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Effective Pair Potentials and Structures of Liquid Rare Earth Metals near the Melting Point

I. Yokoyama*, T. Arai* and Y. Waseda**

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

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

The simple-metal theory may describe the structures of liquid rare earth metals when the pseudopotential parameters are properly selected. Such point has been tested for liquid La, Ce, Pr and Nd near the melting point using the Percus-Yevick integral equation and the Ashcroft empty-core form for the pseudopotential. The core radius was uniquely determined by the density of liquid and the effective valence Z_{eff} was estimated from the value of the plasma parameter which reasonably explains the structural features and some thermodynamic properties coupled with the one-component plasma (OCP) model. The validity of the value of Z_{eff} has been supported by the Gibbs-Bogoliubov variational method using the OCP reference system.

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I. Introduction

The classical one-component plasma (OCP) model is found to reasonably explain the measured structure factors and some thermodynamic properties of liquid transition and rare earth metals⁽¹⁾⁻⁽⁶⁾. In these systematic works we found that the simple-metal theory coupled with the OCP model appears to make some substantial contributions to our understanding of the structures of these metals. The aim of this work is to examine such point for liquid La, Ce, Pr and Nd using the Percus-Yevick integral equation. The calculated structure factors and pair distribution functions are compared with the experimental data.

We have assumed that, as a first approximation to the electronic structure of a rare earth metal with Z valence electrons per ion, Z_0 electrons are incorporated in the non-overlapping ion core, the remaining $Z_{\text{eff}} = Z - Z_0$ electrons per ion are in the free-electron-like states, and their coupling is considered to be weak. This idea for separating the core and conduction electron states corresponds to a proposal by Wills and Harrison (WH)⁽⁷⁾, although the contribution from d- or f-electrons is not explicitly taken into account here. Because of the presence of d or f states it is difficult to perform the first principle calculation of the effective valence Z_{eff} . In this work, the value of Z_{eff} is determined from the plasma parameter. It may be less clear why a theory developed for simple (s-p) metals should be meaningful for liquid transition and rare earth metals. However, according to the recent Regnaut's analysis⁽⁸⁾ of the liquid structure of 3d transi-

tion metals from the WH model, the predictions of the WH potential depend critically on the cancellation between the two large repulsive and attractive terms arising respectively from the simple-metal-like contribution and the d-band contribution. Both the position and the intensity of the attractive well are strongly modified by changing the value of the Ashcroft empty-core radius and these modifications are as large as those induced by the d-band contribution itself. Since the structure factor data, from well below the first peak to high wave-number k , are mainly described by the repulsive part corresponding to the energy of the order of $k_B T$ measured from the bottom of the effective pair potential, it is possible to adjust its gradient by using an empty-core potential with an effective charge. This is the basic idea of the present work.

II. Calculation Procedure

We view a liquid metal as a collection of ions with potential energy described by a structure-independent term $u_0(n)$ and a pairwise interaction $u(r, n)$: both terms depend in principle on n , the number density of the ions. The interatomic pair potential $u(r, n)$, using a standard pseudopotential formalism⁽⁹⁾⁽¹⁰⁾, can be written as (in atomic units)

$$u(r, n) = \frac{Z_{\text{eff}}^2}{r} \left(1 - \frac{2}{\pi} \int_0^\infty \frac{F_N(k, n)}{k} \sin kr dk \right) \quad (1)$$

where

$$F_N(k, n) = \left(\frac{k^2 v(k)}{4\pi Z_{\text{eff}}} \right)^2 \left(1 - \frac{1}{\epsilon(k, n)} \right) \quad (2)$$

is the normalized energy-wavenumber characteristic. Here $v(k)$ is the local pseudopotential and $\epsilon(k, n)$ is the dielectric screening function.

In the present work we employ the Ashcroft empty-core form⁽¹¹⁾

$$v(k) = -(4\pi Z_{\text{eff}}/k^2) \cos kr_c \quad (3)$$

for the pseudopotential, r_c being the core radius, and the Geldart-Vosko expression⁽¹²⁾ is used to describe the electron gas.

III. Results

1. Effective pair potentials

The value of r_c is determined through the relation of $k_0 r_c = \pi/2$, where k_0 denotes the position of the first node of the Ashcroft pseudopotential in k -space and is chosen to get the correct number of degrees of freedom, i.e., $k_0 = (18\pi^2 n)^{1/3}$. This is based on the assumption that all or almost all the elementary excitations in liquid metals can be attributed to the density fluctuations⁽¹³⁾. If we only accept this assumption, the zeroth order picture is of longitudinal phonons with k -vectors occupying an enlarged Debye sphere of radius $k_0 = 3^{1/3} k_D$ where $k_D = (6\pi^2 n)^{1/3}$. Therefore the value of r_c is uniquely determined by the density of liquid La, Ce, Pr and Nd. The density values were taken from the compilation of Gmelin Handbook⁽¹⁴⁾ and numerical data are given in Refs. (15) and (16). The value of Z_{eff} , on the other hand, is estimated from the plasma parameter Γ through the relation of $Z_{\text{eff}} = \sqrt{\Gamma a k_B T}$ with $a = (3/4\pi n)^{1/3}$. Figure 1 shows the pair potentials $u(r, n)$ calculated from the values of r_c and Z_{eff} given in Table 1. It is recognized from Fig. 1 that the minimum of the $u(r, n)$ gets deeper and the repulsive part of the $u(r, n)$ gets harder when the atomic number changes from Ce to Nd (see eq. (1) and the values of Z_{eff} in Table 1) but the size of the ion core

Fig. 1 Effective pair potentials $u(r, n)$ for liquid La, Ce, Pr and Nd near the melting point.

Table 1 Entropy S (in units of Nk_B) and isothermal compressibility χ_T ($10^{-11} \text{ m}^2 \text{ N}^{-1}$) of liquid La, Ce, Pr and Nd. Z_{eff} is the effective valence calculated from the plasma parameter Γ . Both magnetic and electronic contributions⁽¹⁷⁾ are included in the calculated total entropy S_{calc} . For χ_T see Refs. (2) and (3).

	$T(\text{K})$	Γ	Z_{eff}	$r_c(\text{a.u.})$	S_{calc}	S_{expt}	χ_T^{calc}	χ_T^{expt}
La	1243	80	1.12	1.787	13.3	13.0 ^a	5.74	4.29 ^b 4.24 ^c
Ce	1143	80	1.05	1.726	14.9	14.4 ^a	5.66	4.64 ^b 5.30 ^c
Pr	1223	85	1.13	1.734	15.2	15.5 ^a	5.09	5.23 ^b 4.17 ^c
Nd	1323	90	1.20	1.721	15.4	15.7 ^a	4.41	3.41 ^b

a) from Hultgren *et al.*⁽¹⁸⁾

b) from Waseda and Ueno⁽¹⁹⁾

c) from McAlister and Crozier⁽²⁰⁾

Fig. 2 Structure factors $s(k)$: —, Percus-Yevick integral equation; ●, ▲, ■, × experimental data⁽²¹⁾.

remains unchanged. For La, however, the core size is larger than those of Ce, Pr and Nd. We believe that the 5d-electron of La is responsible for this.

2. Structure factors and pair distribution functions

The Percus-Yevick integral equation is employed to calculate the liquid structure factors $s(k)$ and the pair distribution functions $g(r)$ using the effective pair potentials shown in Fig. 1. The calculated results are displayed in Figs. 2 and 3, and are compared with the experimental data⁽²¹⁾. The experimental data involve the uncertainty of 3.2% by estimating from errors in normalization, counting statistics and atomic scattering factors. Full details on the experimental uncertainty are given in the original papers on the structure of liquid rare earth metals by the X-ray diffraction⁽¹⁵⁾⁽¹⁶⁾. As can be seen from these figures, both $s(k)$ and $g(r)$ are rather well described by these pair potentials and the present authors maintain the view that the quality of description is as good as that of the s-p bonded metals, although there are some discrepancies in detail, such as the second-peak region in $s(k)$ and the distinct oscillations in the calculated $s(k)$ in the large- k region. The first-peak height of the calculated

Fig. 3 Pair distribution functions $g(r)$: —, Percus-Yevick integral equation; ●, experimental data⁽²¹⁾.

$g(r)$ is also slightly higher than that of the experimental $g(r)$ in all the cases presently studied. One of the origins for these discrepancies is the values of Z_{eff} , because both the isothermal compressibility χ_T and $s(k)$ are known to be rather sensitive to the values of Z_{eff} .

IV. Discussion

The values of r_c and Z_{eff} used in this work appear to reproduce the basic structural features of liquid La, Ce, Pr and Nd. As is shown in Table 1, those values of Γ coupled with the OCP model can reasonably explain the experimental entropies. For the isothermal compressibilities, the fully quantitative description is difficult because of the lack of knowledge on the density-

derivative of the volume energy which was discussed in Refs. (2) and (3). It is interesting to examine whether the values of Γ (i.e. Z_{eff}) are supported from the Gibbs-Bogoliubov variational method with the OCP reference system⁽¹⁰⁾⁽²²⁾.

The Helmholtz free energy of the system can be written as

$$F = F_{\text{id}} + u_0(n) - T\Delta S_0 + \frac{1}{2} nu(0, n) + \frac{1}{2} \int \frac{dk}{(2\pi)^3} u(k, n)(s_{\text{OCP}}(ka, \Gamma) - 1) \quad (4)$$

where F_{id} is the free energy of an ideal gas, $u_0(n)$ the volume energy and ΔS_0 is the excess entropy

$$\Delta S_0/k_B = -2.83632\Gamma^{1/4} + 0.89770\Gamma^{-1/4} + 0.80049 \ln \Gamma + 1.78559. \quad (5)$$

$u(k, n)$ is the Fourier transform of $u(r, n)$, $u(0, n)$ the $k=0$ limit, and $s_{\text{OCP}}(ka, \Gamma)$ is the OCP structure factor. Detailed expressions of the formalism are given in Ref. (22). Here we employ the OCP structure factor developed by Chaturvedi *et al.*⁽²³⁾⁽²⁴⁾. The structure-dependent part of the Helmholtz free energy for liquid Nd is plotted against Γ in Fig. 4 for the demonstrative purpose. As can be seen from this figure, the position of the minimum of the calculated Helmholtz free energy is close to the Γ value employed in this work, although the difference of the magnitude of about 5 (from 5 to 10 for La, Ce, and Pr) is found. Thus, it may be reasonably said that the thermodynamic variational method based on the OCP reference system supports the validity of the values of Z_{eff} used in this work.

Fig. 4 Structure-dependent part of the Helmholtz free energy F_s versus plasma parameter Γ . $F_s = F - F_{\text{id}} - u_0(n) - nu(0, n)/2$. The position of the minimum of F_s for liquid Nd is found around the value of Γ given in Table 1.

V. Conclusion

The simple-metal theory using the Percus-Yevick integral equation can well describe the essential structural features of liquid La, Ce, Pr and Nd near the melting point when the pseudopotential parameters are properly selected. The present results also suggest that f-electrons in rare earth metals are adequately localized and incorporated in the core electron states.

REFERENCES

- (1) T. Itami and M. Shimoji: J. Phys. F: Met. Phys., **14** (1984), L15.
- (2) H. Itoh, I. Yokoyama and Y. Waseda: J. Phys. F: Met. Phys., **16** (1986), L113.
- (3) I. Yokoyama, S. Naito and Y. Waseda: J. Less.-Common Metals, **136** (1987), 25.
- (4) I. Yokoyama, S. Naito and Y. Waseda: Z. Phys. Chem. Neue Folge, **156** (1988), 469.
- (5) I. Yokoyama and S. Naito: Physica B, **154** (1989), 309.
- (6) I. Yokoyama and S. Naito: Physica B, **168** (1991), 229.
- (7) J. M. Wills and W. A. Harrison: Phys. Rev. B, **28** (1983), 4363.
- (8) C. Regnaut: Z. Phys. B-Condensed Matter, **76** (1989), 179.
- (9) N. W. Ashcroft and D. Stroud: *Solid State Phys.* 33, Academic Press, New York, (1978), p. 1.
- (10) J. Hafner: *From Hamiltonians to Phase Diagrams* (Solid State Sciences 70), Springer-Verlag, Berlin, (1987), p. 34, p. 102.
- (11) N. W. Ashcroft: Phys. Lett., **23** (1966), 48.
- (12) D. J. W. Geldart and S. H. Vosko: Can. J. Phys., **44** (1966), 2137.
- (13) P. Gray, I. Yokoyama and W. H. Young: J. Phys. F: Met. Phys., **10** (1980), 197.
- (14) R. J. Meyer, F. H. Z. Pietsch and A. Kotowski (Editors): *Gmelin Handbuch der Anorganischen Chemie*, Vol. 39, No. B3 Springer-Verlag, Berlin, (1974).
- (15) Y. Waseda and S. Tamaki: Phil. Mag., **36** (1977), 1.
- (16) Y. Waseda and W. A. Miller: Phil. Mag., **38** (1978), 21.
- (17) J. M. Harder and W. H. Young: Phys. Lett., **61A** (1977), 468.
- (18) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly and D. Wagman: *Selected Values of the Thermodynamic Properties of the Elements*, Metals Park, Ohio: Am. Soc. of Metals, (1973), p. 118, p. 278, p. 344, p. 393.
- (19) Y. Waseda and S. Ueno: Sci. Rep. Res. Inst. Tohoku Univ., **34A** (1987), 1.
- (20) S. P. McAlister and E. D. Crozier: Solid State Comm., **40** (1981), 375.
- (21) Y. Waseda: *The Structure of Non-Crystalline Materials*, McGraw-Hill, New York, (1980), p. 282, p. 286, p. 288, p. 290.
- (22) S. Ono and I. Yokoyama: J. Phys. F: Met. Phys., **14** (1984), 197.
- (23) D. K. Chaturvedi, G. Senatore and M. P. Tosi: Lett. Nuovo Cimento, **30** (1981), 47.
- (24) D. K. Chaturvedi, G. Senatore and M. P. Tosi: Nuovo Cimento, B **62** (1981), 375.