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LETTERS

Effects of Temperature on the Energy of the 6.2-keV Mössbauer γ Rays of ^{181}Ta†

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We have found a strong temperature dependence of the energy of the 6.2-keV γ rays from dilute impurities of ^{181}Ta in transition-metal hosts. The observed temperature shifts cover a range of − 32 to + 8 times the expected thermal red shift, and exhibit large variations with the hosts.

The effects of temperature on the energy of Mössbauer γ rays have been studied up to now in detail only for ^{57}Fe [1-4] and ^{119}Sn. [5] For both these Mössbauer resonances the observed variations with temperature are mainly caused by the second-order Doppler (SOD) effect (thermal red shift). [6] Accordingly, information on the variation of the total electron density at the nucleus with temperature could be derived only after dominant corrections for the thermal red shift had been made [5,7]; therefore, this procedure may have introduced large systematic errors, limiting the accuracy of the derived results.

The case of the 6.2-keV γ resonance of ^{181}Ta is quite different, as will be reported in the present paper. Recently this resonance has been applied extensively to high-resolution studies of hyperfine interactions, [8] and its especially high resolving power in the field of isomer shifts has been recognized. [8,9] We have now found that the energy of the 6.2-keV γ rays, emitted from ^{181}Ta as a dilute impurity in transition metals, exhibits a strong temperature dependence far beyond the expected SOD shift. The results underline the exceptional sensitivity of the 6.2-keV γ resonance, and open new possibilities in solid-state applications of isomer-shift studies.

The host metals investigated in this study are Ta, W, Ir, Pt, Nb, Mo, Pd, and Ni. Sources of ^{181}W diffused into these metals were studied at temperatures up to 1000 K, using a single-line Ta metal absorber at room temperature ($\simeq 4$ mg/cm^2 thick). Details of the experimental technique have been presented elsewhere. [10]

Figure 1 shows the experimental variations with temperature of the line positions for five of the sources. It is striking that in the case of the
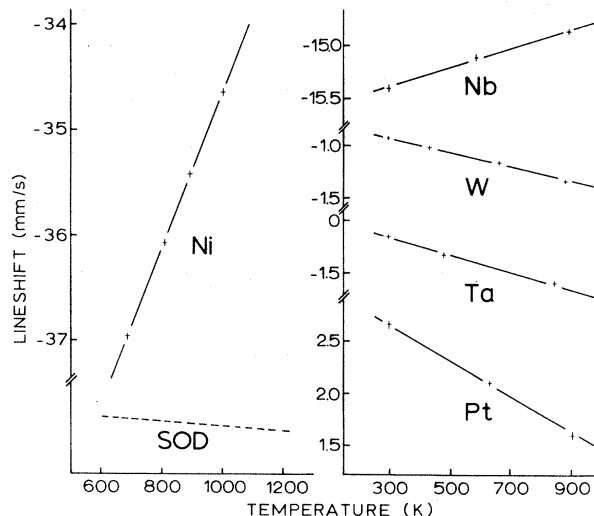

FIG. 1. Temperature dependence of line positions for sources of ^{181}W diffused into Ni, Nb, W, Ta, and Pt. For comparison, the SOD shift, expected for a Debye solid in the limit of high temperatures, is also shown. All curves are plotted on the same scale.

nickel host the transition energy increases with temperature with a slope which is 32 times larger, and of opposite sign, than the one expected from the SOD shift alone. While the slopes of the temperature shifts for W, Ta, and Pt hosts are of the same sign as the SOD shift, they are up to 8 times larger. Within the accuracy of the present experiments the data can be described by a linear relationship between the line shift S and the source temperature T. The solid lines are the results of a least-squares fit of straight lines to the data.

We may write for the experimentally observed temperature variation of the line position S,

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S_{SOD}}{\partial T}\right)_P + \left(\frac{\partial S_{IS}}{\partial T}\right)_V$$
$$+ \left(\frac{\partial S_{IS}}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_P. \quad (1)$$

The first term accounts for the temperature variation of the SOD shift which is given for a Debye solid in the limit of high temperatures by $-2k/2Mc$ cm/sec, amounting to -2.30×10^{-4} mm/sec deg for the present γ transition. The second term represents the explicit temperature dependence of the isomer shift at constant volume due to temperature-induced changes of the total electron density at the nucleus. The third term describes the volume dependence of the isomer shift caused by thermal expansion of the lattice.

Table I summarizes the experimental data, with the line shifts S for both source and absorber at room temperature listed in column 2, and the experimental results for the isobaric temperature variation of the transition energy $(\partial S/\partial T)_P$

presented in column 3. The values for the isobaric temperature dependence of the isomer shift, $(\partial S_{IS}/\partial T)_P$, were derived by subtracting the contribution due to the SOD effect from $(\partial S/\partial T)_P$. In view of the fact that these corrections are small compared to the total temperature shifts, and that the measurements were carried out in the temperature range 300 to 1000 K, where the high-temperature Debye model should approximately hold, this procedure should be sat-isfactory within the present accuracy. Also presented are representative values for the thermal expansion coefficients, $(\partial \ln V/\partial T)_P$ (column 5).

Until now temperature shifts of the 6.2-keV γ rays have been reported only for a W host by Taylor and Storms[11] and their results agree well with the present measurements. In the case of [57]Fe, temperature shifts of the energy of the 14.4-keV γ rays have been measured for dilute impurities of [57]Fe in $3d$, $4d$, and $5d$ transition metals.[3,4] Even though these shifts arise mainly from the SOD effect, the derived values for $(\partial S_{IS}/\partial T)_P$ exhibit characteristics similar to the present case.[7]

A separation of $(\partial S_{IS}/\partial T)_P$ into the explicitly temperature-dependent part and the volume-dependent part of Eq. (1) cannot be carried out quantitatively with the present results alone. The necessary additional information could be obtained from high-pressure isomer-shift studies, which would directly provide values for $(\partial S_{IS}/\partial \ln V)_T$.

For a qualitative discussion we use a value of $\Delta \langle r^2 \rangle \simeq -5 \times 10^{-2}$ fm^2 for the change of the mean squared nuclear charge radius, as recently derived from isomer-shift studies in transition-metal hosts.[9] Since the electron density at the

TABLE I. Summary of experimental results and derived quantities for dilute impurities of [181]Ta in transition-metal hosts.

Host metal	S (mm/sec)	$(\partial S/\partial T)_P$ (10^{-4} mm sec^{-1} deg^{-1})	$(\partial S_{IS}/\partial T)_P$ (10^{-4} mm sec^{-1} deg^{-1})	$(\partial \ln V/\partial T)_P$ (10^{-5} deg^{-1})
Ni	-39.5 ± 0.2[a]	73.2 ± 3.5	75.5 ± 3.5	5.2
Nb	-15.3 ± 0.1	9.2 ± 1.0	11.5 ± 1.0	2.5
Mo	-22.5 ± 0.1	3.6 ± 0.6	5.9 ± 0.5	1.7
Pb	-27.6 ± 0.3	-16.7 ± 7.0	-14.4 ± 7.0	3.5
Ta	-0.075 ± 0.004	-8.0 ± 0.5	-5.7 ± 0.5	2.0
W	-0.86 ± 0.01	-7.1 ± 0.2	-4.8 ± 0.2	1.4
Ir	-1.84 ± 0.04	-10.7 ± 3.3	-8.4 ± 3.3	2.0
Pt	-2.66 ± 0.04	-17.6 ± 0.9	-15.3 ± 0.9	2.9

[a] Extrapolated to room temperature from the temperature dependence of the line position, measured in the range 685 to 1003 K.

nucleus, $|\Psi_0|^2$, should decrease with increasing volume, we expect positive values for $(\partial S_{IS}/\partial \ln V)_T$ in all cases, even though their magnitudes might exhibit large variations, as observed in the case of ^{57}Fe. There, isomer shifts have been measured as a function of pressure for impurities of ^{57}Fe in a series of $3d$, $4d$, and $5d$ transition-metal hosts,[12] and $(\partial S_{IS}/\partial \ln V)_T$ was found to increase with decreasing isomer shift (or increasing $|\Psi_0|^2$), as expected from a scaling of $|\Psi_0|^2$ with volume. We may expect a similar behavior of $(\partial S_{IS}/\partial \ln V)_T$ in the ^{181}Ta case. This means that the negative values of $(\partial S_{IS}/\partial T)_P$, observed for the Pd, Ta, W, Ir, and Pt hosts, originate from an overcompensation of the positive volume shifts by negative contributions due to an explicit temperature dependence of the isomer shift.

Since $|\Psi_0|^2$ is found to increase from $5d$ to $4d$ and to $3d$ hosts in a vertical column of the periodic system,[9] it is expected that $(\partial S_{IS}/\partial \ln V)_T$ is larger for $3d$ than for $5d$ hosts. The large positive value of $(\partial S_{IS}/\partial T)_P$ observed for the nickel host may then be explained by a dominant contribution due to thermal expansion, especially since the thermal expansion coefficient is so large for this metal. For an order-of-magnitude estimate of $(\partial S_{IS}/\partial T)_V$ we take for the conduction electron contribution to $|\Psi_0|^2$ in Ta metal a value of $|\Psi_0|_{ce}^2 \simeq 3.0 \times 10^{26}$ cm^{-3}, and at ^{181}Ta impurities in nickel metal a value of $|\Psi_0|_{ce}^2 \simeq 3.75 \times 10^{26}$ cm^{-3} as estimated from the results of Dirac-Fock calculations for free-ion configurations of Ta[13] and from the measured difference in isomer shifts between hosts of nickel and tantalum metal. With the simple volume scaling assumption

$$\Delta|\Psi_0|^2 \simeq - (\Delta V/V)|\Psi_0|_{ce}^2, \tag{2}$$

we then estimate for $(\partial S_{IS}/\partial \ln V)_T(\partial \ln V/\partial T)_P$ values of $\sim +103 \times 10^{-4}$ mm/sec deg for the nickel host and $\sim +32 \times 10^{-4}$ mm/sec deg for the tantalum host. This results in values of -38×10^{-4} mm/sec deg and -27×10^{-4} mm/sec deg for $(\partial S_{IS}/\partial T)_V$ for the nickel and tantalum hosts, respectively.

We may conclude from this estimate for $(\partial S_{IS}/\partial T)_V$, that the electron density at the nucleus increases in tantalum metal explicitly with temperature by $\simeq 5 \times 10^{21}$ cm^{-3} deg^{-1}, which corresponds to a $d \to s$ electron transfer with increasing temperature of approximately 10^{-5} electrons per

degree. Such effects have been discussed theoretically in connection with the temperature dependence of the Knight shift, and have been interpreted as arising from an effective decrease in the strength of the lattice potential caused by lattice vibrations.[14] In this way, the energy bands become more free-electron-like, leading to an increase in the s character of the wave functions. This effect should exhibit a strong dependence on the electronic structure of the metals. It is to be expected that, as soon as pressure data will be available for the ^{181}Ta γ resonance, the present results will provide very detailed insight into these subtle effects.

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