Pressure Dependence of the Knight Shift in Pt

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The Knight shift K of Pt^{195} in platinum metal was measured as a function of hydrostatic pressure up to about 8000 kg/cm², at three temperatures, 64.8°, 0°, and −78.0°C. $|K|$ decreases with increasing pressure. The pressure dependence of K changes markedly with temperature, following a T^2 law. The temperature dependence of K at constant volume, which has been derived from the previously obtained $K(T)$ at constant pressure and the present pressure-dependence data, may be written as $K=K_0+BT^2+O[(T/T_d)^4]$, where T_d is the degeneracy temperature of the d-band holes. These observations agree with the model proposed by Clogston *et al.* The experimental volume dependence of K_0 and B is analyzed using a standard band model. The volume dependences of (i) the Fermi depths of the s and the d band, (ii) the exchange parameter for the d band, and (iii) the number of the d holes are derived from the experimental data.

1. INTRODUCTION

THE Knight shift K of the Pt^{195} nuclear magnetic resonance (NMR) in platinum metal has negative sign, and its magnitude is strongly dependent on temperature.[1] Clogston *et al.*[2] and Shimizu and Katsuki[3] have explained these anomalous results by comparing the temperature dependences of the susceptibility and the Knight shift in this metal. They also derived some of the band parameters from the analysis.

Since the observed temperature dependence $(\partial \ln K/\partial T)_P$ consists of an explicit dependence $(\partial \ln K/\partial T)_V$, the one to be compared with the theory, and a correction due to thermal expansion

$$(\partial \ln K/\partial \ln V)_V(\partial \ln V/\partial T)_P,$$

it is informative to separate these two contributions experimentally using pressure-dependence data. The deduction of the volume dependence for some of the band parameters from the pressure data is also of interest.

2. EXPERIMENTAL PROCEDURE AND THE RESULTS

The platinum powder (99.99%) was purchased from A. D. McKay, Inc. Since the density of Pt is high and the surface of the powder particles is not easily tarnished, when a pressure is applied the particles tend to contact one another electrically. As a consequence the Q of the surrounding rf coil drops to such an extent as to stop the oscillations of the marginal oscillator in the spectrometer. The same problem was encountered when the pure quadrupole resonance frequency in gallium metal was measured as a function of pressure.[4] In that case the solution was to coat the surface of the Ga particles with a thin layer of glue (Duco cement). In the case of platinum, however, this coating procedure was not successful, probably because the density of the particles is even higher. The degradation of the Q value was prevented by mixing the Pt powder with lead oxide powders (Pb_3O_4) and adding a small amount of viscous silicon grease. The sample was installed in a Be-Cu pressure bomb.[5]

The hydrostatic pressure was generated by a Bridgman-type generator which was purchased from the Harwood Engineering Company. The original package had to be modified to obtain satisfactory operation. The hydraulic ram was directly connected to the pressure bomb through a flexible stainless-steel tubing ($\frac{1}{8}$ in. o.d., 1/40 in. i.d.).[5] The magnetic field from a Varian 12-in. magnet was monitored by a sodium-metal NMR signal using a transistorized marginal oscillator detector. The frequency of this spectrometer was stabilized against the crystal oscillator of a Hewlett-Packard frequency counter through a feedback loop, consisting of a mixer between the crystal and the spectrometer frequency, a frequency-to-voltage converter, an integrator, and a voltage-sensitive diode in the tank circuit of the spectrometer. The monitor Na signal was phase-detected and fed back to the power supply of the magnet. The details of this control system have been described elsewhere.[6]

The temperature of the bomb was kept constant during the runs within ±0.02°C of the three temperatures, 64.8, 0, and −78.0°C.

The Pt^{195} NMR signal was observed with another Pound-type spectrometer, whose frequency was swept over the resonance line, while the magnetic field was kept constant with the control system described above. The center frequency of the resonance line was measured with the Hewlett-Packard frequency counter up to the highest pressures of about 8000 kg/cm². There was no noticeable change in the linewidth. In Fig. 1 the center frequency is plotted as a function of pressure at three different temperatures. The resonance frequency increases with the pressure. Since the Knight shift is

[1] T. J. Rowland, J. Phys. Chem. Solids **7**, 95 (1958).
[2] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964). Note that the definition of α_d in this reference is slightly different from that in the present article.
[3] M. Shimizu and A. Katsuki, J. Phys. Soc. Japan **19**, 614 (1964).
[4] T. Kushida and G. B. Benedek, Bull. Am. Phys. Soc. **3**, 167 (1958).
[5] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).
[6] A. H. Silver and T. Kushida, J. Chem. Phys. **38**, 865 (1963).

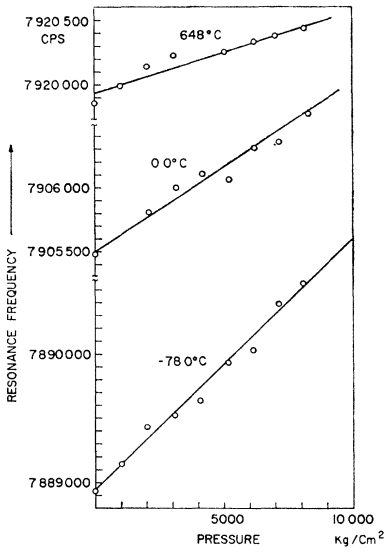

FIG. 1. The NMR frequency of Pt^{195} in platinum metal as a function of hydrostatic pressure at three temperatures. The magnetic field was kept constant during each run. Since the Knight shift K of platinum metal is negative, $|K|$ decreases with the pressure. $\partial K/\partial P$ is markedly temperature-dependent.

negative,[1] the magnitude of the Knight shift *decreases* with pressure. The pressure dependence decreases markedly with increasing temperature. The slope of the curves changes by a factor of 3 for a temperature change of about 140° centered around room temperature.

By using the compressibility of Pt metal[7] and the published values of the Knight shift,[8] one can obtain the volume dependence of the Knight shift in Table I. The $PtCl_6$ solution used as reference sample by Drain[8] is believed to have a paramagnetic shift of 0.7%.[2] The volume dependence of the Knight shift accordingly corrected is shown in the second line of Table I.

3. ANALYSIS OF THE EXPERIMENTAL DATA

Clogston *et al.*[2] have derived the band parameters of platinum metal for the effective-mass approximation.

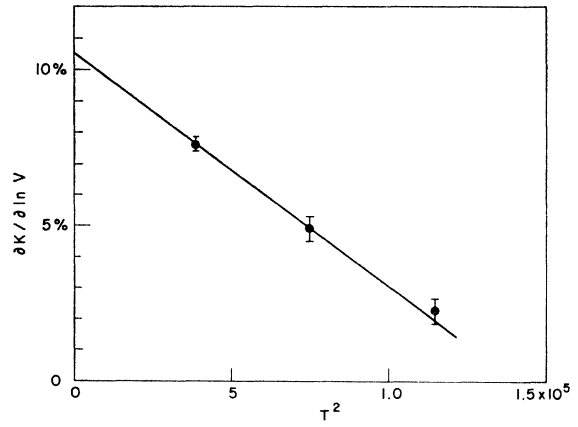

FIG. 2. The temperature dependence of the volume dependence of the Knight shift, $\partial K/\partial \ln V$. $\partial K/\partial \ln V$ changes with the temperature as T^2.

[7] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949).

[8] L. E. Drain, J. Phys. Chem. Solids **24**, 379 (1963).

TABLE I. The volume dependence of the Knight shift K in platinum metal. The third line includes the correction of the Knight-shift value due to the paramagnetic shift of the reference sample (aqueous solution of $PtCl_6$).

	Temperature (°C)		
	−78.0	0.0	+64.8
$\partial \ln K/\partial \ln V$	1.99 ±0.05	1.37 ±0.12	0.68 ±0.13
$(\partial \ln K/\partial \ln V)_{\text{corrected}}$	2.45 ±0.06	1.70 ±0.15	0.85 ±0.16

The same approximation will be used here to analyze the pressure-dependence data. Both the s and the d band are assumed to have standard forms with effective masses m_s^* and m_d^*, respectively. It is also assumed that the effective masses are independent of volume. The volume dependence, as discussed later, is probably small. If their measurements become available, the corresponding corrections can easily be made. The analysis of the present experimental data consists of two parts: (i) the $K(T)$ curve observed at constant pressure is converted into that at constant volume and the validity of the present model is checked, (ii) the volume dependence of some of the parameters in this model is obtained.

According to Ref. 2 the Pt Knight shift can be expressed as

$$K(T)=K_s+K_d(T)+K_{VV}+\delta K_{\text{dia}}. \tag{1}$$

K_s is the contribution from the s-conduction-electron hyperfine interaction, $K_d(T)$ is an indirect Knight shift from the d electrons via the core-polarization effect,[9] K_{VV} is the contribution from orbital paramagnetism, and δK_{dia} the shift due to core-diamagnestism part is negligible for Pt metal. K_s and K_{VV} are positive but smaller than the dominant negative term $K_d(T)$. For K_s and $K_d(T)$ one has[2,9]

$$K_s=(8\pi/3)\chi_s\Omega\langle|\Psi_s(0)|^2\rangle, \tag{2}$$

and

$$K_d(T)=\alpha_d\Omega\chi^d(T). \tag{3}$$

χ_s and χ_d are the volume susceptibilities of the s and the d band, respectively; and Ω is the atomic volume; $\langle|\Psi_s(0)|^2\rangle$ is the probability density for the s electron at the nucleus, averaged over the Fermi surface. The effect of the core polarization due to the exchange interaction between core and d electrons is represented by α_d. Its value has been derived from a comparison of the temperature dependences of the Knight shift and the susceptibility.[2] χ^d is the Pauli susceptibility of d holes $\chi_0^d(T)$ modified by the exchange interaction between d holes,

$$\frac{1}{\chi^d(T)}=\frac{1}{\chi_0^d(T)}-\frac{kT_{\text{ex}}}{n\beta^{*2}}. \tag{4}$$

[9] T. Muto and S. Kobayasi, J. Phys. Soc. Japan **19**, 1837 (1965).

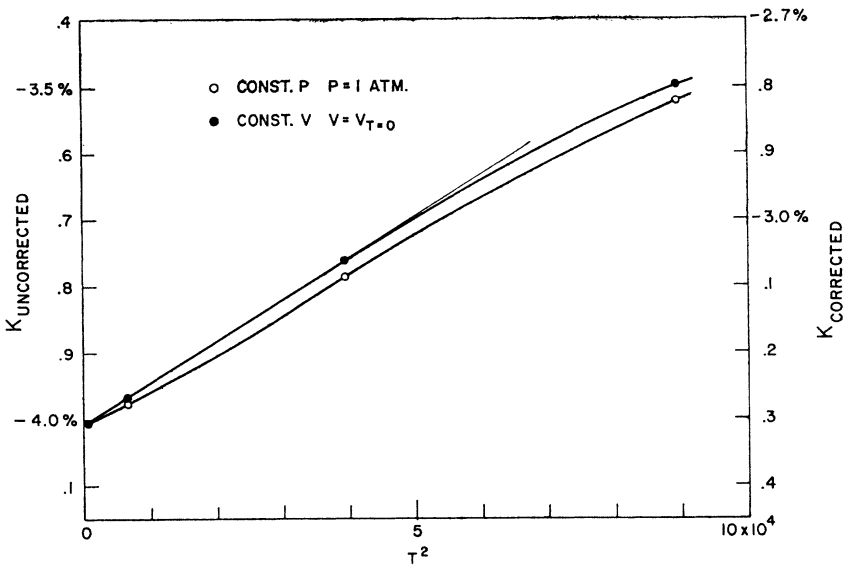

FIG. 3. The temperature dependences of the Knight shift at constant volume and constant pressure.

kT_{ex} is the exchange interaction energy, n is the number of d holes per unit volume, and β^* is an effective spin moment. $\chi_0{}^d(T)$ is given by

$$\chi_0{}^d(T)=\tfrac{3}{2}(n\beta^{*2}/kT_d)(1-\tfrac{1}{12}\pi^2(T/T_d)^2), \quad (5)$$

where kT_d is the Fermi level of the d holes. The standard band model has been used to derive Eq. (5), and the temperature dependence is approximated up to the T^2 terms. It is noted that since the value of T_d ($\approx 1100°K$) is much smaller than the values for the usual metals,[2] the deviation from the quadratic temperature dependence at room temperature is expected to be of the order of $(T/T_d)^4 \approx 1\%$.

Within this approximation, the Knight shift is

$$K(T)=K_s+K_{VV}+\frac{3\alpha_d\Omega n\beta^{*2}}{2k(T_d-\frac{3}{2}T_{ex})} \times\left(1-\frac{\pi^2 T_d}{12(T_d-\frac{3}{2}T_{ex})}\left(\frac{T}{T_d}\right)^2\right) \quad (6)$$

$$\equiv K_0+BT^2. \quad (7)$$

The first three terms in Eq. (6) represents a temperature-independent part. The last one is quadratic in T. It is, therefore, expected that if $K(T)$ is measured at *constant volume*, it follows T^2 at the lower temperature. It would deviate from the quadratic low at higher temperature by the amount mentioned above.

From Eq. (7) the volume dependence of the Knight shift is

$$\frac{\partial K}{\partial \ln V}=\frac{dK_0}{d\ln V}+\frac{dB}{d\ln V}T^2. \quad (8)$$

The observed values of $\partial K/\partial \ln V$ are plotted against T^2 in Fig. 2. They fall on a straight line within experimental error. The volume dependence of the temperature-independent part K_0 is obtained from the zero intercept of the line, its slope gives the volume dependence of B. The results are

$$d\ln K_0/d\ln V=3.2\pm 0.1, \quad (9)$$

and

$$d\ln B/d\ln V=12\pm 2. \quad (10)$$

A. $K(T)$ at Constant Volume

By integrating the thermal expansion coefficient of Pt[10] with respect to the temperature, one obtains the volume at each temperature $V(T)$. Using the values of $\partial K/\partial \ln V$ in Fig. 2, the observed temperature dependence at constant pressure[8] can thus be converted into that at constant volume. In Fig. 3 the explicit temperature dependence of K thus derived from Drain's data is plotted using T^2 as an independent variable. The data at constant pressure are also plotted in this figure. It is noted that the constant V curve is indeed quadratic at low temperature, whereas the constant P curve has a nonmonotonic deviation from quadratic behavior. The constant V curve deviates from the quadratic law by about 1% near the room temperature as expected from the approximation in Eq. (6). The K versus T^2 curves would flatten off at higher temperatures, since $\chi^d(T)\sim 1/T$ in the high-temperature limit. The $O(T^4)$ term neglected in deriving Eq. (6) is a combination of higher derivatives of the density of states with respect to the Fermi level, which are not known experimentally. Their derivation from the standard parabolic band model has little physical significance. Besides a possible explicit temperature dependence of the hf coupling[11]

[10] D. E. Gray, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963).
[11] G. B. Benedek and T. Kushida, J. Phys. Chem. Solids 5, 241 (1958).

could itself give rise to a deviation of the order of a few tenths of a percent. Therefore further pursuit of this point at the moment is unwarranted.

B. Derivation of the Volume Dependence of the Band Parameters

The validity of Eq. (6) being established in the previous section, based on it one can now proceed to derive the volume dependence of the band parameters. The volume dependence of K_s can be written as

$$\frac{d\ln K_s}{d\ln V}=\left(\frac{d\ln K_s}{d\ln V}\right)_1+\left(\frac{d\ln K_s}{d\ln V}\right)_2. \tag{11}$$

The first term in the right side of the equation represents the volume dependence where the number of the s electrons is constant. The second term is the contribution from spill over of d electrons into the s band when the volume is changed.

The upper limit of the first term can be estimated based on the volume dependence of the Knight shift in alkali metals[11]:

$$-1<(d\ln K_s/d\ln V)_1<1. \tag{12}$$

The second term in Eq. (11) is

$$(d\ln K_s/d\ln V)_2=\tfrac{1}{2}(d\ln T_s/d\ln V)_2, \tag{13}$$

where the result of the parabolic band approximation, $\chi_s\propto\sqrt{T_s}$ is used. $(d\ln T_s/d\ln V)_2$ represents the change in T_s due to the spill-over effect.

Since the number of s electrons ($\propto T_s^{3/2}$) is equal to the number of d holes ($\propto T_d^{3/2}$),

$$(d\ln T_s/d\ln V)_2=(d\ln T_d/d\ln V)_2. \tag{14}$$

From Eqs. (11) through (14),

$$d\ln K_s/d\ln V=\pm1+\tfrac{1}{2}(d\ln T_d/d\ln V)_2. \tag{15}$$

There is no experimental value available for $d\ln K_{VV}/d\ln V$. Since the magnitude of K_{VV} is small, one will probably be safe assuming

$$-2\leq d\ln K_{VV}/d\ln V\leq 2. \tag{16}$$

For a parabolic band,

$$(d\ln T_d/d\ln V)_1=-\tfrac{2}{3}, \tag{17}$$

then from Eqs. (9), (15), and (16),

$$d\ln K_{d0}/d\ln V=2.3+0.11(d\ln T_d/d\ln V)\pm0.5, \tag{18}$$

where

$$K_{d0}\equiv\tfrac{3}{2}\alpha_d\Omega n\beta^{*2}/k(T_d-\tfrac{3}{2}T_{ex}), \tag{19}$$

and

$$d\ln T_d/d\ln V=(d\ln T_d/d\ln V)_1+(d\ln T_d/d\ln V)_2. \tag{20}$$

Based on Ref. 2, the following values are used for the components of K_0:

$$K_s=+1.0\%,\quad K_{VV}=+0.4\%,\quad\text{and}\quad K_{d0}=-4.7\%.$$

There are two experimentally derived equations, Eq. (18) and Eq. (10) [with the definition of B given in Eqs. (6) and (7)] and there are five unknown volume derivatives, namely $d\ln T_d/d\ln V$, $d\ln T_{ex}/d\ln V$, $d\ln n/d\ln V$, $d\ln\alpha_d/d\ln V$, and $d\ln\beta^*/d\ln V$.

If the volume dependence of the effective mass of d holes m_d^* can be neglected, the volume dependence of n is

$$d\ln n/d\ln V=\tfrac{3}{2}d\ln T_d/d\ln V. \tag{21}$$

The volume dependence of α_d can be estimated from the pressure-dependence data of the NMR in a ferromagnet and of the saturation magnetization M. The NMR frequency ν in a ferromagnet can be expressed as

$$\nu=\alpha M. \tag{22}$$

The indirect hf coupling constant α of this equation has a form similar to that of α_d. Benedek and Armstrong[12] obtained for the volume dependence of α in iron

$$d\ln\alpha/d\ln V=-0.19. \tag{23}$$

The volume dependence of β^* is related to the volume dependence of the electronic g shift δg. For small values $\delta g\propto\lambda$, the spin-orbit coupling. There is good evidence, at least for insulators, that λ is quite insensitive to volume.[13,14] For large shifts δg is related to the inverse effective mass and again in keeping with the assumption of negligible volume dependence for m_d^*, one is led to assume the same for β^*. Therefore, by neglecting small volume dependence in α_d and β^*, one obtains the volume dependence of T_d and T_{ex} as

$$d\ln T_d/d\ln V=-3.7\pm1.1, \tag{24}$$

and

$$d\ln T_{ex}/d\ln V=-1.1\pm3.0. \tag{25}$$

Since the number of d holes in the atomic volume Ω, n', is proportional to $\Omega T_d^{3/2}$, the spill-over rate, $d\ln n'/d\ln V$, is

$$\begin{aligned}d\ln n'/d\ln V&=1+\tfrac{3}{2}(d\ln T_d/d\ln V)\\&=-4.5\pm1.7.\end{aligned} \tag{26}$$

When the lattice is compressed, the number of holes in the d band increases. The electrons spilled over from the d band go into the s band and increase the depth of the filled part of this band, kT_s. The fractional change in T_s is the same as that of T_d, if the volume dependence of the effective masses of both bands is neglected. In

[12] G. B. Benedek and J. Armstrong, J. Appl. Phys. Suppl. 32, 106S (1961).
[13] L. Rimai, T. Deutsch, and B. D. Silverman, Phys. Rev. 133, A1123 (1964).
[14] W. M. Walsh, Phys. Rev. 122, 762 (1961).

this case

$$d\ln T_s/d\ln V=-3.7\pm1.1. \quad (27)$$

In the present analysis the volume dependence of the effective masses has been neglected. The volume dependence of m_s^* is relatively unimportant in this discussion, since the assumption $d\ln m_s^*/d\ln V=0$ was used only in Eq. (14), which represents only a minor correction. The magnitude of $d\ln m_d^*/d\ln V$ is likely to be of the order of one as seen from the following considerations.

In the tight-binding approximation for the d band,[15] m_d^* varies as $\Omega^{-2/3}S(\Omega)^{-1}$, where S depends on the degree of overlap between neighboring atomic wave functions Ψ,

$$S(R_{ij})=-\int\Psi^*(\mathbf{r}-\mathbf{R}_i)W'(\mathbf{r}-\mathbf{R}_j)\Psi(\mathbf{r}-\mathbf{R}_j)d\tau. \quad (28)$$

W' is the difference between an effective potential in the solid $V(\mathbf{r})$ and the atomic potential $W(\mathbf{r})$

$$W'(\mathbf{r}-\mathbf{R}_j)=V(\mathbf{r})-W(\mathbf{r}-\mathbf{R}_j).$$

The form of Eq. (28) suggests that S would vary as $T_{ex}^{1/2}$ when the volume is changed. Therefore

$$d\ln m_d^*/d\ln V=-\tfrac{2}{3}-d\ln S/d\ln V\approx-1. \quad (29)$$

If $d\ln m_d^*/d\ln V$ is included in Eq. (21),

$$d\ln n/d\ln V\approx\tfrac{3}{2}d\ln T_d/d\ln V-\tfrac{3}{2},$$

and one obtains,

$$d\ln T_d/d\ln V=-3.0,$$
$$d\ln n'/d\ln V=-3.5,$$
$$d\ln T_{ex}/d\ln V=+0.7.$$

The values are still within the uncertainties quoted in Eqs. (24), (25), and (26). This result supports the conclusion that the quoted uncertainties would adequately account for possible volume dependence of the effective masses. The estimate of $d\ln T_{ex}/d\ln V$ is less reliable, because it is the difference between the two quantities with comparable magnitudes.

4. CONCLUSION

Knight-shift measurement in Pt metal as a function of volume at three different temperatures revealed a volume dependence extremely sensitive to the temperature. The temperature dependence at constant volume of the Knight shift agrees with the model which predicts quadratic dependence at low temperature and a slight flattening off around room temperature. It is shown that the nonmonotonic deviation from the T^2 law in the previously observed temperature dependence is caused by the effect of thermal expansion. The experimental data are analyzed using the standard band model with the assumption that the effective masses of the d and s band are independent of volume.

The volume dependence of the band parameters are:

(i) for the Fermi depth of the d band holes, $d\ln T_d/d\ln V=-3.7\pm1.1$,

(ii) for the Fermi depth of the s band, $d\ln T_s/d\ln V=-3.7\pm1.1$,

(iii) for the exchange parameter, $d\ln T_{ex}/d\ln V=-1.1\pm3.0$,

(iv) for the spill-out rate of the d holes, $d\ln n'/d\ln V=-4.5\pm1.7$.

ACKNOWLEDGMENTS

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[15] For instance, J. R. Reitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. I, p. 48.