Sound Velocity and its Temperature Coefficient of Liquid La, Ce and Pr

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ABSTRACT

The sound velocity and its temperature coefficient in liquid La, Ce and Pr have been estimated using an improved Rosenfeld's approach. The temperature coefficient of the sound velocity in liquid Ce is positive, which is quite different from that of La and Pr. To reproduce the positive temperature coefficient of the sound velocity in liquid Ce, it is necessary to take into account the effect caused by electrons. The present calculations based on Ascarelli's approach suggest an increase in delocalization of the 4f electrons with temperature in the liquid state of Ce. This is consistent with the results given by McAlister and Crozier

Keywords: Sound velocity, Temperature coefficient, Light rare earth metals

1. INTRODUCTION

The velocity of sound in liquid metals is one of the most basic thermodynamic properties. Although there is a pioneering work of Ascarelli /1/, information on the sound velocity of liquid rare earth metals has been very limited, because of their chemical reactivity and higher melting point. In nearly all liquid metals, the temperature coefficient of the sound velocity is negative, which is interpreted as a loosening of the structure with increasing temperature. Liquid La and Pr are included in this category. However, liquid Ce represents a very different case, as seen from a decrease in adiabatic compressibility with temperature/2/. Such anomalous behavior of the sound velocity and compressibility of liquid Ce attracts our attention.

The purpose of this work is to investigate the sound velocity and its temperature coefficient in liquid La, Ce and Pr by means of an improved Rosenfeld's approach /3,4/ based on the hard-sphere model. Next, we examine the role of electrons so as to produce the positive temperature coefficient of the sound velocity in liquid Ce using Ascarelli's approach /1,5/. The calculated results are compared with the experimental results of McAlister and Crozier /2/. Discussion of the effective valence will be made using free electron theory.

2. MODEL THEORIES

2.1 Improved Rosenfeld's Approach (Hard-Sphere Model)

The velocity of sound, V_S, is defined by /3,4/

$$MV_S^2 = (\partial p/\partial n)_S = (\partial p/\partial n)_T + T[(\partial p/\partial T)_V]^2/(n^2 C_V/N), \quad (1)$$

where M is the mass of an ion, V is the volume, T is the

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absolute temperature, N is the total number of ions and n is the number density of ions. p and S denote the pressure and the entropy, respectively. C_V stands for the heat capacity at constant volume which is purely kinetic, $C_V = (3/2)Nk_B$ for a system of hard spheres, with k_B being the Boltzmann constant. Then the velocity of sound , V_S , is given by

$$V_S = s(\xi)^{new}(k_B T/M)^{1/2}, \quad (2)$$

where ξ is the packing fraction defined by

$$\xi = \pi n \sigma^3/6, \quad (3)$$

and

$$s(\xi)^{new} = (p(\xi) + \xi p'(\xi) + (2/3)(3\xi p'(\xi) (\partial \ln \sigma/\partial \ln T)_V + p(\xi))^2)^{1/2}. \quad (4)$$

In Eq.(3), σ is a hard-sphere diameter. $p(\xi)$ and $p'(\xi)$ are given by the Carnahan-Starling expression /6/ as

$$p(\xi) = (1+\xi+\xi^2-\xi^3)/(1-\xi)^3 , \quad (5)$$

and

$$p'(\xi) \equiv dp(\xi)/d\xi = 2(2+2\xi-\xi^2)/(1-\xi)^4 \quad (6)$$

The temperature dependence of σ is estimated by the use of the empirical formula proposed by Protopapas et al. /7/:

$$\sigma(T) = 1.126\ \sigma_m [1 - 0.112(T/T_m)^{1/2}], \quad (7)$$

in which σ_m is the value of σ at the melting point, T_m , and

$$(\partial \ln \sigma/\partial \ln T)_V = - (0.056\sigma_0/\sigma(T))(T/T_m)^{1/2} , \quad (8)$$

in which σ_0 is given by $\sigma_0 = 1.0878(n_m)^{-1/3}$ with n_m being the number density of ions at T_m. We can extract the value of ξ through the excess entropy, as explained in Refs. /8,9/, which is 0.463 for liquid metals near the melting point. With $\xi = 0.463$, as shown in Ref. /9/, we can reasonably well account for the structural, thermodynamic, transport, and surface properties of liquid metals near the melting point on the basis of a hard-sphere model.

2.2 Ascarelli's Approach

Ascarelli /1/ used a model of hard spheres immersed in a uniform (without gradients) potential and the total binding energy E (per atom) of a metal can be conveniently separated into the following two terms /10,11/, when calculated to the second order in a perturbation scheme,

$$NE = NE_0 + (1/2)\sum_{i \neq j} V(r_{ij}) , \quad (9)$$

where E_0 is a quantity dependent on the volume of the system but independent of the positions of the ions, and $V(r)$ is an effective pair interaction energy. As the structure of liquid metals is largely determined by the short-range repulsive forces, we approximate $V(r)$ by a simple hard-sphere potential. The total binding energy E of a metal is completely determined by E_0, which while supplying the cohesion to the hard-sphere system, does not change the equilibrium configurations of the ions.

We now approximate E_0 by the sum of two terms : the kinetic energy of a free-electron gas, and a negative energy term, $-B/V^{1/3}$, which contains the energy of the interaction of valence electrons with the ion, and the energy of the interaction of valence electrons with themselves. B is a constant to be determined by considering the pressure of the system to be zero at the melting point. For simplicity in the following, we write B in terms of a dimensionless constant A defined by

$$B = 3A(V_m)^{1/3}k_B T_m. \quad (10)$$

We then write the pressure as /1/

$$pV/(Nk_B T) = p/(n k_B T) = (2/5)(zE_F/(k_B T)) - A(V_m/V)^{1/3}(k_B T_m/(k_B T)) + p_h V/(Nk_B T), \quad (11)$$

where z is the number of valence electrons per atom(valency), V_m is the volume at the melting point and E_F is the Fermi energy. p_h is the pressure of the hard-sphere system, which is well described by the Carnahan-Starling equation of states as given by Eq. (5).

Now assuming the total pressure $pV/(Nk_BT) = 0$ under normal condition at the melting point in Eq.(11), we find

$$A = p_h/(n_m k_B T_m) + (2/5)(zE_F(T_m)/(k_B T_m))$$
$$=(1 + \xi_m + \xi_m^2 - \xi_m^3)/(1 - \xi_m)^3$$
$$+ (2/5)(zE_F(T_m)/(k_B T_m)), \quad (12)$$

where ξ_m is the packing fraction at the melting point which is 0.463 as mentioned in the section *2.1*. A is a constant which is independent of n and T in the following calculations. We can then write, after a simple differentiation of the pressure with respect to the volume and the temperature,

$$(\partial p/\partial n)_T/(k_B T) = (2/3)(zE_F/(k_B T))$$
$$-(4/3)A(n/n_m)^{1/3}(k_B T_m/(k_B T)) + p(\xi) + \xi p'(\xi), \quad (13)$$

$$(\partial p/\partial T)_V/(n k_B) = p(\xi)$$
$$+ 3\xi p'(\xi)(\partial \ln\sigma/\partial \ln T)_V . \quad (14)$$

In the derivation of Eq.(13), we assumed $(\partial\sigma/\partial n)_T = 0$. Then, substituting Eqs. (13) and (14) into Eq.(1), we obtain

$$V_S/(k_B T/M)^{1/2} = [(2/3)(zE_F/(k_B T))$$
$$-(4/3)A(n/n_m)^{1/3}(k_B T_m/(k_B T))$$
$$+p(\xi) + \xi p'(\xi) + (2/3)\{p(\xi)$$
$$+ 3\xi p'(\xi)(\partial \ln\sigma/\partial \ln T)_V\}^2]^{1/2}. \quad (15)$$

There are four differences between Ascarelli's original approach and the present one, which are summarized as follows:

(1) The different values of ξ_m were used (0.45 by Ascarelli, while 0.463 in this work),
(2) A different equation of states was used (Ascarelli used Reiss et al.'s /1/ but we used the Carnahan-Starling equation of states),
(3) The temperature dependence of σ employed in this work differs from Ascarelli's approach,
(4) We did not assume that $Cp/Cv = 1.15$ for all metals employed by Ascarelli.

3. RESULTS

The value of σ at T_m is extracted from Eq.(3) by using $\xi_m = 0.463$ and the measured density. Then, the temperature dependences of σ and $(\partial \ln\sigma/\partial \ln T)_V$ are estimated by Eqs.(7) and (8). The values of ξ at elevated temperatures are determined from Eq.(3) using Eq.(7) and the experimental density data.

Using Eq.(2), the sound velocity and its temperature dependence were estimated for liquid La, Ce and Pr. The results are summarized in **Tables 1, 2 and 3**, together with the input and experimental data. The calculated values of V_S are found to be in reasonable agreement with the experimental data. A comparison of the calculated values with the experimental data is demonstrated in **Figs. 1 and 2.**

The sound velocity, V_S, is described by the improved approach of Rosenfeld /3/, although there is a rather large difference in the temperature dependence. Particularly, the calculated values do not explain the positive temperature dependence of V_S for liquid Ce. This strongly suggests that the effect caused by electrons should be included in the case of Ce using Ascarelli's approach. As an effective valence, z_{eff}, (i.e.,the effective number of free electrons per atom) of liquid Ce, we employed 1.15 ,which was determined from a plasma parameter Γ of the classical one-component plasma model (see Ref./12 / in detail). The results are shown in **Table 4.** As seen from the table, the present theoretical value at the melting point agrees well with the experimental one. However, no improvement can be obtained for the positive temperature dependence. Therefore, we again estimated the sound velocity values of liquid Ce by introducing the variation of the effective valence with increasing temperature.

The results are displayed in Fig. 2 for comparison. When considering the variation of the effective valence as a function of temperature, the positive temperature coefficient of the sound velocity for liquid Ce can be reproduced in the framework of Ascarelli's approach.

4. DISCUSSION

From Eq.(1), the sound velocity V_S is given by

$$V_S^2 = (1/M)(\partial p/\partial n)_S = (1/Mn)(1/\kappa_S), \quad (16)$$

where κ_S is the adiabatic compressibility. Then, the temperature derivative of κ_S at constant pressure is given by

Table 1

Input density data and sound velocity results of liquid La (improved Rosenfeld's approach). Experimental data are taken from Ref./ 2 /, but the thermal expansion coefficient is taken from Ref./13/.

T (K)	ρ (10^3kgm^{-3})	α_P (10^{-4}K^{-1})	ξ	$(\partial \ln\sigma/\partial \ln T)_V$	Vs^{calc} (ms^{-1})	Vs^{expt} (ms^{-1})	Vs^{calc}/Vs^{expt}
1193 (T_m)	5.96	0.40	0.463	-0.063	1960	2023	0.97
1240	5.95		0.459	-0.065	1948	2019	0.96
1273	5.94		0.456	-0.066	1942	2016	0.96
1320	5.93		0.452	-0.067	1933	2013	0.96
1373	5.92		0.447	-0.069	1923	2008	0.96

Table 2

Input density data and sound velocity results of liquid Ce (improved Rosenfeld's approach). Experimental data and the thermal expansion coefficient are taken from Ref./ 2 /.

T (K)	ρ (10^3kgm^{-3})	α_P (10^{-4}K^{-1})	ξ	$(\partial \ln\sigma/\partial \ln T)_V$	Vs^{calc} (ms^{-1})	Vs^{expt} (ms^{-1})	Vs^{calc}/Vs^{expt}
1068 (T_m)	6.69	0.354	0.463	-0.063	1846	1693	1.09
1143	6.67		0.455	-0.066	1829	1706	1.07
1250	6.65		0.446	-0.069	1815	1725	1.05
1323	6.63		0.439	-0.072	1801	1738	1.04

Table 3

Input density data and sound velocity results of liquid Pr (improved Rosenfeld's approach). Experimental data are taken from Ref./ 2 /, but the thermal expansion coefficient is taken from Ref./13/.

T (K)	ρ (10^3kgm^{-3})	α_P (10^{-4}K^{-1})	ξ	$(\partial \ln\sigma/\partial \ln T)_V$	Vs^{calc} (ms^{-1})	Vs^{expt} (ms^{-1})	Vs^{calc}/Vs^{expt}
1208 (T_m)	6.61	0.38	0.463	-0.063	1958	1925	1.02
1240	6.60		0.460	-0.064	1951	1922	1.02
1273	6.59		0.457	-0.065	1945	1920	1.01
1320	6.58		0.453	-0.067	1937	1916	1.01
1373	6.57		0.449	-0.068	1928	1911	1.01

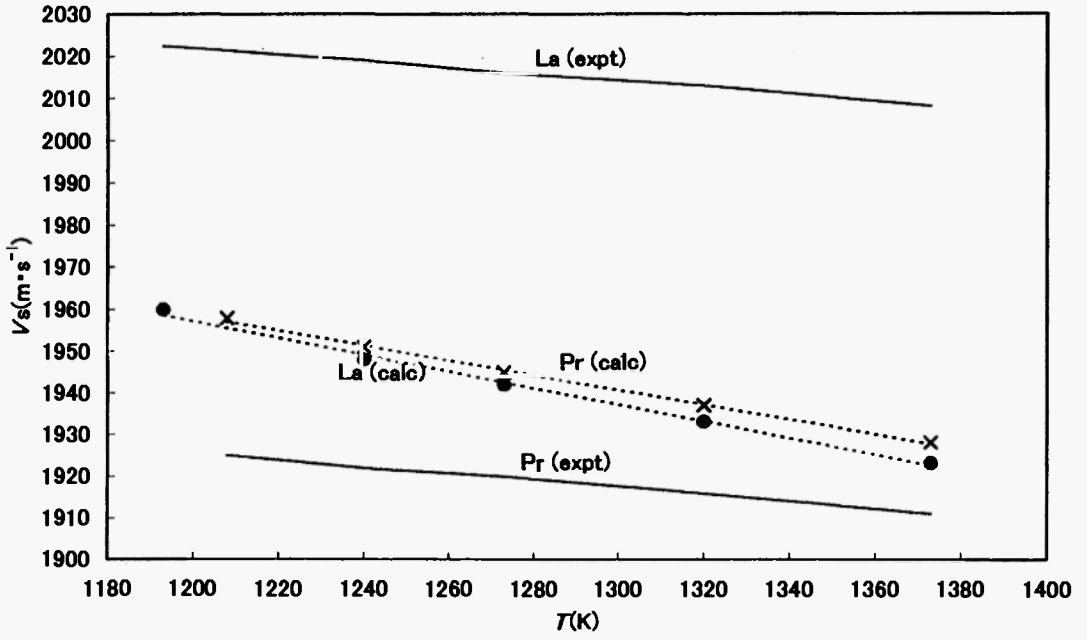

Fig. 1: Comparison between theory and experiment for the sound velocity in liquid La and Pr. The solid lines denote the experimental data. The broken lines denote the calculated results. The experimental temperature coefficient of the sound velocity /2/ $(\partial Vs/\partial T)_p$ is –0.078±0.004 $ms^{-1}K^{-1}$ for liquid La and – 0.084±0.007 $ms^{-1}K^{-1}$ for liquid Pr , respectively.

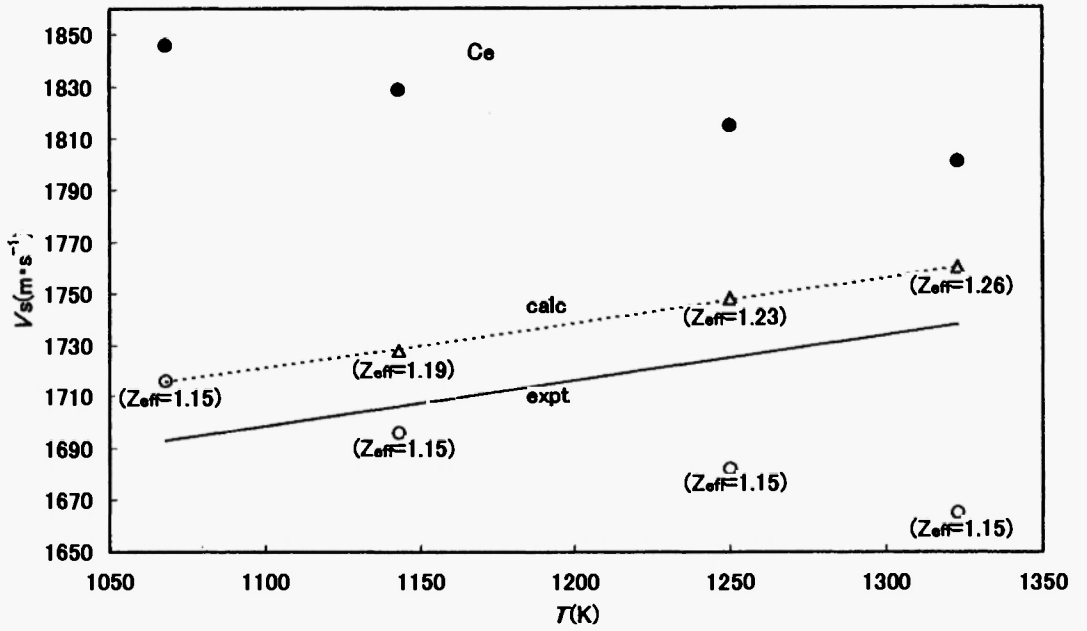

Fig. 2: Comparison between theory and experiment for the sound velocity in liquid Ce. The solid lines denote the experimental data. •:improved Rosenfeld's approach, o: Ascarelli's approach (z_{eff} = 1.15; fixed), Δ Ascarelli's approach (z_{eff} ; varied). The experimental temperature coefficient of the sound velocity /2/ $(\partial Vs/\partial T)_p$ is + 0.177±0.005 $ms^{-1}K^{-1}$. The calculated temperature coefficient of the sound velocity is + 0.175±0.005 $ms^{-1}K^{-1}$.

Table 4

Input density data and sound velocity results of liquid Ce (Ascarelli's approach). Experimental data are taken from Ref./ 2 /. Z_{eff} is the effective valence. The value of 1.15 is taken from Ref./12/. The values given by parenthesis are the calculated results when considering the variation of the effective valence with temperature.

T (K)	ξ	$(\partial \ln\sigma/\partial \ln T)_V$	z_{eff}	A	V_S^{calc} (ms^{-1})	V_S^{expt} (ms^{-1})	V_S^{calc}/V_S^{expt}
1068 (T_m)	0.463	-0.063	1.15	28.966	1716	1693	1.01
1143	0.455	-0.066	1.15		1696	1706	0.99
			(1.19)		(1728)		(1.01)
1250	0.446	-0.069	1.15		1682	1725	0.98
			(1.23)		(1748)		(1.01)
1323	0.439	-0.072	1.15		1665	1738	0.96
			(1.26)		(1760)		(1.01)

$$(1/\kappa_S)(\partial \kappa_S/\partial T)_P = (1/\kappa_T)(\partial \kappa_T/\partial T)_P , \quad (17)$$

where κ_T is the isothermal compressibility and the ratio of the specific heats is assumed constant over the range of temperature of interest. We will try to explain the positive temperature coefficient of V_S in liquid Ce using the framework of the free electron theory /1/. For a non-interacting free electron gas, κ_T is given by /14/

$$\kappa_T = 3/(2n\, z\, E_F) \quad (18)$$

where z is the valence and E_F is the Fermi energy

$$E_F = (h^2/(8\pi^2 m))(3\pi^2 zn)^{2/3} , \quad (19)$$

where m is the mass of an electron and h is the Planck constant. From Eq.(19), we obtain

$$(\partial E_F/\partial T)_P = (2/3)\, E_F\, ((1/z)(\partial z/\partial T)_P - \alpha_P), \quad (20)$$

and

$$(\partial (nzE_F)^{-1}/\partial T)_P = -5\,((\partial z/\partial T)_P - z\alpha_P)/(3nz^2E_F), \quad (21)$$

where α_P is the thermal expansion coefficient defined by

$$\alpha_P = (1/V)(\partial V/\partial T)_P = -(1/n)(\partial n/\partial T)_P . \quad (22)$$

Therefore, the temperature derivative of κ_S at constant pressure is given by

$$(1/\kappa_S)(\partial \kappa_S/\partial T)_P = -5\,((\partial z/\partial T)_P - z\alpha_P)/(3z) . \quad (23)$$

On the other hand, we obtain from Eq. (16)

$$(1/\kappa_S)(\partial \kappa_S/\partial T)_P = \alpha_P + 2\beta_P , \quad (24)$$

where β_P is defined by

$$\beta_P \equiv -(1/V_S)(\partial V_S/\partial T)_P . \quad (25)$$

Since Eq. (23) is equal to Eq. (24), the following relation can be obtained,

$$-5\,((\partial z/\partial T)_P - z\alpha_P)/(3z) = \alpha_P + 2\beta_P , \quad (26)$$

and

$$\beta_P = (1/3)\alpha_P - (5/6)(1/z)\,(\partial z/\partial T)_P . \quad (27)$$

If $(\partial V_S/\partial T)_P > 0$, $\beta_P < 0$ from Eq. (25). Then, from Eq. (27),

$$\alpha_P < (5/2)(1/z)\,(\partial z/\partial T)_P . \quad (28)$$

Since $\alpha_P > 0$, $(\partial z/\partial T)_P > 0$ from Eq. (28). Therefore, if $(\partial V_S/\partial T)_P$ is positive, then $(\partial z/\partial T)_P$ must be positive.

This enables us to provide an origin for the anomalous behavior of the sound velocity of liquid Ce first reported by McAlister and Crozier /2/.

On the other hand, $(\partial V_S/\partial T)_P$ is negative for liquid La and Pr and then β_P is positive, so that,

$$\alpha_P > (5/2)(1/z)(\partial z/\partial T)_P. \quad (29)$$

From Eq. (29), the relation of $(\partial z/\partial T)_P = 0$ is suggested. This means the valence for liquid La and Pr is found to be constant, irrespective of temperature.

5. CONCLUSION

The sound velocity and its temperature dependence in liquid La and Pr are reasonably well explained by the improved Rosenfeld's approach based on the hard-sphere model. However, in order to reproduce the positive temperature coefficient of the sound velocity in liquid Ce, the effective valence given in Ascarelli's approach .must be introduced as a function of temperature. The present work for liquid Ce clearly supports the variation of the effective valence with temperature, resulting from the promotion of the 4f electrons into the 5d conduction band. Such an idea was first suggested by McAlister and Crozier /2/ to explain the experimental data.

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