[1]The Ratio of Specific Heats of Some Liquid Rare Earth Metals

T. Arai, I. Yokoyama and Y. Waseda [2]

Department of Mathematics and Physics,
National Defense Academy,
Yokosuka 239, Japan

[2]*Institute for Advanced Materials Processing,*
Tohoku University, Sendai 980, Japan

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Introduction

Recently Yokoyama and Naito /1/ reported that the collective coordinate method using the temperature derivative of the one-component plasma structure factor is capable of describing specific heats C_v and C_p, including the ratio of specific heats, of liquid 3d transition metals near the melting points. In the course of work on liquid rare earth metals, however, we encountered a puzzling problem regarding the ratio of specific heats, γ, of liquid La, Ce, Pr and Nd. In the following Table we show this using the results obtained by Yokoyama et al. /2/. We can deduce from the fourth column in Table 1 that the γ of these metals is larger than 1.1. On the other hand, we can evaluate γ using the well-known thermodynamic relation:

$$\gamma = C_P/C_V = 1 + \frac{\alpha^2 V T}{\chi_S C_P} \qquad (1)$$

where α denotes the thermal expansion coefficient, V the volume, T the absolute temperature, χ_S the adiabatic compressibility and C_p the specific heat at constant pressure. We employ the values of χ_S obtained by Yokoyama et al. /2/ and use the experimental values of α and C_p. The experimental values of C_p are due to work done by Hultgren et al. /4/ and those of α, available only for liquid La, Ce, Pr and Nd, are taken from the recent compilation by Iida and Guthrie /5/. The calculated values of γ from Eq. 1 and listed in the last column in Table 1 are smaller than 1.1 for liquid La, Ce and Pr.

Discussion

The purpose of the present communication is to comment on this puzzling problem in terms of the collective coordinate method successfully applied to liquid 3d transition metals. According to this method, the specific heats C_v and C_p are calculated by the following formulae:

$$C_V = C_V^0 + C_V^{1'} + C_V^{1''} + C_V^{elec} \qquad (2)$$

where

$$\frac{C_V^2}{Nk_B} = \frac{9}{2} J_0 \left\{ 1 + \left(\frac{\partial \ln a(k/k_0)}{\partial \ln T} \right)_V \right\} (k/k_0)^2 d(k/k_0)$$

TABLE 1
Ratio of specific heats γ of liquid La, Ce, Pr and Nd. ρ is the mass density.

	T(K)	ρ(g.cm^{-3})	γ	
			a	b
La	1243	5.95	1.11	1.03
Ce	1143	6.67	1.13	1.02
Pr	1223	6.61	1.12	1.02
Nd	1323	6.92	1.14	1.12

a calculated from $\chi_T^{expt}/\chi_S^{calc}$ where the experimental isothermal compressibility χ_T^{expt} are due to Waseda and Ueno /3/ and the calculated adiabatic compressibility χ_S^{calc} are due to Yokoyama et al. /2/.

b calculated from Eq. 1 using the experimental data /4-5/.

$$\frac{C_V^{1'}}{Nk_B}=\frac{81}{32}\int_0^1\frac{d(k/k_0)}{(k/k_0)}\int_0^1\frac{d(k'/k_0)}{(k'/k_0)} \tag{4}$$
$$\times\left[\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}^2\eta_1-2\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}\eta_3+\eta_5\right]$$

$$\eta_n=\int_{\frac{|k-k'|}{k_0}}^{\frac{k+k'}{k_0}}\left(\frac{\partial\ln a(q/k_0)}{\partial\ln T}\right)_V a\left(\frac{q}{k_0}\right)\left(\frac{q}{k_0}\right)^n d\left(\frac{q}{k_0}\right)$$

n=1, 3, 5

$$\frac{C_V^{1''}}{Nk_B}=\frac{81}{32}\int_0^1\frac{d(k/k_0)}{(k/k_0)}\int_0^1\frac{d(k'/k_0)}{(k'/k_0)} \tag{5}$$
$$\times\left[\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}^2\chi_1-2\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}\chi_3+\chi_5\right]$$

$$\chi_n=\int_{\frac{|k-k'|}{k_0}}^{\frac{k+k'}{k_0}}\left[\left(\frac{\partial\ln a(q/k_0)}{\partial\ln T}\right)_V^2+\left(\frac{\partial^2\ln a(q/k_0)}{\partial(\ln T)^2}\right)_V\right]$$
$$a\left(\frac{q}{k_0}\right)\left(\frac{q}{k_0}\right)^n d\left(\frac{q}{k_0}\right)$$

n=1, 3, 5

and

$$\frac{C_V^{elec}}{Nk_B}=\frac{S_{elec}}{Nk_B}. \tag{6}$$

Here C_V^0 describes the independent-phonon contribution (i.e., harmonic term) and $C_V^{1'}$ and $C_V^{1''}$ are due to the phonon-phonon interaction. C_V^{elec} denotes the electronic contribution and this is equal to the electronic entropy S_{elec}. The numerical values of S_{elec} are taken from work by Harder and Young /6/.

For C_p,

$$C_P=C_P^0+C_P^{1'}+C_P^{1''}+C_P^{elec}. \tag{7}$$

where

$$\frac{C_P^0}{Nk_B}=\frac{9}{2}\int_0^1\left\{1+\frac{2\alpha T}{3}+\left(\frac{\partial\ln a(k/k_0)}{\partial\ln T}\right)_P\right\} \tag{8}$$
$$(k/k_0)^2 d(k/k_0),$$

$$\frac{C_P^{1'}}{Nk_B}=\frac{81}{32}\int_0^1\frac{d(k/k_0)}{(k/k_0)}\int_0^1\frac{d(k'/k_0)}{(k'/k_0)} \tag{9}$$
$$\times\left[\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}^2\Phi_1-2\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}\Phi_3+\Phi_5\right]$$

$$\Phi_n=\int_{\frac{|k-k'|}{k_0}}^{\frac{k+k'}{k_0}}\left(\frac{\partial\ln a(q/k_0)}{\partial\ln T}\right)_P a\left(\frac{q}{k_0}\right)\left(\frac{q}{k_0}\right)^n d\left(\frac{q}{k_0}\right)$$

n=1, 3, 5

$$\frac{C_P^{1''}}{Nk_B}=\frac{81}{32}\int_0^1\frac{d(k/k_0)}{(k/k_0)}\int_0^1\frac{d(k'/k_0)}{(k'/k_0)} \tag{10}$$
$$\times\left[\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}^2\xi_1-2\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}\xi_3+\xi_5\right]$$

$$\xi_n=\int_{\frac{|k-k'|}{k_0}}^{\frac{k+k'}{k_0}}\left[\left(\frac{\partial\ln a(q/k_0)}{\partial\ln T}\right)_P^2+\left(\frac{\partial^2\ln a(q/k_0)}{\partial(\ln T)^2}\right)_P\right]$$
$$a\left(\frac{q}{\kappa_0}\right)\left(\frac{q}{\kappa_0}\right)^n d\left(\frac{q}{\kappa_0}\right)$$

n=1, 3, 5

and

$$\frac{C_P^{elec}}{Nk_B}=\frac{S_{elec}}{Nk_B}. \tag{11}$$

In Eqs. 3-10, $a(k/k_0)$ denotes the static structure factor normalized with $k_0=(18\pi^2N/V)^{1/3}$, and α in Eq. 8 is the thermal expansion coefficient. In the present formalism, the difference between C_V and C_p is attributed mainly to the difference between $(\partial\ln a(k/k_0)/\partial\ln T)_V$ and $(\partial\ln a(k/k_0)/\partial\ln T)_p$ (see Table 3 below). In order to perform calculations of C_V and C_p, we need the temperature derivative of the structure factor which is not known to us either theoretically or experimentally. However,

TABLE 2
Calculated specific heats C_v, C_p (in units of Nk_B) and ratio of specific heats γ of liquid La, Ce, Pr and Nd. α is the thermal expansion coefficient ($10^{-4}K^{-1}$) compiled by Iida and Guthrie /5/. Γ denotes the plasma parameter with which the observed structure factor data /3,11/ can be moderately well described by the one-component plasma structure factor /8-10/.

	T(K)	α	Γ	C_v	C_p	γ
La	1243	0.40	100	3.34	3.55	1.06
Ce	1143	0.34	95	3.43	3.59	1.05
Pr	1223	0.38	90	3.22	3.42	1.06
Nd	1323	0.79	110	3.35	3.81	1.14

TABLE 3
Details of calculated specific heats (in units of Nk_B). The values of the electronic specific heats C_v^{elec} and C_p^{elec} are taken from Harder and Young /6/.

	C_v^0	$C_v^{1'}$	$C_v^{1''}$	C_v^{elec}	C_v	C_p^0	$C_p^{1'}$	$C_p^{1''}$	C_p^{elec}	C_p
La	2.83	0.01	0.00	0.5	3.34	3.03	0.01	0.01	0.5	3.55
Ce	2.82	0.01	0.00	0.6	3.43	2.98	0.01	0.00	0.6	3.59
Pr	2.81	0.01	0.00	0.4	3.22	3.00	0.01	0.01	0.4	3.42
Nd	2.84	0.01	0.00	0.5	3.35	3.27	0.01	0.03	0.5	3.81

Yokoyama et al. /7/ showed that the classical one-component plasma structure factor $a_{OCP}(k)$ developed by Chaturvedi et al. /8-10/ can reproduce moderately well the experimental structure data /3,11/ for liquid rare earth metals. Therefore, we evaluate $(\partial \ln a(k/k_0)/\partial \ln T)_v$ and $(\partial \ln a(k/k_0)/\partial \ln T)_p$ using the $a_{OCP}(k)$ in the same way as employed by Yokoyama and Naito /1/. In this approximation we obtain

$$\left(\frac{\partial \ln a(k)}{\partial \ln T}\right)_v = -\frac{\Gamma\left(\frac{\partial a_{OCP}(x,\Gamma)}{\partial \Gamma}\right)_x}{a_{OCP}(x,\Gamma)}, \tag{12}$$

and

$$\left(\frac{\partial \ln a(k)}{\partial \ln T}\right)_p = \frac{1}{3a_{OCP}(x,\Gamma)} \times \left\{\alpha x T\left(\frac{\partial a_{OCP}(x,\Gamma)}{\partial x}\right)_\Gamma - \Gamma(3+\alpha T)\left(\frac{\partial a_{OCP}(x,\Gamma)}{\partial \Gamma}\right)_x\right\} \tag{13}$$

where $x \equiv ka$, with a being ion-sphere radius given by $a=(3/4\pi n)^{1/3}$ with n the number density of ions and Γ is the plasma parameter.

We now quote the numerical results in Table 2. As shown in Table 2, the calculated values of γ from the collective coordinate method well support those obtained from Eq. 1. Table 3 shows the details of the calculated specific heats. Harmonic effects are dominant in the description of the specific heats. Because of the presence of the factor $(k/k_0)^2$ in Eqs. 3 and 8, the most important region of wavenumber k-space is $k_D<k<k_0\equiv 3^{1/3}k_D$ where k_D is the radius of the Debye sphere. The difference in calculated C_v and C_p comes largely from the difference between $(\partial \ln a(k/k_0)/\partial \ln T)_v$ and $(\partial \ln a(k/k_0)/\partial \ln T)_p$ in this k-region.

Conclusion

On looking closely at Eqs. 1, 8 and 13 we can understand that α plays an important role for predicting γ. If the values of α for La, Ce and Pr are larger than those given in Table 2, the problem we have raised will be solved and the three routes to γ will give much the same results. However, if the experimental values of α are right, the following conclusion can be drawn from the present study. The ratio of specific heats of liquid Nd is definitely larger than 1.1, whereas those of liquid La, Ce and Pr will be smaller than 1.1 in contrast with those of liquid alkali, polyvalent and 3d transition metals. Accurate values of α for liquid La, Ce and Pr are highly desirable in order to confirm the present conclusion.

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