Thermodynamic and Electronic Properties of 3d-transition Metals in the Liquid State*

Yoshio WASEDA, Shigeru TAMAKI** and Yoshimi TSUCHIYA**

The Research Institute of Mineral Dressing and Metallurgy

(Received December 11, 1976)

Synopsis

An analytic solution of the Percus-Yevick equation for the hard sphere model is applied to the thermodynamic properties of liquid 3d-transition metals dear the triplepoint. Agreement between theory and experiment is fairly good for the therma pressure coefficient. The recent method has been used to evaluate the electronic contributions to entropies and specific heat. The density of states of the d-band at the Fermi level and the heat of vapourization for liquid 3d-transition metals are also discussed.

I. Introduction

A systematic investigation on the structure of 3d-transition metals in the liquid has recently been reported[1]. The obtained results are shortly given below. The structure factor of 3d-transition metals in the liquid state has a typical form with good symmetry and sequently it has suitably agreed with that the Percus-Yevick Hard Sphere (P-Y-H-S) model[2,3]. The hard sphere diameter σ and the packing fraction η to be suited to the experimental results are shown in

Table 1. Hard sphere diameters and packing fractions of liquid 3d-transition metals at temperature T K.

	$T(K)$	density (g/cm^3)	hard sphere diameter (Å)	packing fraction (η)	n_1 (atoms)	$\frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3\frac{\rho}{\eta}$
Sc	1833	2.92	2.75	0.43	10.5	1.01
Ti	1973	4.15	2.53	0.44	10.9	0.99
V	2173	5.36	2.37	0.44	11.0	1.00
Cr	2173	6.27	2.25	0.44	11.2	1.02
Mn	1533	5.97	2.33	0.44	10.9	1.02
Fe	1823	7.01	2.25	0.45	10.6	1.00
Co	1823	7.70	2.24	0.46	11.4	0.99
Ni	1773	7.72	2.21	0.45	11.6	1.01
Cu	1423	7.92	2.25	0.45	11.3	1.00

* The **280th** report of the Research Institute of Mineral Dressing and Metallurgy. A preliminary result of this work has been reported in J. Phys. F: Metal Phys., **6** (1976), L89.

** Permanent address: Department of Physics, Faculty of Science, Niigata University, Niigata 950-21, Japan.

(1) Y. Waseda and S. Tamaki, Phil. Mag., **32** (1975), 273.

(2) H.L. Frisch and J.L. Lebowitz, *The Equilibrium Theory of Classical Fluids*, 1964, New York, Benjamin.

(3 H Reiss Adv. Chem. Phys., **9** (1965), 1.

Table 1 together with that of liquid Sc at 1560°C.[4] It was concluded that the nearest neighbours number are almost equal to 11 in all 3d-series and that the packing fraction of each metal is nearly equal to 0.45.

The present authors have preliminary reported[5] that the thermodynamic properties of 3d-series in the liquid state are considerably explained by the P-Y-H-S model. In this paper, we will present a detail of calculation of the previous results and will discuss the electronic structures of 3d-transition metals in the liquid state. To proceed the calculation for both atomic and electronic properties, the idea proposed by Meyer, Stott and Young[6] that the density of state at Fermi level could be derived from the excess entropy is worthwhile and we shall apply it to some extent.

II. Percus-Yevick-Hard-Sphere Model

Before proceeding with the calculation, we show the validity for the values of the hard sphere diameter and the packing fraction. According to the Born-Green theory[7], the interatomic potential $\phi(r)$ in liquid metals is given by the following relation,

$$\phi(r) = U(r) + \frac{\pi\rho}{r}\int \frac{d\phi(s)}{ds} g(s)ds \times \int_{-s}^{s} (s^2-t^2)(t+r)\,[g(|t+r|)-1]\,dt, \tag{1}$$

where $U(r) = -k_B T \cdot lng(r)$, $g(r)$ being the radial distribution function obtained by diffraction experiments. Using the structural data, the interatomic potential of the $3d$-transition metals in the liquid state is obtained as shown in Fig. 1. It is also found that the potentials of Cr, Fe and Co are similar to that of Ni. A numerical solution in this work is based on the combination of a linearized simultaneous equation (LSE) method[8] and the iteration method of Johnson-March scheme[9]. Several discussions (see for example, Gaskell[10], Kumaravadival et al.[11] Ailawadi et al.[12]) have been given on the method of solving the Born-Green equation by numerical calculation. However there is no problem on the hard part of the obtained pair potential. Very recently, De Angelis and March[13] have

(4) Y. Waseda and S. Tamaki, Phil. Mag., **35** (1977), in press.
(5) S. Tamaki and Y. Waseda, J. Phys. F: Metal Phys., **6** (1976), L89.
(6) A. Meyer, M.J. Stott and W.H. Young, Phil. Mag., **33** (1976), 381.
(7) M. Born and H.S. Green, Proc. Roy. Soc., **A188** (1946), 10.
(8) Y. Waseda and K. Suzuki, Phys. Stat. Sol. (b), **47** (1971), 203.
(9) M.D. Johnson, P. Hutchinson and N.H. March, Proc. Roy. Soc., **A282** (1964), 283.
(10) T. Gaskell, Proc. Phys. Soc., **89** (1966), 231.
(11) R. Kumaravadivel, R. Evans and D.A. Greenwood, J. Phys. F: Metal Phys., **4** (1974), 1839.
(12) N.K. Ailawadi, P.K. Banerjee and A. Choudry, J. Chem. Phys., **60** (1974), 2571 and 5124.
(13) De Angelis and N.H. March, Phys. Lett., **55A** (1976), 287.

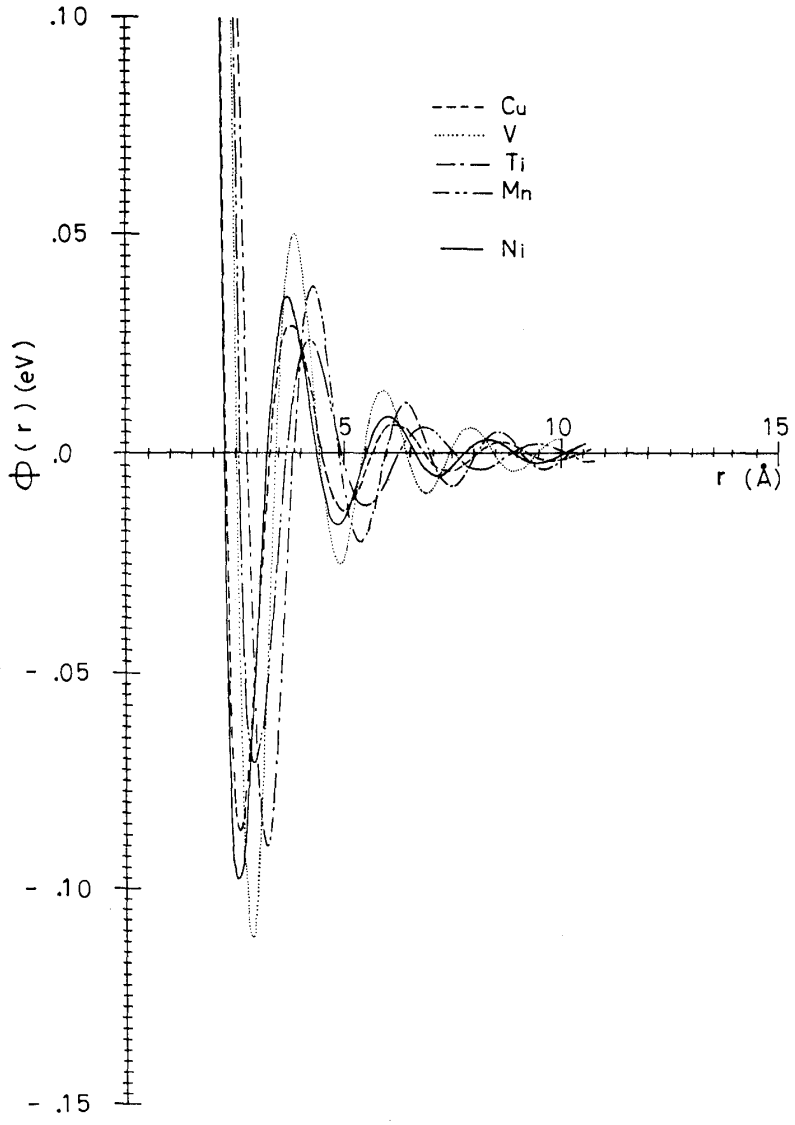

Fig. 1. Effective pair potential of 3*d*-transition metals in the liquid state.

Table 2. Parameters of analytical form for the pair potentials of liquid 3*d*-transition metals derived from measured structural data[14]

	r_0 (Å)	A (eV)	B	C	E (eV)	F	G
Ti	3.17	0.0986	9.447	−0.7136	2.386	8.822	−20.07
V	2.82	0.1345	8.855	−0.6948	70.49	6.420	−14.93
Cr	2.58	0.1271	7.069	−0.6152	292.3	7.867	−17.83
Mn	2.67	0.0879	6.835	−0.5991	187.8	7.669	−17.53
Fe	2.58	0.1148	6.966	−0.6062	322.9	7.796	−18.14
Co	2.56	0.1101	6.861	−0.6002	36.84	5.923	−13.78
Ni	2.53	0.1173	6.983	−0.6072	277.6	7.581	−17.63
Cu	2.57	0.1003	6.785	−0.5965	814.5	9.301	−21.14

$$\phi_{\text{eff}}^{\text{obs}}(r) = A\left(\frac{r_0}{r}\right)^3 \cos\left[B\left\{\left(\frac{r}{r_0}\right)+C\right\}\right] E\exp\left[F+G\left(\frac{r}{r_0}\right)\right]$$

also suggested that all three theories of P-Y, H-N-C and B-G lead to the same result for extracting $\phi(r)$ from the structural data in a zeroth order approximation. The parameters of analytical form for the pair potentials of Fig. 1 are listed in Table 2[14]. The hard core size in Fig. 1 is nearly equal to that obtained so as to fit to the experimental structure factor using P-Y-H-S model. The hard sphere diameter and the packing fraction used satisfy also the equation $\rho(4/3)\pi(\sigma/2)^3 1/\eta=1$ as seen in Table 1.

On the basis of the hard sphere model, the equation relating to the isothermal compressibility is given by (see for example Egelstaff[15]),

$$\rho k_B T \chi_T = S(0) = \frac{(1-\eta)^4}{(1+2\eta)^2} \tag{2}$$

where ρ is the number density, k_B is the Boltzmann constant, $S(0)$ is the long wave limit of the liquid structure factor and η is the packing fraction defined by $\eta=(\pi/6)\rho\sigma^3$, σ being hard sphere diameter.

The expression for the pressure is not unique[16] but here we use the equation derived from the compressibility:

$$p = \rho k_B T \frac{1+\eta+\eta^2}{(1-\eta)^3} . \tag{3}$$

The temperature dependence of the thermal pressure coefficient, γ_v can be obtained from eq. (3) as

$$\gamma_v = \rho k_B \left\{ \frac{1+\eta+\eta^2}{(1-\eta)^3} + \frac{(2+\eta)^2}{(1-\eta)^4} T \left(\frac{\partial \eta}{\partial T} \right)_v \right\} . \tag{4}$$

The temperature dependence of η is derived by Hasegawa[17] and Shimoji[18] using equation (2). Assuming the temperature dependence of both sides of equation (2) is equal then

$$\left(\frac{\partial \eta}{\partial T} \right)_v = - \frac{(1+2\eta)^3}{4(1-\eta)^3(2+\eta)} \rho k_B \chi_T \left[1 + T \frac{\partial \ln \chi_T}{\partial T} \right] . \tag{5}$$

For liquid 3d-transition metals, the temperature dependence of $\ln\chi_T$ at constant volume is not known but this might be negligibly small compared with unity, since even for liquid alkali metals they are very small[19]. Then the thermal pressure coefficient becomes,

$$\gamma_v = \rho k_B \left\{ \frac{(1+\eta+\eta^2) - \frac{1}{4}(1+2\eta)(2+\eta)}{(1-\eta)^3} \right\} . \tag{6}$$

(14) Y. Waseda and S. Tamaki, Metal Phys. Seminar, **1** (1976), 133.
(15) P.A. Egelstaff, *An Introduction to the Liquid State*, 1967, London, Academic Press.
(16) E. Thile, J. Chem. Phys., **39** (1963), 474.
(17) M. Hasegawa and M. Watabe, J. Phys. Soc. Japan, **32** (1972), 14; ibid., **36** (1974), 1510.
(18) M. Shimoji, *The Properties of Liquid Metals*, 1973, London, Taylor and Francis, p 421.
(19) O.J. Kleppa, J. Chem. Phys., **18** (1950), 1331.

Table 3. Structure factor at the long wave limit S(0), isothermal compressibility χ_T, temperature dependence of η at constant volume, thermal expansion coefficient α_v and thermal pressure coefficient γ_v of liquid 3d-transition metals at temperatures mentioned in Table 1. Observed thermal expansion coefficients are taken from the reference (Saito et al.[20]).

	S(O)	χ_T (10^{-12} cm²/dyne)	$-\left(\frac{\partial\eta}{\partial T}\right)_v$ (10^4 drg^{-1})	α_v (10^{-4})	α_v^{obs} (10^{-4})	γ_v (bar·K^{-1})
Sc	0.0305	3.08	0.60	1.36		44
Ti	0.0278	1.98	0.56	0.93	1.39	47
V	0.0278	1.98	0.49	1.15	0.95	58
Cr	0.0278	1.73	0.50	1.14	1.52	66
Mn	0.0278	2.68	0.70	1.61	1.71	60
Fe	0.0253	1.80	0.58	1.33	1.36	74
Co	0.0231	1.58	0.58	1.30	1.46	82
Ni	0.0253	1.77	0.60	1.38	1.62	78
Cu	0.0253	2.31	0.74	1.71	1.18	74

The thermal expansion coefficient α_v is directly obtained by the relation

$$\alpha_v = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \chi_T \cdot \gamma_v .$$

Numerical results of these thermodynamic functions of liquid 3d-transition metals are tabulated in Table 3. Magnitudes of the calculated thermal pressure coefficients agree with the experimental ones[20].

In simple liquid metals, the entropy is given in the following expression,

$$S = S_{\text{ideal gas}} + S_E , \tag{7}$$

$$S_E = Nk_B\left\{\frac{3}{2}\ln(1-\eta) - \frac{6\eta}{1-\eta} - \frac{9}{2}\frac{\eta^2}{(1-\eta)^2} + \frac{1-\eta^3}{(1-\eta)^3}\right\} , \tag{8}$$

$$S_{\text{ideal gas}} = Nk_B\left\{\frac{5}{2} + \ln\left[\frac{e}{n}\left(\frac{mk_BT}{2\pi h^2}\right)\right]^{3/2}\right\} , \tag{9}$$

where $S_{\text{ideal gas}}$ is the entropy of ideal gas in the liquid state and S_E is the excess entropy. The notation is identical to the one in the work of Silbert et al.[21] The specific heat at constant volume, $C_v = T(\partial S/\partial T)_v$ is then,

$$C_v = Nk_B\left[\frac{3}{2} - \left\{\frac{3}{2}\frac{1}{1-\eta} + \frac{6}{(1-\eta)^2} - \frac{3(1-2\eta)}{(1-\eta)^3}\right\} T\left(\frac{\partial\eta}{\partial T}\right)_v\right] . \tag{10}$$

The first term in the square bracket corresponds to the ideal gas entropy and the others are from the excess one. Using both thermodynamic equations, $C_p/C_v = \chi_T/\chi_s$ and $\chi_T - \chi_s = T\alpha_v^2/\rho C_p$, we can obtain the specific heat at constant pressure, C_p

(20) T. Saito, Y. Shiraishi and Y. Sakuma, Trans. Iron, Steel Inst. Japan, **9** (1969), 118.
(21) M. Silbert, I.H. Umar, M. Watabe and W.H. Young, J. Phys. F: Metal Phys., **5** (1975), 1262.

Table 4. Excess entropy S_E and specific heat C_v and C_p.

	$-S_E$ (cal K^{-1} mol^{-1})	$-S_E^{obs}$ †(cal K^{-1} mol^{-1})	C_v †(cal mol^{-1})	C_p (cal mol^{-1})	C_p^{obs} †(cal mol^{-1})
Sc	5.87	4.24	7.07	7.16	10.6
Ti	6.27	4.10	7.21	7.31	8.8
V	6.27	4.24	7.21	7.35	9.5
Cr	6.27	4.41	7.21	7.28	9.4
Mn	6.27	2.83	7.21	7.28	11.0
Fe	6.59	3.41	7.34	7.41	10.5
Co	7.01	3.30	7.57	7.64	9.0
Ni	6.59	4.00	7.34	7 41	9.2
Cu	6.59	6.77	7.34	7.40	7.5

† Data are taken from the reference book by Hultgren et al.[22].

as follows,

$$C_p = C_v + T\alpha_v^2/\rho\chi_T \ . \tag{11}$$

The estimated values for S_E, C_v and C_p of 3d-transition metals are listed in Table 4. The observed values of the entropy in the liquid state are estimated using the data from Hultgren et al.[22] and Dinnison et al.[23] and the density data of Saito et al.[20] The discrepancy between the theoretical values of the excess entropy and the specific heat and the experimental ones for 3d-transition metals seems to be due to the effect of the 3d- electron at the Fermi level. This inference is positively understood by the fact that the theoretical values of these quantities of liquid Cu are very close to the experimental ones because the contribution from d electron in liquid Cu is much smaller than that in liquid 3d-transition metals.

III. Density of 3d-electron states

Meyer et al.[6] have proposed a new method to derive the density of states at the Fermi level. The first order in k_BT, the electronic entropy is written

$$S_{elec} = \frac{1}{3}\pi^2 N(E_F) k_B^2 T \tag{12}$$

where $N(E_F)$ is the appropriate density of states (two per space orbital) at the Fermi level. Rigorously speaking, the total entropy at temperature T is given by the sum of S_{elec}, the ideal gas entropy S_{gas} and that of the hard-sphere part S_E, however, the actual value of S_{elec} for simple metals is very small and then the total entropy is given by the summation of S_E and S_{gas}. For transition metals, the density of states originated from the *d*-band is much larger than that from the conduction electron. Then we can not neglect the contribution of S_{elec}. This

(22) R. Hultgren, R.L., Orr, P.D. Anderson and K.K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, 1963, New York, John Wiley & Sons.

(23) D.H. Dennison, Jr. K.A. Gschneider and A.H. Daane, J. Chem. Phys., **44** (1966), 4273.

Table 5. Density of states of 3d-transition metals at the Fermi level, obtained from electron entropy.

Element	$N(E_F)$ (eV)$^{-1}$	Element	$N(E_F)$ (eV)$^{-1}$
Sc	1.8	Fe	3.2
Ti	2.2	Co	3.7
V	2.0	Ni	2.6
Cr	1.8	Cu	0
Mn	3.4		

is the reason why $S_E(=S-S_{gas})$ does not agree with the observed value S_E^{obs} $(=S-S_{gas}-S_{elec})$. The estimated values of $N(F_F)$ for 3d-transition metals are tabulated in Table 5.

The specific heat of 3d-electron is given by $(\partial S_{elec}/\partial T)_T$ which is equal to S_{elec} itself. Therefore, we can derive the density of state of 3d-band from the observed specific heat, using the same procedure mentioned above. However we would prefer to adopt the curve for the density of state derived from the electronic entropy S_{elec}, because it is selfconsistent with the bonding energy or heat of vaporization.

As shown in Table 1, the nearest neighbours number of atoms does not change in 3d-series at all. This fact suggests that the shapes of the $3d$-electron's density of states are much the same. In addition, the rigid band model seems to be a good model for Cr, Mn, Fe, Co, Ni and Cu in the liquid state because all the interatomic distances are nearly equal, although a little variations in the d-band width are expected because the nearest neighbour distance r_1 goes to decrease on going from Sc to Cr.

For a crude but useful approximation, we have estimated the density of 3d-electron's states as below. The electronic state of 3d-transition metal is assumed to be $3d^x\ 4s^1$ (from $x=2$ for Sc to $x=10$ for Cu) which is considerably justified by the case of solid state[24]. Using the estimated value of $N(E_F)$, the density of 3d-electron's state $N_d(E)$ is written as in Fig. 2. As seen in the figure, the density of states has two maxima near the Fermi level of Ti and Co. Within the short range space, the structure of 3d-transition metals in the liquid state seems to be close to a cubic configuration as stressed in section 1. In fact, the present density of state is nearly split into two part like $d\varepsilon$- and $d\gamma$-bounding as in the cubic symmetry.

From the figure of the density of states, the centre of the energy of $d\varepsilon$ bonding corresponds to the Fermi level of Ti and that of $d\gamma$ corresponds to E_F of Co. Weighing for the levels of $d\varepsilon$ and $d\gamma$, the averaged energy level is obtained, which is apart from the zero energy level by only the band shift. A relation among these energy level is also shown in Fig. 2.

(24) J.O. Dimmock, *Solid State Physics*, **26** (1971), 103; New York, Academic Press.

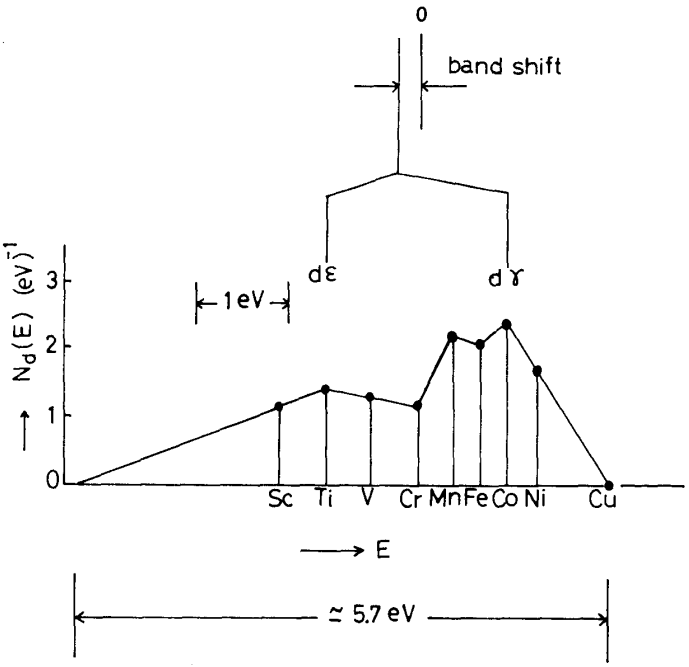

Fig. 2. Density of states of 3d-transition metals in the liquid state. Band shift energy is assumed to be 0.25 eV[25].

IV. Heat of vaporization

The bonding energy of 3d-transition metals in the liquid state is approximately expressed by the heat of vapourization. In this section, we shall estimate the bonding energy of 3d-transition metals in the liquid state, using the obtained density of states in the preceeding section. The bonding energy of 3d-transition metals is given by the following relation,[25]

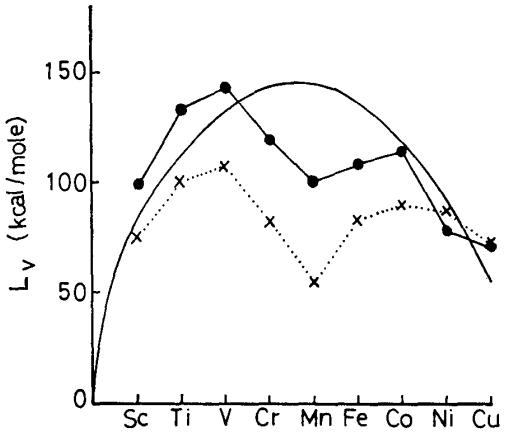

Fig. 3. Experimental and theoretical heat of vaporization. —— band theoretical one using a rectangular density of states[25].
—— • —— band theoretical one with hard sphere model. —— × —— experimental.

(25) J. Friedel, *The Physics of Metals* I, 1969, Cambridge.

$$E_{\text{bond}} = pE_1 + \int_{-\infty}^{E_F} EN(E)dE \tag{13}$$

where p is the number of 3d-electron and E_1 is the band shift energy. The estimated values are little bit larger than the observed ones. However the qualitative feature is much better than that of rectangular density of states as proposed by Friedel[25]. For reference, all these estimated values are shown in Fig. 3.

V. Discussions

Büsch et al.[26] have measured the magnetic susceptibility of Mn, Fe, Co, Ni and Cu in the liquid state. Since the d-band of Cu is completely filled, its susceptibility is very small, whereas that of liquid Mn has large value as $\chi_d = 7.2 \times 10^{-4}$ CGS emu/mol. The non-magnetic susceptibility of d-band is expressed in the following form[27],

$$\chi_d = \frac{2\mu_B^2 N(E_F)}{1 - U_{\text{eff}} N(E_F)} \tag{14}$$

where U_{eff} means the effective interaction between electrons in d-band. In the solid state, Wohlforth and Cornwell[28] have shown that the best value of U_{eff} is 0.617 eV. If it is assumed that this value is valid in liquid Mn, we obtain its density of state at Fermi level as 2.79 $(\text{eV})^{-1}$ which is in adequate agreement with that derived in this work.

In order to know the electronic structure of 3d-transition metals in the liquid state, the Tight-Binding method and APW method are powerful, but it is impossible to see the energy separation by the orbital symmetry if the observed or calculated pair distribution function $g(r)$ should be used in those methods, in other words, the spherical symmetry were used. So far it is desirable to calculate the band structure of 3d-transition metals in the liquid state as in a quasicrystalline model.

In conclusion, it is therefore worthwhile to mention that the hard sphere model seems to be useful for the discussion of the thermodynamic properties of liquid 3d-transition metals, since the derivation of them from the first principle including the electron theory are difficult at the present time. In addition, the electronic structure can be also obtained from the application of hard sphere model based on the experimental structure data.

Acknowledgements

The authors wish to thank Professor W.H. Young for his fruitful correspondence in this work. One of us (Y.W.) is indebted to Professors M. Ohtani and Y. Shiraishi for their support and encouragement in this study.

(26) G. Büsch, H-J Güntherodt, H.U. Kunzi and H.A. Meier, *The Properties of Liquid Metals*, 1973, London, Taylor and Francis, p 263.
(27) E.C. Stoner, Proc. Roy. Soc., **154** (1936), 656.
(28) E.P. Wohlfarth and J.F. Cornwell, Phys. Rev., **126** (1962), 517.