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Perturbation treatment of Percus-Yevick equation and its application to liquid platinum and palladium metals

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An analytical expression for the structure factor has been derived by using the square well potential as a perturbation over the hard sphere potential. Expressions for the isothermal pressure derivatives of the structure factor have been obtained in the $\rho^{-1/3}$ model. From these expressions the third and the fourth order structure functions are derived. Transport properties are calculated using two different methods. Calculated structure factor values for liquid platinum and palladium are in excellent agreement with the available experimental data.

1. Introduction and Theory

(A) *Structural Properties*

With the advent of the solution of the Percus-Yevick equation for the hard sphere potential by Wertheim (1963) and Thiele (1963) rapid strides have been made in explaining the properties of liquids using their results. The direct correlation function (D.C.F.), $C(r)$ obtained by Wertheim can be written as

$$C(r) = -(1-\eta)^{-4}\{(1+2\eta)^2-6\eta(1+\eta/2)^2(r/\sigma)+(1+2\eta)^2(\eta/2)(r/\sigma)^3\} \quad \ldots (1)$$

where $\eta = \pi\rho\sigma^3/6$, $\rho\,(= N/V)$ being the average number density and σ, the hard-sphere diameter.

We propose to perturb this solution with the square well attractive tail. The S.W. potential can be defined as

$$\begin{aligned} U(r) &= \infty, & r &< \sigma \\ &= -\epsilon, & \sigma &< r < \lambda\sigma \\ &= 0, & r &> \lambda\sigma \end{aligned} \quad \ldots (2)$$

here λ and ϵ corresponds to the breadth and depth of the S.W. used. Following March (1968) and Lebowitz & Percus (1966), we assume that

$$C(r) = -U(r)/k_BT, \qquad r > \sigma \quad \ldots (3)$$

where k_B is the Boltzmann constant and T the temperature in the absolute scale.

Using eqs. (1)-(3), we immediately write down the Fourier Transform of the D.C.F. as

$$\begin{aligned}\rho\widetilde{C}(K) = & -24\eta(1+2\eta)^2(1-\eta)^{-4}(k\sigma)^{-3}(\sin k\sigma - k\sigma \cos k\sigma) \\ & +144\eta^2(1+\eta/2)^2(1-\eta)^{-4}(k\sigma)^{-4}(-k^2\sigma^2)\cos k\sigma + 2k\sigma \sin k\sigma + 2\cos k\sigma - 2) \\ & -12\eta^2(1+2\eta)^2(1-\eta)^{-4}(k\sigma)^{-6}\times(-k^4\sigma^4 \cos k\sigma + 4k^3\sigma^3 \sin k\sigma + 12k^2\sigma^2 \\ & \cos k\sigma - 24k\sigma \sin k\sigma - 24\cos k\sigma + 24) \qquad \ldots \quad (4)\end{aligned}$$

Now the structure factor, $S_2(k)$ is related to the Fourier Transform of the total correlation function $C(k)$ as

$$S_2(k) = (1-\rho\widetilde{C}(k)]^{-1} \qquad \ldots \quad (5)$$

The potential parameters can be obtained by using the compressibility formula. However, we prefer to use the experimental first maxima as has been done by Ashcroft & Leckner (1966) in the case of the liquid rubidium for obtaining those parameters.

Using eqs. (4) and (5), we can easily show that

$$\rho\widetilde{C}(0) = 1-(1+2\eta)^2(1-\eta)^{-4}+8\eta\epsilon(k_BT)^{-1}(\lambda^3-1) \qquad \ldots \quad (6)$$

and

$$S_2(0) = [(1+2\eta)^2(1-\eta)^{-4}-8\eta\epsilon(k_BT)^{-1}(\lambda^3-1)]^{-1} \qquad \ldots \quad (7)$$

But $S_2(0)$ is related to the isothermal compressibility χ_T by the expression (Barton 1974)

$$S_2(0) = \rho k_B T \chi_T \qquad \ldots \quad (8)$$

using (7) and (8), we can calculate χ_T.

Egelstaff *et al* (1971) have proposed a method for determining the triplet and quadruplet correlation functions, $g_3(r, s)$ and $g_4(r, s, t)$ of liquids through the isothermal pressure derivatives of the structure factor, $S_2(k)$. The so called $\rho^{-1/3}$ model in which the interparticle distances in a liquid are assumed to vary inversely as the cube root of the average number density, ρ for isothermal changes of pressure describes the correlation functions well at or near the triple point.

Following Egelstaff (1971) the relation between $[\partial S_2(k)/\partial P]_T$ and the correlation term $H(\mathbf{r}, \mathbf{s})$ over the superposition approximation can be written as

$$\begin{aligned}&\rho^2 \int_v \exp\,(i\mathbf{k}.\mathbf{r})\,d\mathbf{r}.\int_v \mathbf{H}(\mathbf{r}, \mathbf{s})d\mathbf{s} \\ &= (2\pi)^{-3}\rho^{-1}[S_2(k)-1]^*[S_2(k)-1]^2+[S_2(k)-1][S_2(0)+S_2(k)-1] \\ &\qquad\qquad -\rho k_BT[\partial S_2(k)/\partial P] \\ &\equiv \widetilde{H}(k)\end{aligned}$$

where $\quad A^*B \equiv \int_v A(\mathbf{k}-\mathbf{k}')B(\mathbf{k}')d\mathbf{k}' \qquad \ldots \quad (10)$

In the $\rho^{-1/3}$ model, $[\partial S_2(k)/\partial P]_T$ becomes

$$\rho k_B T\left[\frac{\partial S_2(k)}{\partial P}\right]_T = -\frac{1}{3}kS_2(0)\left[\frac{\partial S_2(k)}{\partial k}\right]_T \qquad \ldots (11)$$

Using eqs. (4) and (5), we have

$$\rho k_B T\left[\frac{\partial S_2(k)}{\partial P}\right]_T = 8S_2(0)[S_2(k)]^2\eta(k\sigma)^{-6}\times$$

$$[\alpha(k\sigma)^3\{(k^2\sigma^2-3)\sin k\sigma+3k\sigma\cos k\sigma\}+\beta(k\sigma)^2\{(4k^2\sigma^2-8)\cos k\sigma$$
$$+(k^2\sigma^2-8)k\sigma\sin k\sigma+8\}+\gamma\{(k^4\sigma^4-12k^2\sigma^2+24)\times 6\cos k\sigma+$$
$$+(k^4\sigma^4-24k^2\sigma^2+144)\times k\sigma\sin k\sigma-144\}-(\epsilon/k_BT)(k\sigma)^3\times\{(\lambda^2k^2\sigma^2-3)\sin\lambda k\sigma$$
$$+3\lambda k\sigma\cos\lambda k\sigma+(3-k^2\sigma^2)\sin k\sigma-3k\sigma\cos k\sigma\}] \qquad \ldots (12)$$

Following Egelstaff *et al* (1972), we can show that the quadruplet correlation function is related to the second pressure derivative of $S_2(k)$ as

$$(\rho k_BT)^2\left[\frac{\partial^2 S_2(k)}{\partial P^2}\right]_T = \rho k_BT\left[\frac{\partial S_2(k)}{\partial P}\right]_T +$$

$$[1-S_2(k)]\times\rho k_BT\left[\frac{\partial S_2(0)}{\partial P}\right]_T+[3S_2(0)-2S_2^2(0)]\times[1-S_2(k)]$$

$$+\rho\int_v\exp(i\mathbf{k}.\mathbf{r})d\mathbf{r}.\rho\int_v d\mathbf{s}\rho k_BT\left[\frac{\partial g_3(r,s)}{\partial P}-\frac{\partial g(s)}{\partial P}-\frac{\partial g(r-s)}{\partial P}\right] \qquad \ldots (13)$$

Using eqs. (4) and (5), we have

$$(\rho k_BT)^2[\partial^2 S_2(k)/\partial P^2]_T = -\tfrac{8}{3}\eta[S_2(k).S_2(0)]^2(k\sigma)^{-6}\times$$
$$[\alpha(k\sigma)^3\times\{(k^2\sigma^2-12)k\sigma\cos k\sigma+(12-5k^2\sigma^2)\sin k\sigma\}+\beta(k\sigma)^2\times$$
$$\{(k^4\sigma^4-20k^2\sigma^2+40)\cos k\sigma+(20-3k^2\sigma^2)\times 2k\sigma\sin k\sigma-40\}+$$
$$+\gamma\{(k^6\sigma^6-42k^4\sigma^4+504k^2\sigma^2-1008)\cos k\sigma+(-k^4\sigma^4+21k^2\sigma^2-126)\times$$
$$8k\sigma\sin k\sigma+1008\}-(\epsilon/k_BT)(k\sigma)^3\{(12-5\lambda^2k^2\sigma^2)\sin\lambda k\sigma+(\lambda^2k^2\sigma^2-12)\times$$
$$\lambda k\sigma\cos\lambda k\sigma+(5k^2\sigma^2-12)\sin k\sigma+(12-k^2\sigma^2)k\sigma\cos k\sigma\}]$$

$$-\tfrac{2}{3}\rho k_BT\left[\frac{\partial S_2(k)}{\partial P}\right]_T\times[2S_2(0)-3\rho k_BT\times S_2^{-1}(k)\left[\frac{\partial S_2(k)}{\partial P}\right] \qquad \ldots (14)$$

Using eqs. (9)-(14), we can calculate $[\partial S_2(k)/\partial P]_T$, $[\partial^2 S_2(k)/\partial P^2]_T$ and the integrals in eqs. (9) and (13).

Using the general theory of fluctuations of thermodynamic variables developed by Callen (1960), Ballentine & Lakshmi (1975) have recently evolved a method of evaluating higher order structure functions in the long wavelength limit. They have shown that the so-called n-th order structure function $S_n(k_1, k_2, \ldots, k_{n-1}, 0)$ is given by

$$S_n(k_1, k_2, \ldots, k_{n-1}, 0)$$

$$= \rho k_B T \left[\frac{\partial}{\partial P} S_{n-1}(k_1, \ldots, k_{n-1})\right]_T + S_2(0).S_{n-1}(k_2, \ldots, k_{n-1}) \qquad \ldots \quad (15)$$

For $n = 3$, we have :

$$S_3(k, -k, 0) = \rho k_B T[\partial S_2(k)/\partial P]_T + S_2(0).S_2(k) \qquad \ldots \quad (16)$$

and for $n = 4$, in a limiting case,

$$S_4(k, -k, 0, 0) = \rho k_B T[\partial^2 S_2(k)/\partial P^2]_T + \rho k_B T\{S_2(k)[\partial S_2(0)/\partial P]_T + 3S_2(0) \times [\partial S_2(k)/\partial P]_T\} + S_2^2(0).S_2(k) \qquad \ldots \quad (17)$$

They have also shown that

$$S_3(0, 0, 0) = S_2^2(0).\{2 + \chi_T^{-2}[\partial \chi_T/\partial P]_T\} \qquad \ldots \quad (18)$$

and

$$S_4(0, 0, 0, 0) = S_2^3(0) \times \{6 + 7\chi_T^{-2}[\partial \chi_T/\partial P]_T + \chi_T^{-3}[\partial^2 \chi_T/\partial P^2]_T\} \qquad \ldots \quad (19)$$

We can use these equations to calculate $S_3(k, k, 0)$ $S_4(k, -k, 0, 0)$, $S_3(0, 0, 0)$ and $S_4(0, 0, 0, 0)$ using this model using the same potential parameters as are used to compute $S_2(k)$.

(*B*) *Transport properties*

It is important to note that the structure factor data are very useful in evaluation of certain transport properties of liquids. The following equations developed by Davis *et al* (1961) and J. Palyvos *et al* (1967) have been utilised for the evaluation of shear-viscosity η_S, bulk viscosity η_B, thermal conductivity λ_T and self-diffusion co-efficient D from the computed structure factor data. It may be mentioned that we have used effective mass m^* instead of ordinary mass m by them. The significance of m^* will be explained in what follows

$$\eta_s = \frac{5}{16\sigma^2}\left(\frac{m^* k_B T}{\pi}\right)^{\frac{1}{2}} \times \left\{ \frac{\left(1 + \frac{8}{3}\eta[g(\sigma) + \lambda^3 g(\lambda\sigma)\psi]\right)^2}{g(\sigma) + \lambda^2 g(\lambda\sigma)\left[\Xi + \frac{1}{6}\left(\frac{\epsilon}{k_B T}\right)\right.} + \frac{48}{25\pi}(4\eta)^2[g(\sigma) + \lambda^4 g(n\sigma)\Xi] \right\} \qquad \ldots \quad (20)$$

$$\eta_B = \frac{16\eta}{\pi\sigma^2}\left(\frac{m^* k_B T}{\pi}\right)^{\frac{1}{2}}[g(\sigma) + \lambda^4 g(\lambda\sigma)\Xi] \qquad \ldots \quad (21)$$

$$\lambda_T = \frac{75}{64\sigma^2}\left(\frac{k_B{}^3T}{\pi m^*}\right)^{\frac{1}{2}} \left\{ \frac{\left(1+\frac{12}{5}\eta[g(\sigma)+\lambda^3 g(\lambda\sigma)\psi]\right)^2}{g(\sigma)+\lambda^2 g((\lambda\sigma)\left[\,\Xi+\frac{11}{16}\times(\epsilon/k_BT)^2\,\right]} \right.$$

$$\left. +\frac{32}{25\pi}(4\eta)^2[g(\sigma)+\lambda^4(\lambda\sigma)\,\Xi\,] \right\} \qquad \ldots \quad (22)$$

$$D = \frac{3}{8\rho\sigma^2}\times\left(\frac{k_BT}{\pi m^*}\right)^{\frac{1}{2}}[g(\sigma)+\lambda^2 g(\lambda\sigma)\Xi]^{-1} \qquad \ldots \quad (23)$$

Here m^* is the effective mass of atoms and ψ and Ξ have been defined as

$$\Psi = 1-\exp(\epsilon/k_BT)+(\epsilon/2k_BT)\left(1+\frac{4}{\sqrt{\pi}}\exp(\epsilon/k_BT)\right)$$

$$\times\int_{(\epsilon/k_BT)^{\frac{1}{2}}}^{\infty}\exp(-x^2)x^2dx \qquad \ldots \quad (24)$$

and

$$\Xi = \exp(\epsilon/k_BT)-\epsilon/k_BT-2\int_0^{\infty}x^2(x^2+\epsilon/k_BT)^{\frac{1}{2}}\exp(-x^2)dx \qquad \ldots \quad (25)$$

It may be pointed out that the $g(r)$ values at $r=\sigma$ and $r=\lambda\sigma$ can be obtained from a smooth graph of $g(r)$ versus r which in turn can be computed by the Fourier inversion of $S(k)$. The ψ and Ξ values can be obtained from the literature (Luks *et al* 1966).

Also equations developed by Rao *et al* (1976) have been used for calculating surface tension, γ_s, shear viscosity η_s, self-diffusion co-efficient D. These equations are :

$$\gamma_s = -\frac{\pi\rho^2k_BT\sigma^4}{8}[g(\sigma)-\lambda^4(1-\exp(-\epsilon/k_BT))g(\lambda\sigma)] \qquad (26)$$

$$\eta_s{}^2 = \frac{4\pi m^*k_BT\sigma^3\rho^{7/3}}{7.848\times15}\times[\sigma\{g'(\sigma)+(1-\exp(\epsilon/k_BT))\times\lambda^4g'(\lambda\sigma)\}$$

$$-5\{g(\sigma)+(1-\exp(\epsilon/k_BT))\lambda^3g(\lambda\sigma)\}] \qquad \ldots \quad (27)$$

$$D = \frac{kT}{2m^{*\frac{1}{2}}\sigma}\left(\frac{\pi\rho k_BT}{3}\right)^{-1/2}\times[g'(\sigma)+(1-\exp(\epsilon/k_BT))\times g'(\lambda\sigma)] \quad \ldots \quad (28)$$

Here, m^* the effective mass is given by

$$m^* = m\eta g(\sigma)(l'/\sigma)^3 \qquad \ldots \quad (29)$$

where l^* is the so-called correlation length. $g'(r)$ can be computed from the relation

$$g'(r) = -[g(r)-1]/r + (2\pi^2\rho)^{-1} r^{-1} \int^{\infty} S(k)-1]k^2 \cos kr\, dk \qquad \ldots (30)$$

$g'(\sigma)$ and $g'(\lambda\sigma)$ can be obtained from a smooth curve obtained by plotting $g'(r)$ against r.

2. RESULTS AND DISCUSSIONS

$S_2(k)$ values of liquid platinum at 1780°C and liquid palladium at 1580°C calculated from eqs. (4) and (5) are shown in figure 1 along with experimental points obtained by Waseda (1975). Potential parameters used are shown in table 1. The argument between calculated and experimental values is excellent. This fact leads us to conclude that the present model is by far the best available one to explain the structural properties of liquid platinum metals. Values of the isothermal compressibility, χ_T of these metals are also calculated using eqs.

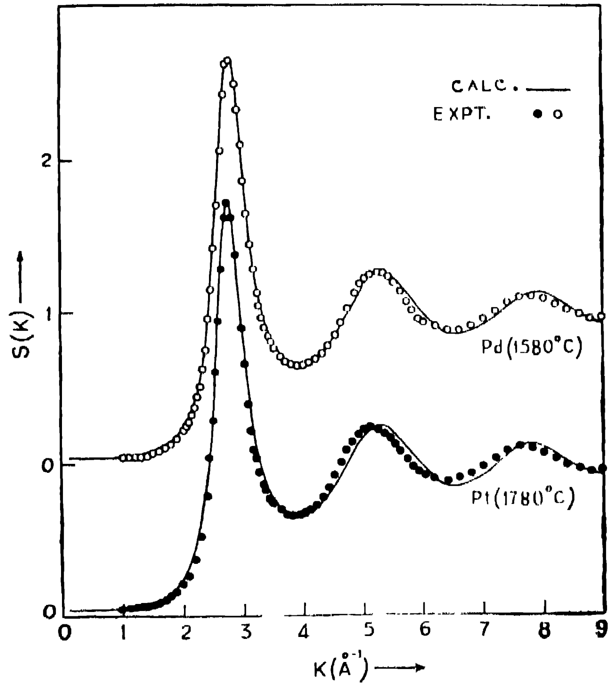

FIG. 1. Structure factor $S(k)$ for liquid platinum and palladium are plotted against k.

(7) and (8). These values are also shown in table 1. Unfortunately no experimental data are available uptil now to compare with our results.

$$[\partial S_2(k)/\partial P]_T, \quad [\partial^2 S_2(K)/\partial P^2]_T,$$

$\tilde{H}(k)$ and the integral in eq. (13) are calculated by using eqs. (12), (14), (9) and (13) respectively and are shown in figures 2, 4, 3 and 5 respectively. The convolution in equation (9) has been performed by a Fourier transform technique as followed by Egelstaff (1971) taking care to ensure the orthogonality of the discrete sine transforms e.g. (Lado 1971). The general shapes of the curves in all the cases are similar to those obtained by Egelstaff *et al* (1971) and Rao *et al* (1975) and endorsed by experimental observations of Egelstaff *et al* (1971). In the absence of experimental data, we have every reason to believe our results.

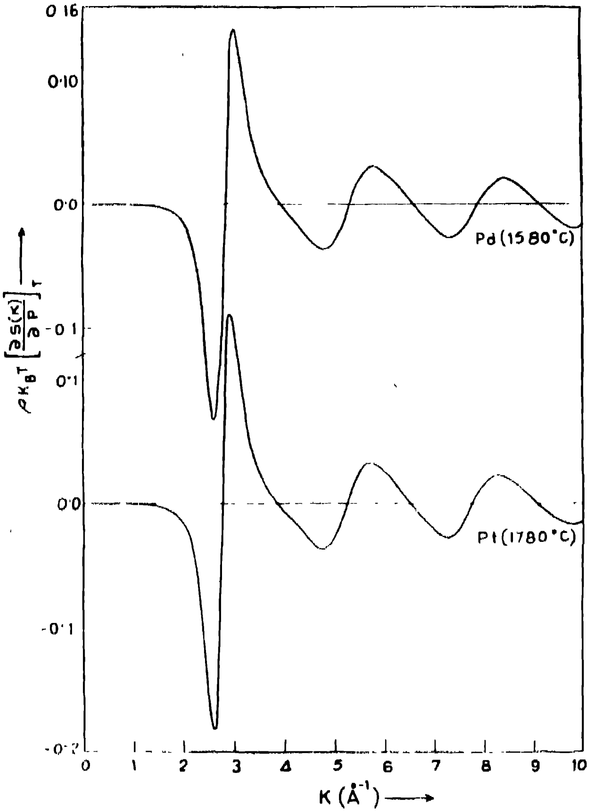

Fig. 2. $Pk_BT \left[\frac{\partial S_2(k)}{\partial P}\right]_T$ vs. k curves for liquid platinum and palladium.

Table 1 Potential parameters, isothermal compressibility and structure functions in the long wavelength unit of liquid platinum and palladium.

Liquid	Temperature (°K)	ρ (atom Å^{-3})	σ_e (Å)	ϵ/k_B (°K)	λ	$\chi_T \times 10^{12}$ cm. sec^2 gm^{-1}	$S_2(o) \times 10^2$	$S_3(0, 0, 0) \times 10^3$	$S_4(0, 0, 0,0) \times 10^4$
Platinum	2053	0.0577	2.42	332.28	1.52	1 983	3.243	−3.206	5.470
Palladium	1853	0.0594	2.40	245.49	1.50	2.078	3.157	−3.031	4.990

Table 2 Transport properties of liquid platinum and palladium using the methods of Davis et al and Rao et al.

Liquid	$\eta_S \times 10^2$ (Poise)		$\eta_B \times 10^3$ (Poise)		$\lambda_T \times 10^4$ (cal cm^{-1}sec^{-1} deg K^{-1})	$D \times 10^5$ cm^2/sec.		$\gamma_S \times 10^{-2}$ (dyne cm^{-1})
	Davis et al	Rao et al	Davis et al	Rao et al	Davis et al	Davis et al	Rao et al	Rao et al
Platinum	4.184	1.787	6.393	—	2.416	5.960	5.151	1.517
Palladium	3.050	1.247	4.611	—	3.196	7.462	6.568	1.614

It may be mentioned that $\rho^{-1/3}$ model gives a worng value for $\rho k_B T[\partial S_2(0)/\partial P]$ But in this model, the value of $\rho k_B T \left[\frac{\partial S_2(0)}{\partial P}\right]_T$ does not come wrong as it is calculated using eq. (7).

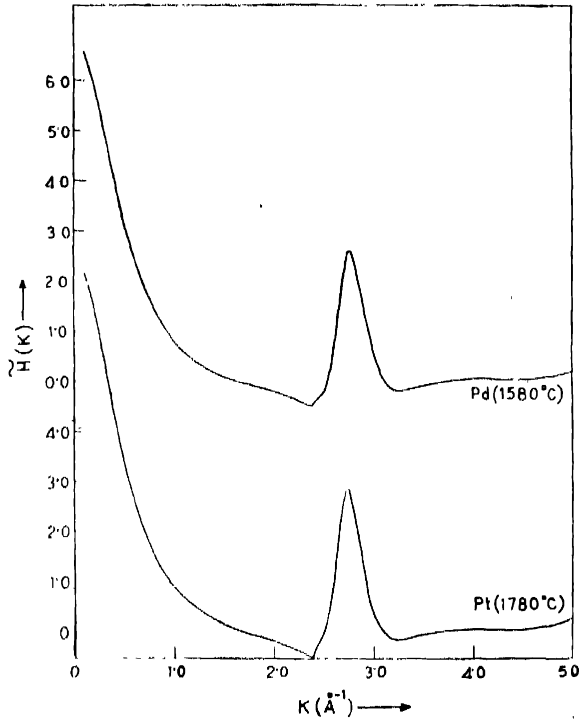

FIG. 3. $\bar{H}(k)$ vs. k curves for liquid platinum and palladium.

$S_3(k, -k, 0)$ and $S_4(k, -k, 0, 0)$ calculated from eqs. (16) and (17) respectively are shown in figures 6 and 7 respectively. Values of $S_3(0, 0, 0)$ and $S_4(0, 0, 0, 0)$ are calculated from equations (18) and (19) respectively. Unfortunately no experimental data are available uptil now. But we note that the shapes of the curves and the values of $S_3(0, 0, 0)$ and $S_4(0, 0, 0, 0)$ are very similar to those obtained by Ballentine & Lakshmi (1975).

Transport properties are calculated using eqs. (20)-(30) are shown in Table 2. Unfortunately no experimental data are available upto date. But it is gratifying to note that the values are of the expected order of the liquid metals and the values calculated by two different methods are close to each other. Hence these results are self-consistent.

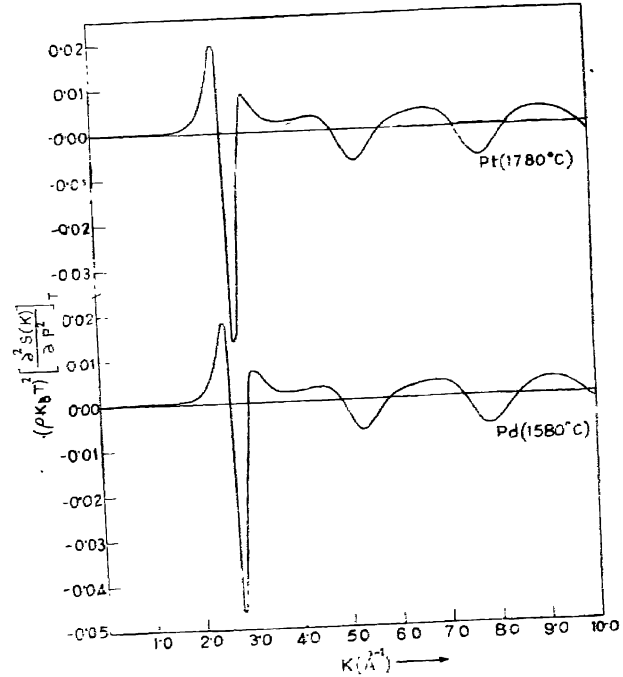

Fig. 4. $(\rho k_B T)^2 \left[\frac{\partial^2 S_2(k)}{\partial P}\right]_T$ vs. k curves for liquid platinum and palladium.

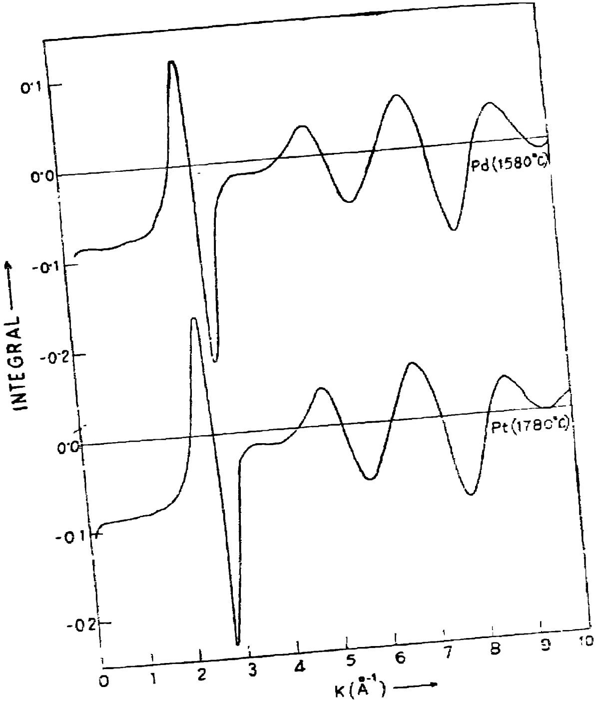

Fig. 5. Integral in Eqn. 5 vs. k curves for liquid platinum and palladium.

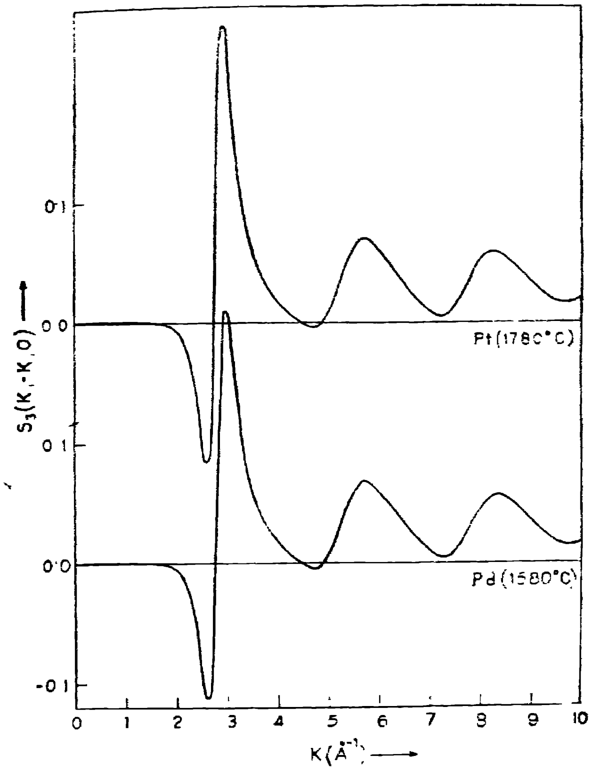

FIG. 6. S_3 $(k, -k, 0)$ vs. k curves for liquid platinum and palladium.

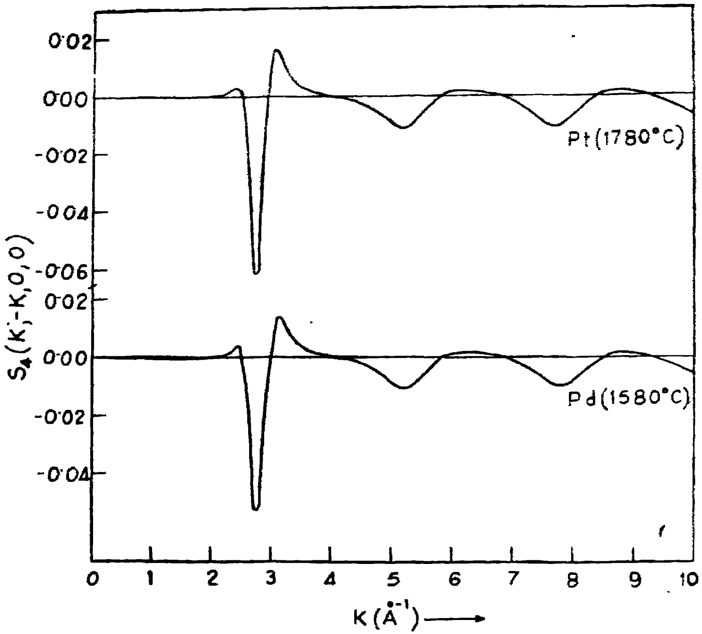

FIG. 7. S_4 $(k, -k, o, o)$ vs. k curves for liquid platinum and palladium.

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