ	0.005 08±0.012 31		
5XY	-0.002 57±0.010 78		
6XX	-0.012 93±0.004 76		
6YZ	-0.006 57±0.012 55		
7XX	-0.000 42±0.010 70		
7YY	-0.010 34±0.012 90		
7ZZ	-0.003 25±0.003 99		
7YZ	-0.001 38±0.002 18		
7XZ	-0.002 08±0.003 27		
7XY	-0.004 15±0.003 08		
8XX	0.000 52±0.009 47		
8YY	0.010 25±0.009 38		

ed in Table II. Notice that the shear moduli c_{44} and $\frac{1}{2}(c_{11}-c_{12})$ differ by almost a factor of 4. This implies that fcc La, like γ -Ce, is very anisotropic with regard to the propagation of elastic waves.

Using the force constants listed in Table II we evaluated the phonon density of states of fcc La at 660 and 1100 K by the method of Raubenheimer and Gilat.¹³ The phonon spectrum obtained with the use of the data at 660 K is shown in Fig. 4. The overall width of the phonon spectrum and the position of the main peak (at ~ 2.4 THz) are in relatively good agreement with the results¹⁴ obtained by Nücker from measurements on polycrystalline samples. Comparison of the phonon spectrum with the results of tunneling measurements^{6,7} could provide information about the energy dependence of the electron-phonon interaction matrix elements. Unfortunately, however, tunneling measurements have been performed to date only on junctions with measured superconducting transition temperatures characteristic of the dhcp phase.^{6,7}

Since the dispersion curves of most solids have been measured only at room temperature, it has

been customary to assume that the phonon density of states obtained from the room-temperature data is independent of temperature. In this harmonic approximation the contribution to the specific heat arising from the temperature dependence of the phonon spectrum is neglected. In many cases, in particular for fcc La which is stable only at relatively high temperatures, this contribution can be significant especially at high temperatures. To evaluate the lattice specific heat, taking into account the temperature dependence of the phonon spectrum, however, one must have both the frequencies and their temperature derivatives at each temperature.¹⁵ Since for fcc La the frequencies have been determined only at two temperatures, an appropriate interpolation scheme is required and we adopted that used first¹⁶ by Miiller and Brockhouse. Since this method has been described in considerable detail in the literature,¹⁶⁻¹⁸ only a brief outline of the calculations will be presented.

Since the measured frequency shifts are quite small, the temperature dependence of the phonon frequencies was assumed to be linear:

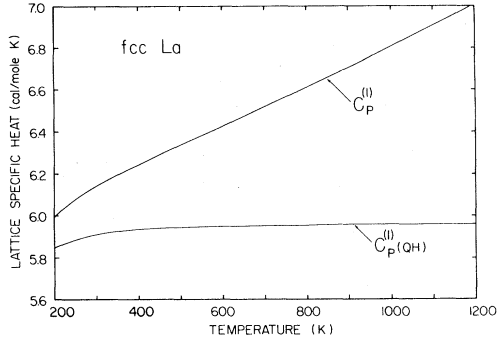


FIG. 5. Temperature dependence of the calculated lattice specific heat at constant pressure $C_p^{(l)}$. $C_p^{(l)}(\text{QH})$ is the quasiharmonic lattice specific heat.

$$\begin{aligned}\omega_\sigma(T) &= \omega_\sigma(T_1) f(T) \\ &= \omega_\sigma(T_1) [1 - A(T - T_1)],\end{aligned}$$

where $T_1 = 660$ K, σ stands for the wave-vector and branch index, and A is determined from the experimental data at 660 and 1100 K. With this assumption the lattice specific heat at constant pressure $C_p^{(l)}$ can be evaluated with the use of the frequency spectrum $g(\omega, T_1)$ at 660 K:

$$C_p^{(l)} = 3Nk \left[1 - T \frac{f'(T)}{f(T)} \right] \int g(\omega, T_1) \frac{x^2}{\sinh^2 x} d\omega, \quad (1)$$

where $x = (\hbar\omega/2kT)f(T)$. The calculated specific heat at constant pressure $C_p^{(l)}$ and the quasiharmonic contribution $C_p^{(l)}(\text{QH})$ [the first term of Eq. (1)] are plotted in Fig. 5. The equivalent Debye temperature Θ_D as a function of temperature obtained by equating the quasiharmonic contribution to the Debye expression of the specific heat is plotted in Fig. 6.

The temperature dependence of Θ_D at low temperature (Fig. 6) obtained in the present analysis is in quite good agreement with that obtained by Johnson and Finnemore from low-temperature specific-heat measurements.⁴ In particular, the 0-K Debye temperature (133.7 K) obtained in the present work is to be compared with that (140 K) obtained by Johnson and Finnemore.⁴ The agreement is quite good in view of the approximations involved in the analysis and the possible presence of some amount of the dhcp phase (which has a higher Debye temperature than the fcc phase) in the samples used for the low-temperature heat-capacity measurements.

At high temperatures there is a significant contri-

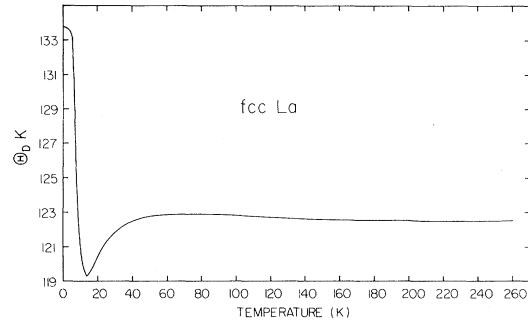


FIG. 6. Temperature dependence of the effective Debye temperature of fcc La.

bution (Fig. 5) to the lattice specific heat arising from the temperature dependence of the phonon frequencies. Unfortunately, no band calculations of the electronic contribution are presently available to allow detailed comparison of the results of the present analysis with measurements of the total specific heat C_p of fcc La. At high temperatures, however, the bare electronic density of states can be used to estimate the electronic contribution, since the electron-phonon mass enhancement is negligible¹⁹ at temperatures higher than about twice the Debye temperature. Using the electronic density of states $N(E_F)$ evaluated by Pickett, Freeman, and Koelling⁸ we obtain an appropriate coefficient for the electronic specific heat of 4.76 mJ/mole K^2 . Using this value we estimate an electronic contribution to the specific heat of 1.14 cal/mole K at 1000 K. Using this estimate we obtain a total specific heat at 1000 K of 7.9 cal/mole K , a value in good agreement with measurements of the total specific heat of fcc La at high temperatures.^{20,21} Thus it does not seem that vacancy formation, as has been suggested,²¹ contributes significantly to the high-temperature specific heat of fcc La.

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