

## Microscopic Observation of the $s \rightarrow d$ Transition in Metallic Cesium under High Pressure

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Using the  $^{133}\text{Cs}$  high-pressure Mössbauer effect technique, we were able for the first time to investigate on a microscopic level the pressure effects on the electronic charge densities and lattice dynamics in metallic cesium. A quantitative analysis of the experimental results reveals direct evidence for a gradual pressure-induced  $6s \rightarrow 5d$  electronic transition in metallic cesium in agreement with band structure calculations. From the pressure-induced change of the Debye-Waller factor at 4.2 K, we obtain a new value of the Debye temperature  $\theta_D$  for metallic Cs of 64(2) K at  $p=6$  GPa ( $V/V_0=0.33$ ).

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The high-pressure behavior of metallic cesium and other alkali metals such as Rb and K has been intimately connected to the change in the character of the lowest energy conduction electron band from  $s$ -like to  $d$ -like. This transition was recognized to be the main cause for the very soft behavior of the equation of state and for the structural phase transitions occurring in the heavy alkali metals under pressure. Cesium, being the heaviest of the alkali metals, shows these effects at relatively low pressures ( $p \leq 10$  GPa). In this pressure range Cs undergoes five structural phase transitions. The most unusual one is the isostructural electronic transition (fcc  $\rightarrow$  fcc) at 4.22 GPa with a 9% volume collapse [1-4]. The role played by the electronic  $s \rightarrow d$  transition in causing high-pressure structural transitions in metallic Cs has recently been the subject of great interest both in experimental [5-8] and theoretical [9-12] investigations.

Modern band structure calculations for cesium suggest that both the isostructural (high-pressure) transitions and the unusual softness of the low-pressure isotherm are related to a gradual evolution of the valence electrons from  $6s$  to  $5d$  states [12]. Thus, this process is not an abrupt collapse in the size of the Cs atoms, as might directly explain the isostructural transition. It is rather of a continuous nature extending over a wide range in volume.

On the experimental side, macroscopic high-pressure experiments, such as x-ray diffraction, e.g., [13] or optical reflectivity [14], delivered *indirect* support to the  $s \rightarrow d$  transition in Cs. However, no *direct* microscopic experimental evidence for such a transition has been reported so far.

In this work we were able to investigate on a microscopic level the effect of pressure on the electronic densities and on lattice dynamics in metallic Cs. Here, we have used for the first time the  $^{133}\text{Cs}$  high-pressure Mössbauer effect (ME) spectroscopy. The ME technique allows one to detect simultaneously pressure-induced changes of both the  $s$ -electron density at the Cs nuclei  $\rho(0)$  via the  $^{133}\text{Cs}$  ME isomer shift  $S$  and of the Mössbauer's Debye-Waller factor ( $2w$ ) via the recoilless fraction  $f = \exp(-2w)$  which is proportional to the area

of the ME spectrum.  $S(p)$  is a sensitive parameter to the pressure-induced  $s \rightarrow d$  transition in Cs metal and thereby allows one to estimate the amount of such a transition and to compare it with theoretical calculations [12], whereas  $f(p)$  is related to pressure-induced changes of the lattice dynamics and can be used to deduce the value of the Debye temperature  $\theta_D$  [15] as a function of volume. Thus, the pressure dependence of both physical quantities offers the possibility to investigate the  $s \rightarrow d$  transition in metallic Cs and to check its possible connection to lattice dynamics as theoretically suggested [10].

Our experimental results supply a direct microscopic evidence of the  $6s \rightarrow 5d$  transition in metallic cesium in good quantitative agreement with modern band structure calculations [12]. Furthermore, we obtain a new value of the Debye temperature for metallic Cs:  $\theta_D = 64(2)$  K at  $V/V_0 = 0.33$ .

The main reason for the lack of  $^{133}\text{Cs}$  Me studies on metallic Cs and also on other Cs compounds since the first observation of the ME in  $^{133}\text{Cs}$  in 1965 [16] is the following: The value of the fraction of the recoilless absorption ( $f$ ) of the 81 keV  $\gamma$  transition in metallic Cs is extremely small ( $5.5 \times 10^{-5}$  at 4.2 K [16]). This is due to both the high recoil energy ( $E_r$ ) associated with the 81 keV  $\gamma$  transition and the very low Debye temperature of Cs metal ( $\theta_D \approx 40$  K [16,17]),

$$f = \exp(-3E_r/k_B\theta_D), \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $\theta_D$  is the Debye temperature as deduced from the Mössbauer measurement. This problem has been solved by preparing a special Mössbauer source that exhibits both a high activity and a high  $f$  value. This source consists of a stack of about 4 mm diam Mo foils implanted on both sides with a low dose of about  $5 \times 10^{13}$  atoms/cm<sup>2</sup> of  $^{133m} + ^{133}\text{Xe}$ . The concentration of the source activity on small diameter Mo foils was necessary for the high-pressure measurements since the sample has a diameter of only 4 mm. The source used decays to  $^{133}\text{Cs}$  with a half-life of 2.2 d. The emission spectrum of this source consists predominantly of a single line with some shoulders (see Fig. 1 for  $p=0$

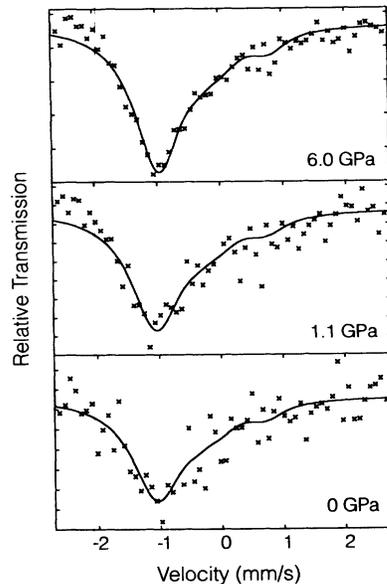


FIG. 1.  $^{133}\text{Cs}$  Mössbauer absorption spectra of Cs metal at 4.2 K and at pressures of 0, 1.1, and 6.0 GPa. The percentage absorption depth of the spectra is about  $10^{-4}$ .

GPa), which originates from vacancy associated sites in addition to the substitutional site (main line) [18]. We have avoided annealing of the Mo foils after implantation in order to keep the probability of the vacancy associated sites as low as possible. The line shape of the source including both main line and vacancy associated sites (source parameter) was considered in the analysis of the all measured absorption spectra of metallic Cs. The spectra were thus fitted with constant source parameters throughout each series, thereby allowing an accurate determination of  $S$  and  $\Theta_D$ .

The  $^{133}\text{Cs}$  high-pressure ME experiments were performed up to 6 GPa, which corresponds to a volume change  $V/V_0=0.33$  at 4.2 K using a modified high-pressure setup with  $\text{B}_4\text{C}$  anvils. The detailed description of the high-pressure setup is published elsewhere [19]. Cs metal (99.95%) was located in the hole of the gasket under silicon oil, which was used as a pressure transmitting medium, and was covered on top and bottom with 50  $\mu\text{m}$  sodium borate sheets. The pressure was determined at 4.2 K by putting a  $^{119}\text{Sn}$  foil ( $< 10 \mu\text{m}$ ) on the top of the cell and by measuring the known change of  $^{119}\text{Sn}$  ME isomer shift with pressure [20].

Figure 1 shows  $^{133}\text{Cs}$  Mössbauer absorption spectra obtained at  $p=0, 1.1,$  and  $6.0$  GPa and 4.2 K. The volume-induced change of the isomer shift has been obtained from the analysis of the ME line and by using the experimental equation of state at the two measured values [6,7]. The results are plotted in Fig. 2 (dashed line). The relatively large errors in  $S$  are caused by the extremely low absorption depth ( $f$  fraction) of the resonance absorption spectra ( $\sim 10^{-4}$ ).

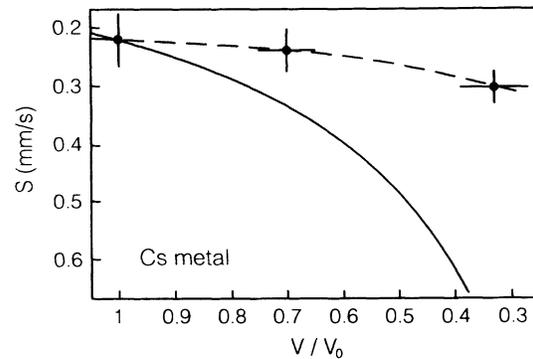


FIG. 2. Volume dependence of the isomer shift  $S$  in metallic Cs. The values of  $S$  are given with respect to CsCl at ambient pressure. Dashed line through the experimental data points is only a guide to the eye. The solid line displays a hyperbolic behavior of  $S$  with decreasing volume assuming a uniform compression of the  $6s$  electrons without  $6s \rightarrow 5d$  transfer.

As shown in Fig. 2 (dashed line) there is a slight increase of the isomer shift with decreasing volume which indicates a corresponding increase of  $\rho(0)$ . In metallic Cs a volume-induced change of  $\rho(0)$  mainly originates from the following mechanisms: (i) a uniform compression of the  $s$ -like conduction electrons (mainly  $6s$  electrons); i.e.,  $\Delta\rho(0) \approx -\rho(0)(\Delta V/V_0)$ . This leads to a hyperbolic increase of  $\rho(0)$  (or  $S$ ) with reducing volume; and (ii) a change of the number of the  $s$  electrons at the expense of the more localized non- $s$  band electrons (mainly  $5d$  electrons). This would lead to a decrease of  $\rho(0)$  in the case of a  $6s \rightarrow 5d$  transfer.

In order to gain a deeper insight into the relative importance of these two mechanisms (i) and (ii) in changing  $\rho(0)$  in Cs metal, one has to correlate changes of the volume-induced values of  $S$  with corresponding changes in the number of the  $s$  electrons in metallic Cs. For this reason we recall the general expression for the isomer shift [21]:

$$S = \frac{2\pi Ze^2}{3} \Delta\langle r^2 \rangle [\rho_a(0) - \rho_s(0)], \quad (2)$$

where  $Ze$  is the charge of the atomic nucleus,  $\Delta\langle r^2 \rangle$  is the difference of the mean square of the nucleus radius between the ground and excited states, and  $\rho_a(0)$  and  $\rho_s(0)$  are the electronic charge densities at the Cs nucleus of the absorber and source, respectively. Since  $\rho(0)$  is a measure of the change of the  $s$ -electron density at the ME nucleus, a quantitative interpretation of ME isomer shift requires knowledge of  $\Delta\langle r^2 \rangle$  for the 81 keV,  $5/2 \rightarrow 7/2$  transition in  $^{133}\text{Cs}$ . Previous  $^{133}\text{Cs}$  ME studies [16] of the systematics of  $S$  in a series of Cs compounds have led to a value of the change of  $S$  [ $\Delta S = 0.121(63)$  mm/s] corresponding to one  $6s$  electron. This value has been obtained from the difference of the measured isomer shifts between Cs metal,  $S(\text{Cs}) = -0.164(57)$  mm/s with respect to a  $\text{BaAl}_4$  source, assuming a configuration for

TABLE I. Analysis of the volume-induced change of the isomer shift  $\Delta S$  in terms of the  $6s \rightarrow 5d$  transfer. The theoretical value of the amount of the  $6s \rightarrow 5d$  transfer at  $V/V_0=0.3$  is taken from Ref. [12].

$p$ (GPa)	$V/V_0$	$\Delta S$ (mm/s)	Expected	Estimated amount of	
			$\Delta S$ if no $6s \rightarrow 5d$ transfer (mm/s)	$6s \rightarrow 5d$ transfer	This work Theory [12]
1.1	0.70(5)	0.018(24)	0.095(24)	0.3(1)	...
6.0	0.33(6)	0.082(20)	0.450(20)	0.67(6)	0.8

the Cs ion as  $5p^6 6s^n$  with  $n=1.23$  [22] and that of the most ionic compound  $\text{CsMnF}_3$  [ $S = -0.313(6)$  mm/s] with  $n=0$ . On the other hand, we obtain from our  $^{133}\text{Cs}$  ME isomer shift measurements on Cs metal at ambient pressure a value of  $S=0.222(37)$  mm/s with respect to  $\text{CsCl}$  or  $S=0.266(43)$  mm/s with respect to  $\text{CsMnF}_3$ . This measured value of  $S=0.266(43)$  mm/s is considerably larger and more accurate than the previous one [ $S=0.149(63)$  mm/s [16]]. If the present result is utilized in calculating the relation giving the change in  $S$  per unit equivalent  $6s$ -electron change, a value of  $0.216(43)$  mm/s is obtained.

On this basis we analyze the volume-induced change of isomer shift in Cs metal in terms of corresponding changes of the number of the  $6s$  electrons. The analysis of the experimental data is shown in Table I. The third column in Table I presents the volume-induced changes of the isomer shift relative to the value of  $S$  for Cs metal at ambient pressure. These values are compared (fourth column) with the corresponding shifts that are expected in the case of a uniform compression of the  $6s$  electrons [mechanism (i); see above]. This expected behavior of  $S$  is displayed by a full line in Fig. 2. Thus, the hyperbolic change of  $S$  with  $V/V_0$  according to mechanism (i) clearly deviates from the experimental results and thereby shows a clear case of  $6s$ -electron deficiency (i.e.,  $6s \rightarrow 5d$  transfer). The amount of this deficiency with respect to normal pressure is given in the fifth column.

Next, we compare the amount of the  $6s \rightarrow 5d$  transfer with that estimated from band structure calculations [12]. The general result of the band structure calculations is that the  $s \rightarrow d$  transition is gradual and starts very close to normal pressure or that even at normal pressure there might already be some  $s \rightarrow d$  transfer which causes a distortion of the Fermi surface of cesium [9]. Our results, indicating a loss of  $6s$  character which increases linearly with compression, clearly point to a process in which the  $6s$ -electron deficiency grows gradually with pressure. The theoretical estimate for the amount of the transfer gives a value of  $0.8$   $6s$  electron transferred at  $V/V_0=0.3$  [12]. The experimental value of  $0.67$  which we obtain at  $V/V_0=0.33$  is in good agreement with this value. The indication for a gradual growth in the elec-

tron deficiency which we observe can be interpreted in terms of the gradual and smooth overlap between the  $5d$  and  $6s$  bands as postulated by McMahan [12]. Additionally, very recent theoretical calculations on metallic Cs [8] show that a compression below  $V/V_0=0.3$  causes an expansion of the  $5p$  band so that it approaches the Fermi level. At such a higher compression the effect of  $5p \rightarrow 5d$  hybridization would influence the properties of the metal [8]. We, thus, would expect that this process would influence the behavior of the isomer shift by a change in the shielding of the  $5s$  electrons, which would lead to an increase of the  $s$ -electron density at the nucleus and therefore an increase in the apparent  $6s$ -electron number. The experimental results, however, show that in our pressure range this is not the case, probably due to the large separation of the  $5p$  band from the Fermi level. We believe that experiments at higher compression down to  $V/V_0=0.25$  might demonstrate this effect, which may cause an upturn in the isomer shift as the volume decreases further.

Finally, we want to refer to another interesting aspect of our study regarding the effect of the pressure on the lattice dynamics in metallic Cs. As mentioned above, the pressure-induced changes of the recoilless fraction  $f(p)$  reflect any corresponding changes of the Debye temperature  $\theta_D(p)$  [see Eq. (1)]. In order to avoid large errors in our result, we do not include the area of a deformation of the pressure cell in the pressure range  $0 \leq p \leq 0.6$  GPa that changes the thickness of the absorber. We therefore estimate the value of  $\theta_D$  at 6 GPa or at  $V/V_0=0.33$  in the following way. From Ref. [13], we used the experimental value of the Grüneisen parameter  $\gamma = -d \times \ln \theta_D / d \ln V = 0.45$  at 1.1 GPa or  $V/V_0=0.7$ , from which we estimate a value of  $\theta_D(1.1 \text{ GPa}) = 57(1)$  K with respect to  $\theta_D(0 \text{ GPa}) = 49(1)$  K [15]. We then calculate from the experimental value  $\ln(f_2/f_1) = 2.5(1)$  ( $f_2$  and  $f_1$  are the values of the recoilless fraction at 6.0 and 1.1 GPa, respectively) a value of  $\theta_D(6.0 \text{ GPa}) = 64(2)$  K. This new value of  $\theta_D$  (6 GPa), which is measured well below the Debye temperature at ambient pressure [ $T \approx 0.1 \theta_D(0 \text{ GPa})$ ], represents real changes of the phonon spectrum of metallic Cs at  $V/V_0=0.33$ . We hope that this result will stimulate further theoretical and experimental efforts.

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