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***Ab initio* calculations of superconductivity in palladium under pressure**

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We have calculated the phonon dispersion and the electron-phonon interaction in palladium at ambient and under pressure using *ab initio* methods and evaluated superconducting transition temperature on the basis of the BCS theory. At ambient pressure, we have evaluated the electron-phonon coupling constant to be $\lambda = 0.377$ by the use of the density-functional perturbation theory, and estimated the spin fluctuation effect in relation to the experimental data of specific heat. The vanishing of the superconducting transition at ambient pressure is resulted from the spin fluctuation effect. The spin fluctuation effect reduces with increasing pressure, and the superconductivity appears under pressure.

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Superconductivity in platinum metals, palladium (Pd), platinum (Pt), and rhodium (Rh), has been investigated with interest in the triplet pairing.¹⁻⁴ Rh becomes superconductor at the lowest transition temperature in all elements $T_c = 325 \mu\text{K}$,⁵ while, in Pd and Pt, superconductivity has not been observed.

The spin fluctuation effect has been thought to play an important role in these metals and to provide a reason for the absence of superconductivity in Pd and Pt. Irradiated Pd film and Pt powder, however, can be transformed into superconductors.^{6,7} The transition temperature of pure Pd film which is irradiated with He^+ ions is 3.2 K at the highest and depends on thickness of the film and conditions of irradiation. The compacted, high purity Pt powder of average grain size $\sim 2 \mu\text{m}$ can also become a superconductor. Its transition temperature T_c strongly depends on the compression of the powder: those were found to be $0.62 \leq T_c \leq 1.38 \text{ mK}$ for the packing fraction $0.8 \geq f \geq 0.5$.

The above experimental results suggest that the weakening of the spin fluctuation might lead to the superconducting transition. In irradiated Pd film the defects produced by the irradiation might smear out the sharp peak in the density of state at the Fermi level $N(E_F)$, which would reduce the Stoner enhancement factor and hence the spin fluctuation. The decrease in $N(E_F)$, however, would lead to decrease in the electron-phonon coupling (BCS phonon parameter λ) and this would be detrimental to the superconductivity. On this point some theoretical studies^{8,9} have shown that in irradiated Pd the decrease in spin fluctuation does not accompany the decrease in $N(E_F)$. It has been further reported that in Pt powder spin-orbit scattering might weaken the spin fluctuation to the extent that superconducting transition can occur in single Pt granule.¹⁰

The influence of magnetic impurity upon proximity effect in platinum metals has also been investigated.¹¹ The proximity effect in Pt and Pd is greatly suppressed if these metals include magnetic impurity. When Pt does not include mag-

netic impurity, the proximity effect is observed. The screening length may increase with decreasing temperature and reach a value which is expected in copper. With magnetic impurity, the magnetic moment of the impurity is enhanced by the spin fluctuation and causes the pair-breaking effect which may suppress the proximity effect.

In this paper we evaluate the superconducting transition temperature, assuming phonon-mediated superconductivity and take spin fluctuation effect into account. Since the spin fluctuation effect would decrease with increasing pressure, we expect the superconducting transition in Pd under pressure. We calculate the phonon dispersion and the electron-phonon coupling constant using the linear response theory on the basis of *ab initio* calculation methods which have been used to evaluate the T_c of some other substances.¹²⁻¹⁴

In Ref. 15 we reported a preliminary results of the lattice dynamics calculations and the superconducting transition temperatures in Pd at ambient pressure and at 50 GPa based on the local density approximation (LDA). We have, in the present work, performed the similar calculations in the generalized gradient approximation (GGA) in addition to the LDA and studied the pressure dependencies of the superconducting transition temperature. In the calculations we have paid special attention to the muffin-tin radius which is one of the parameters used in the band theoretical calculation. Some values of the muffin-tin radii cause numerical errors and considerably affect the results of both the phonon frequency and the electron-phonon coupling constant. At some pressures we have checked the results by changing the value of the radius a little, obtained smooth pressure dependences of the results, and revised the results of the previous work.

Here we briefly summarize the methods we use. We use the full-potential linear muffin-tin orbital (FP-LMTO) method¹⁶ for the band theoretical calculation. The phonon frequencies are calculated based on the linear response theory.¹⁷ For the GGA we adopt the formula proposed by Perdew *et al.*¹⁸ with the expression of the exchange-correlation functional by Vosko *et al.*¹⁹ We use

FIG. 1. Phonon dispersions of palladium for the fcc structure at ambient pressure. The LDA ($\square$), GGA ($\triangle$), and experimental data points ($\bullet$) (Ref. 20) are shown. The line connecting the calculated data points are for guide to the eyes.

$3k\text{-}spd\text{-}LMTO$ basis sets with the one-center expansion inside the muffin-tin spheres up to $l_{\max}=6$. We express the induced charge densities and the screened potentials inside the muffin-tin spheres by the spherical harmonics up to $l_{\max}=6$ and those in the interstitial region by the plane waves with the cutoff corresponding to the (24,24,24) fast-fourier-transform mesh in the unit cell of the real space. For the electronic states calculation we use the k -point mesh (16,16,16) over the Brillouin zone and calculate the phonon frequencies at irreducible q points on the (8,8,8) mesh.

Before the lattice dynamics calculations we carried out the total energy calculations and compared those between the fcc and bcc structure at several pressures. We have confirmed that the fcc structure is energetically more favorable than the bcc at least up to 50 GPa. Observing this result, we carry out the lattice dynamics and subsequent calculations on the fcc lattice.

We study the phonon dispersion in both LDA and GGA. In Fig. 1 we show the results along some high symmetry lines at ambient pressure with the experimental data points.²⁰ The LDA curves are in good agreement with the experimental data, while the GGA ones are somewhat lower than the experiments. In Table I, we list the values of the phonon frequencies at the equilibrium volume for some q points, where our LDA and GGA results are compared with experimental²⁰ and other theoretical¹² ones. The equilibrium volumes V obtained by our calculation are given by the ratio

TABLE I. The phonon frequencies of palladium for the fcc structure at equilibrium volume. The equilibrium volumes are given by the ratio V/V_0 , where V is the theoretically obtained value of the volume and V_0 the experimental one at ambient pressure. The phonon frequencies of experimental (Ref. 20) and those by another theoretical study (Ref. 12) are also shown for comparison.

	X_L [THz]	X_T [THz]	L_L [THz]	L_T [THz]	V/V_0
LDA	6.69	4.82	7.12	3.44	0.973
GGA	5.77	4.24	6.13	3.03	1.052
Exp. (Ref. 20)	6.72	4.64	7.02	3.34	
LDA (Ref. 12)	7.17	5.01	7.39	3.60	0.975

FIG. 2. Phonon DOS of palladium for the fcc structure at ambient pressure and at 50 GPa. The results of the LDA are shown.

V/V_0 , where V_0 is the experimental value of the volume at ambient pressure. Our LDA results are in better agreement with the experiments than the other theoretical ones. In the subsequent studies we mainly show the results of the LDA calculations.

In Fig. 2 we show the phonon density of state (DOS) obtained by the LDA at ambient pressure and at 50 GPa. The phonon frequencies increase with increasing pressure and no phonon anomalies have been observed.

Then we carry out the calculation of the electron-phonon matrix elements using the same (8,8,8) mesh over the Brillouin zone. In Table II, we show the electron-phonon coupling constant λ with the Hopfield parameter η at each pressure. In the same table, the lattice constants a , electronic DOS at the Fermi level $N(E_F)$, the averaged phonon frequencies $\langle\omega^2\rangle^{1/2}$, and the logarithmic-averaged phonon frequencies $\omega_{\log}$ are also shown. (See Ref. 21 for the definitions of $\langle\omega^2\rangle^{1/2}$ and $\omega_{\log}$.)

We first evaluate the transition temperature T_c using the electron-phonon coupling constant and the phonon frequency obtained above. We use the Allen-Dynes formula²¹

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^* (1 + 0.62\lambda)}\right), \quad (1)$$

where μ^* denotes the effective screened Coulomb repulsion constant. If we assume the μ^* to be 0.10, which is the value usually taken for transition metals, we obtain the superconducting transition temperature T_c , 0.514 K at ambient pressure, where our value of λ is 0.377. This value of the λ is close to other works.^{12,22} If we assume 0.15 for the value of μ^* , we obtain a much reduced T_c of 0.084 K.

In the experimental studies at ambient pressure, however, the superconducting transition in Pd has not been observed so far. There exists a speculation that the transition might be suppressed by the effects of spin fluctuation or magnetic impurity. The spin fluctuation effect, however, may reduce under pressure, and the phonon-mediated superconductivity suppressed at ambient pressure may appear under pressure.

We estimate the spin fluctuation effect by the treatment of Mazin *et al.*²³ using the following modified Allen-Dynes formula:

TABLE II. Pressure dependencies of the lattice constants a , the electronic DOS at the Fermi level $N(E_f)$, the averaged phonon frequencies $\langle\omega^2\rangle^{1/2}$, the logarithmic-averaged phonon frequencies $\omega_{\log}$, the electron phonon coupling constant λ , the Hopfield parameter η , the superconducting transition temperature without and with taking into account spin fluctuation effect T_c, T_c^{SF} , respectively. For the calculations of superconducting transition temperature T_c , the effective screened Coulomb repulsion constant μ^* is assumed to be 0.15–0.10, while for the calculations of T_c^{SF} , μ^* is fixed at 0.10. The results are obtained by the LDA calculations.

P[GPa]	a [a.u.]	$N(E_f)\left[\frac{\text{states}}{\text{Ry} \times \text{cell}}\right]$	$\langle\omega^2\rangle^{1/2}$ [K]	$\omega_{\log}$ [K]	λ	η [Ry/a.u. ²]	T_c [K]	T_c^{SF} [K]
0	7.26545	33.653	197.10	173.87	0.3773	0.05700	0.084–0.514	0.000
5	7.21663	32.613	213.86	188.67	0.3568	0.06345	0.046–0.384	0.002
10	7.17180	31.741	223.21	196.99	0.3454	0.06692	0.031–0.318	0.016
15	7.12956	31.182	229.22	200.94	0.3362	0.06869	0.021–0.264	0.022
20	7.09026	30.672	235.88	205.62	0.3274	0.07083	0.014–0.218	0.024
30	7.02305	29.548	248.78	216.28	0.3122	0.07513	0.006–0.152	0.024
40	6.96582	28.478	260.60	225.70	0.2994	0.07906	0.003–0.107	0.021
50	6.91489	27.552	271.63	234.63	0.2906	0.08338	0.001–0.082	0.018

$$T_c^{SF} = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1 + \lambda + \lambda_{SF})}{\lambda - \lambda_{SF} - \mu^* [1 + 0.62(\lambda + \lambda_{SF})]}\right), \quad (2)$$

The parameter λ_{SF} represents the effect of ferromagnetic spin fluctuation.

At ambient pressure, we evaluate the λ_{SF} by the relation $\lambda_{SF} = \lambda_{s-h} - \lambda$ using the equation $1 + \lambda_{s-h} = 3\gamma/2\pi^2 k_B N(E_f)$, where γ is the electronic part of the specific-heat coefficient and $N(E_f)$ the electronic density of state at the Fermi level. We obtain the $\lambda_{s-h} = 0.612$ using the experimental data^{24,25} ($\gamma = 9.4$ mJ/mole K^2), and our results of electronic density of state at the Fermi level. With the value of λ_{s-h} and $\lambda = 0.377$, we evaluate λ_{SF} to be 0.235, at ambient pressure. This value of λ_{SF} , 0.235, suppresses the superconducting transition, because the denominator of the exponent in Eq. (2) is almost zero. This means that the vanishing of the superconducting transition at ambient pressure results from large spin fluctuation effect and is consistent with the experimental facts.

To evaluate the λ_{SF} in Eq. (2) under pressures, we follow again Mazin *et al.*'s treatment within the framework of the Stoner model, assuming the relation,

$$\lambda_{SF} = \frac{\alpha}{1 - IN(E_f)}, \quad (3)$$

where I and $N(E_f)$ are the Stoner factor and the density of state at the Fermi level, and α is a parameter which characterizes the band structure and q dependence of the bare magnetic susceptibility. Since Pd has been believed to be very close to ferromagnetic instability at ambient pressure, we tentatively assume the value of $IN(E_f)$ to be 0.98, from which we determine the value $\alpha = 0.0047$ through Eq. (3) using the value of $\lambda_{SF} = 0.235$. Then we determine the value of I using our value of $N(E_f)$ at ambient pressure.

Using $N(E_f)$ at each pressure and assuming I and α to be independent of pressure in Eq. (3), we obtain the λ_{SF} at each pressure and evaluate the T_c^{SF} using Eq. (2). The T_c^{SF} at 50 GPa evaluated by this procedure is 0.018 K. In Table II, we list our results of the superconducting transition temperatures T_c^{SF} at several pressures and compared with those obtained from Eq. (1). The above results of the T_c and the T_c^{SF} are plotted in Fig. 3.

If we assume $IN(E_f) = 0.93$ (this corresponds to the Stoner enhancement factor 15),²⁶ the transition temperatures decrease to $T_c^{SF} < 0.1$ mK under pressure. This result shows that if the system is near the ferromagnetic instability at ambient pressure, the spin fluctuation effect may decrease rapidly with increasing pressure and higher transition temperature is expected under pressure. Though our results of T_c^{SF} in Pd under pressure are different from the result of Ref. 27, the T_c^{SF} would increase toward the values evaluated by the

FIG. 3. Pressure dependencies of superconducting transition temperatures in palladium for the fcc structure. The result (●) is obtained from band structure calculations in the LDA and the spin fluctuation effect is taken into account. The T_c^{SF} values are scaled by a factor 10. The results obtained both in the GGA (▲) and the LDA (■) without the spin fluctuation effect are also shown.

Eq. (1) if the spin fluctuation effect in Pd would decrease enough in certain pressure regions.

We have calculated the phonon dispersions and the electron phonon matrix elements all over the Brillouin zone at various volumes using the linear response theory on the basis of *ab initio* calculations and obtained the electron phonon coupling constants. The calculated superconducting transition temperature is 0.514 K at ambient pressure, if we use the Allen-Dynes formula and disregard the spin fluctuation effect, and it gradually decreases with increasing pressure to 0.082 K at 50 GPa. The large spin fluctuation effect is

expected, when we evaluate its parameter using its relation with the experimental data of specific-heat, and it suppresses the superconducting transition at ambient pressure. But our results of rather high T_c without the spin fluctuation effect may suggest the possible observation of the superconductivity in Pd under pressure, though more detailed studies of the pressure dependence of the spin fluctuation effect are necessary.

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