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TEMPERATURE DEPENDENCE OF THE 6.2 keV MÖSSBAUER RESONANCE OF $^{181}$Ta AT LOW TEMPERATURE

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Résumé. — Nous décrivons la variation en fonction de la température de la résonance Mössbauer de 6.2 keV du $^{181}$Ta pour des sources de $^{181}$W(W) et $^{181}$W(Ta). Les mesures ont été faites entre 15 K et 457 K. Elles révèlent dans le cas de $^{181}$W(W) une nette déviation par rapport à la variation linéaire anormalement élevée observée antérieurement à haute température. Déduisant l'effet Doppler de second ordre, on obtient un terme dont la variation avec la température est pratiquement proportionnelle à la dilatation thermique du W. La signification de ce résultat est discutée. La variation en fonction de la température dans le cas de $^{181}$W(Ta) est plus linéaire et l'analyse est beaucoup moins évidente.

Abstract. — The temperature dependence of the 6.2 keV Mössbauer resonance of $^{181}$Ta is reported for sources of $^{181}$W(W) and $^{181}$W(Ta). The measurements cover the temperature range from 15 K to 457 K. For $^{181}$W(W) they show substantial deviation from the anomalously large linear dependence observed previously at high temperature. Subtraction of the second order Doppler shift leaves a residual whose temperature dependence is closely proportional to the thermal expansion of W. The implications of this result are discussed. The temperature dependence for $^{181}$W(Ta) is more nearly linear and the analysis is much less straightforward.

1. Introduction. — The 6.2 keV $\gamma$-ray transition of $^{181}$Ta holds particular appeal for Mössbauer studies. The relatively long half-life of 6.8 µs for the excited state and the very low $\gamma$ energy should lead to an effect of almost 100 % with the very narrow natural linewidth of $\Gamma_0 = 6.7 \times 10^{-11}$ eV. Furthermore, the rather large hyperfine splittings and isomer shifts recently observed [1-3] for this Mössbauer nucleus together with the narrow line suggest that Mössbauer studies of unprecedented sensitivity should be possible.

Unfortunately, this very combination of narrow natural linewidth and large splittings and shifts makes the $\gamma$ resonance extremely vulnerable to unresolved splittings and broadenings from impurities and lattice defects. Nevertheless, it has been recently demonstrated [1-3] that high resolution Mössbauer studies are indeed possible with $^{181}$Ta, although even the best measurements have produced linewidths of order 20 times the natural width and resonance dips of only a few percent. The measurements of Kaindl and Salomon [1] have demonstrated that the $\gamma$-ray energy from sources of $^{181}$W in various metallic hosts shows an extraordinarily large temperature dependence in the temperature range from 300 K to 900 K. The observed temperature shifts varied linearly with temperature and were ~ 32 to + 8 times the normal thermal redshift which has been found to dominate the temperature dependence of all previously studied Mössbauer resonances when a change in valence does not occur.

In this paper we report studies of the temperature dependence of the 6.2 keV Mössbauer resonance of $^{181}$Ta for sources of $^{181}$W(W) and $^{181}$W(Ta). The measurements were made in the temperature range from 15 K to 457 K. For $^{181}$W(W) they show a large and well-defined deviation from the linear behavior previously observed at high temperature. For $^{181}$W(Ta) the low temperature data have poorer statistics but are consistent with a straight line behavior down to $T = 0$. Such a behavior is most unusual and suggests that the local electronic configuration for a W impurity in Ta metal changes explicitly with temperature.

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2. Experimental procedure. — The $^{181}$W source activity was prepared by neutron irradiation of 1 mg of 93 % enriched $^{180}$W in a neutron flux of $3 \times 10^{15}$ n/cm$^2$ for a period of 4 weeks. The W and Ta hosts were in the form of 6 mm diameter disks approximately 0.8 mm thick cut from a large grain polycrystalline W rod and a single-crystal Ta rod. The $^{181}$W activity was dissolved in a concentrated HNO$_3$ : HF, diluted with H$_2$O, and then dropped into a shallow crater etched on the face of the disk. The active solution was evaporated to dryness and the host crystal was suspended in a high vacuum r. f. annealing furnace. Reduction of the $^{181}$W activity to metallic form was achieved in 1/4 atmosphere of H$_2$ and with the crystal at 950°C. The activity was then diffused into the host for a period of about 1/2 hour in a vacuum of about $10^{-9}$ torr, at a temperature of 2 400°C for $^{181}$W(W) and 2 200°C for $^{181}$W(Ta).

The absorbers were Ta metal foils 4 mg/cm$^2$ thick annealed at 1 900°C in a vacuum of $10^{-6}$ torr for a period of about 8 hours. The thickness of 4 mg/cm$^2$ was achieved either a) through a process of successive annealings and rollings of 0.13 mm thick Ta strips (99.996 % purity, MRC Marz grade) or b) by purchase of foils of the desired thickness (Goodfellow Metals Ltd., Ruxley Towers, Claygate-Esher, Surrey, England). No significant difference in quality was observed for absorbers produced from these different starting materials. Further details of the preparation of these sources and absorbers have been given previously [3, 4]. Also, the Mössbauer cold-finger cryostat shown in figure 1 has been described [5], so the rest of the experimental discussion will be confined to techniques pertinent to high precision measurements on the $^{181}$Ta resonance.

It is useful at this point to consider the precision required by the experiment. The total deviation from a linear temperature dependence for a $^{181}$W(W) source was not expected to exceed 15 % at liquid helium temperature and to be much smaller than this near room temperature. To measure such deviations with an accuracy of only $\pm 7$ % requires a velocity calibration good to about $\pm 0.5$ %, if the statistical definition of the line position is also $\pm 0.5$ % ($\pm 0.004$ mm/s). Typically, our results for the $^{181}$W(W) source have a one standard deviation statistical error (including both the calibration of line position and statistical errors) of $\pm 0.003$ mm/s, and a reproducibility only slightly worse than this. Fortunately, the two inner lines of the magnetic hyperfine spectrum of $^{57}$Fe lie very close to the line position observed for the $^{181}$W(W) source. Therefore a 5 mC source of $^{57}$Co(Cu) was mounted on the absorber carriage, and the absorption spectrum obtained with a 0.025 mm natural Fe metal absorber mounted at room temperature was used to provide a convenient, accurate, and simultaneous velocity calibration.

For the $^{181}$W(Ta) source a highly accurate velocity calibration is not required since the line position is so close to zero velocity; therefore calibrations were taken only at the beginning and end of the runs. The experiments on $^{181}$W(Ta) were done with a weak source and do not yet have the statistical precision of the $^{181}$W(W) results. If higher precision experiments on $^{181}$W(Ta) are carried out they would require better calibration in order to achieve optimum precision.

The desired temperatures in the cryostat were maintained with the use of liquid helium, liquid nitrogen, liquid methane, a dry ice-alcohol mixture, and water at its normal boiling point. Temperatures above that of boiling water were obtained with a regulated hot oil bath, and a few low temperature points were obtained by resistively heating the copper cold-finger. Temperatures at the source site were measured with a calibrated carbon resistance thermometer and the copper cold-finger temperature was monitored with a chromel-alumel thermocouple above 100 K. Temperature gradients between the copper cold-finger and the source were generally only a few percent of the quantity (T-300 K). However, at the lowest (and highest) temperatures there was a sizable gradient between the bath and the copper cold-finger. (For instance, liquid helium at 4.2 K generally cools the cold-finger to 17 K and the source to 18 K.)

The 6.2 and 14.4 keV $\gamma$-rays from the $^{57}$Co and $^{181}$W sources each passed through three or four Be windows 0.08 mm thick, mounted on radiation shields and on the outer wall of the cryostat. The outer Be windows were sealed to the chamber with indium O-rings. The absorbers were mounted on the outer windows and were therefore at room temperature. The arrangement is shown schematically in the expanded view of figure 1.

The 6.2 keV $\gamma$-ray was detected with a double
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window proportional counter filled to a pressure of 1.5 atmospheres with a mixture of 90 % argon and 10 % methane gas. The Mössbauer γ-ray was partially resolved [4] at a counting rate of 1 000 counts/s, as obtained with the weak 181W(Ta) source, but it was completely unresolved at the rate of 90 000 counts/s from the hot 181W(W) source. In the latter case the γ-ray window was set approximately from knowledge of the γ-ray peak at lower counting rates. The window was then adjusted to optimize the Mössbauer effect by trial and error since only a few minutes was required to obtain a well-defined effect. Naturally, the poor resolution resulted in an appreciable decrease in the effect, but this was more than offset by the good statistics from the large increase in counting rate.

3. Results and discussion. — Figure 2 shows typical Mössbauer spectra obtained with the 181W(W) source at several temperatures. Figure 3 shows the experimental line positions derived from the spectra for sources of 181W(Ta) and 181W(W) at various temperatures from 15 K to 457 K. The 181W(W) data show substantial deviation at low temperature from the anomalously large linear behavior observed previously at high temperature [1]. The dashed lines through the data have the slopes reported previously for the two sources [1].

Figure 4 shows the lineshift for the 57Co(Cu) source and Fe metal absorber. These data were taken simultaneously with the 181W(W) points shown in the bottom of figure 3. The velocity calibration for both sets of data was the splitting of the two inner lines of the six-line 57Fe spectrum. For the case of the W source in a W host, the thermal second order Doppler shift (SOD) and recoil free fractions can be calculated [6] from the experimentally determined phonon spectrum of W metal [7]. Since the results for the recoil free fractions have now been experimentally verified for 182W, 184W and 186W [8], the correction for the SOD for 181W(W) can be made with some confidence. Table I summarizes the experi-

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**Fig. 2.** — Typical absorption spectra for a source of 181W(W) at various temperatures and a Ta metal absorber at room temperature.

**Fig. 3.** — Uncorrected data of the lineposition versus temperature for sources of 181W(W) and 181W(Ta) with a Ta metal absorber at room temperature. The dashed lines, which give the high-temperature slopes from reference [1], have an uncertainty of about 10 %.

**Fig. 4.** — Lineposition versus temperature for a source of 57Co(Cu) and an 57Fe metal absorber at room temperature. These data were accumulated simultaneously with those for 181W(W) and the velocity calibrations for both were derived from the splitting of the inner two lines of the Fe spectrum.
mental data for the lineshift $S$ of the $^{181}W(W)$ source and the appropriate SOD corrections extrapolated from the work of Raj and Puri [6]. The temperature dependence of the difference (shown in figure 5 for $^{181}W(W)$) can be expressed

$$\frac{\partial(S - \text{SOD})}{\partial T} = \left(\frac{\partial S_{IS}}{\partial T}\right)_{V} + \left(\frac{\partial \ln V}{\partial T}\right)_{p}$$ \tag{1}

Table I

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$S$ (mm/s)</th>
<th>SOD (*) (mm/s)</th>
<th>S - SOD (mm/s)</th>
<th>Error (*) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>457</td>
<td>0.923 6</td>
<td>-</td>
<td>0.106 0</td>
<td>0.015 8</td>
</tr>
<tr>
<td>410</td>
<td>0.895 7</td>
<td>-</td>
<td>0.096 9</td>
<td>0.002 5</td>
</tr>
<tr>
<td>365.5</td>
<td>0.876 2</td>
<td>-</td>
<td>0.086 0</td>
<td>0.003 2</td>
</tr>
<tr>
<td>363</td>
<td>0.866 4</td>
<td>-</td>
<td>0.085 0</td>
<td>0.002 5</td>
</tr>
<tr>
<td>298</td>
<td>0.836 2</td>
<td>-</td>
<td>0.071 1</td>
<td>0.003 2</td>
</tr>
<tr>
<td>298</td>
<td>0.830 4</td>
<td>-</td>
<td>0.071 6</td>
<td>0.002 3</td>
</tr>
<tr>
<td>203</td>
<td>0.791 2</td>
<td>-</td>
<td>0.051 0</td>
<td>0.003 2</td>
</tr>
<tr>
<td>203</td>
<td>0.780 5</td>
<td>-</td>
<td>0.051 6</td>
<td>0.002 6</td>
</tr>
<tr>
<td>119</td>
<td>0.751 3</td>
<td>-</td>
<td>0.036 1</td>
<td>0.003 5</td>
</tr>
<tr>
<td>82</td>
<td>0.736 9</td>
<td>-</td>
<td>0.030 1</td>
<td>0.002 2</td>
</tr>
<tr>
<td>82</td>
<td>0.736 5</td>
<td>-</td>
<td>0.030 1</td>
<td>0.002 1</td>
</tr>
<tr>
<td>40</td>
<td>0.729 0</td>
<td>-</td>
<td>0.027 0</td>
<td>0.002 8</td>
</tr>
<tr>
<td>40</td>
<td>0.723 0</td>
<td>-</td>
<td>0.027 0</td>
<td>0.003 4</td>
</tr>
<tr>
<td>20</td>
<td>0.723 7</td>
<td>-</td>
<td>0.026 5</td>
<td>0.002 5</td>
</tr>
<tr>
<td>18</td>
<td>0.724 2</td>
<td>-</td>
<td>0.026 5</td>
<td>0.003 7</td>
</tr>
</tbody>
</table>


(\(\frac{\partial S}{\partial T}\)) is based on ref. [2] and the assumption that the variation of the measured lineshift with applied hydrostatic pressure gives \((\frac{\partial S}{\partial P})_p\) in the absence of other interfering contributions. If analysis \(b\) is correct then \((\frac{\partial S}{\partial T})_V\) must have a temperature dependence closely proportional to the thermal expansion.

Either of these possibilities must be considered somewhat surprising: the first, because the explicit transfer of \(d \rightarrow s\) electrons in the conduction band with increasing temperature is widely assumed to be large enough to produce a sizable value of \((\frac{\partial S}{\partial T})_V\); the second, because there is no apparent reason to expect this explicitly volume independent term to have the same temperature dependence as the volume.

Suppose possibility \(a\) is valid. Then eq. (2) gives \(b \approx (\frac{\partial S}{\partial ln V})_V = 23 \text{ mm/s} \) which is of the opposite sign and more than a factor of six smaller than the value derived from hydrostatic pressure measurements on a source of $^{181}W(W)$ [2]. However, in a recent pressure experiment it has been reported that the resonance line does not return to its original position upon return to zero pressure [10]. This hysteresis indicates that an irreversible change may be induced in the active area close to the surface of the host crystal and suggests

![Graph showing lineshift corrected for second order Doppler shift (SOD) versus temperature for a source of $^{181}W(W)$. The curve drawn through the points is proportional to the volume expansion of W metal.](image)
that the measured shifts may not be indicative of \( \frac{\partial S_{\text{W}}}{\partial \ln V} T \).

Now consider possibility b), namely that

\[ \frac{\partial S_{\text{W}}}{\partial \ln V} T \]

is large and its temperature dependence is closely proportional to the thermal expansion. Although such a simple scaling with thermal expansion is unexpected in view of the complex results generally found from temperature dependent band structure calculations [11, 12], it must be emphasized that such calculations have been concerned primarily with properties related to the electronic properties at the Fermi surface. It is quite possible that a rather less complex behavior may be found if attention is paid to the total electron density at the nucleus. Indeed, the factor which contains the entire temperature dependence of the band structure is \( \exp(-W) \) where \( \exp(-2W) \) is the usual Debye-Waller factor [10, 11].

The fact that these factors on Fermi surface properties is generally complex because of the complexity of the Fermi surface itself. There seems to be no compelling reason to expect the reduction of the effective lattice potential to have such a complex effect on the total electron density at the nucleus.

Our data for \( ^{181}\text{W(Ta)} \) are less precise, and we have not concentrated on this analysis because of our feeling that an understanding of the simpler \( ^{181}\text{W(W)} \) system is a necessary prerequisite to an understanding of more complicated systems. In the \( ^{181}\text{W(Ta)} \) case the \( ^{181}\text{W} \) is an impurity in the Ta metal host; consequently, the SOD correction for \( ^{181}\text{W(Ta)} \) is less certain than for \( ^{181}\text{W(W)} \) at low temperatures. However, it is expected to show a smaller deviation from linearity. Subtraction of such an estimated correction leaves a residual S—SOD which is still approximately a straight line, but with a slope only about 60% as large as observed for the lineshift. This approximately linear temperature dependence is, of course, not proportional to the thermal expansion at low temperature and suggests that \( \frac{\partial S_{\text{W}}}{\partial T} T \) is non-zero for this source.

We have also made preliminary low temperature measurements on two \( ^{181}\text{W(Nb)} \) sources. At the present time the uncertainties in our measured lineshifts are only slightly smaller than the entire temperature dependence expected below room temperature. Thus, improved measurements are needed before an analysis is undertaken in this case.

4. Conclusions and recommendations. — The results presented here demonstrate that the \( ^{181}\text{Ta Mössbauer resonance has high enough resolution to monitor thermally induced changes in the electron density at the nucleus. Such changes were previously found to lead to a linear variation with temperature in the range 300 K < T < 900 K. We have shown that for 15 K < T < 457 K significant deviations from linearity can occur. The close proportionality between the thermal expansion of W metal and our values of \( \frac{\partial (S—SOD)}{\partial T} \) for a source of \( ^{181}\text{W(W)} \) suggest that \( \frac{\partial S_{\text{W}}}{\partial T} T \) may be close to zero for this source. This is not the only possible explanation for these results and theoretical calculations are needed in order to clarify the situation.

The data for a source of \( ^{181}\text{W(Ta)} \) are less precise but suggest that \( \frac{\partial S_{\text{W}}}{\partial T} T \) is non-zero and shows a variation with temperature which cannot be proportional to the thermal expansion.

References