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Calibration and interpretation of Mössbauer isomer shift of the 81-keV transition in ^{133}Cs

H. Muramatsu, E. Tanaka, H. Ishii, H. Ito, and M. Misawa
Department of Chemistry, Faculty of Education, Shinshu University, Nagano 380-8544, Japan

T. Miura, Y. Fujita, K. Omata, and S. Muto
High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

M. Koizumi, A. Osa, and T. Sekine
Department of Materials Science, Japan Atomic Energy Research Institute, Takasaki 370-1292, Japan

M. Yanaga
Department of Chemistry, Faculty of Science, Shizuoka University, Shizuoka 422-8529, Japan

K. Endo
Showa College of Pharmaceutical Sciences, Tokyo 194-8543, Japan

H. Nakahara
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Tokyo 192-0397, Japan

M. Fujioka
Cyclotron and Radioisotope Center, Tohoku University, Sendai 980-8578, Japan

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Radioactive ^{133}Xe was implanted into five host materials (Al, V, Cr, Rh, Mo) by means of an isotope separator. Internal conversion electron spectra of the 81-keV transition in ^{133}Cs were measured with an iron-free magnetic spectrometer and Mössbauer spectra were recorded independently. From the correlation between the weighted-mean Mössbauer isomer shifts and the intensity ratios of $(O+P)$-shell to N_1-shell conversion electrons, the change of the nuclear charge radius of the 81-keV transition in ^{133}Cs was deduced to be $\Delta R/R=+(1.5\pm 0.5)\times 10^{-4}$ for a uniform charge distribution of $R=1.2\times A^{1/3}$ fm or, equivalently, $\Delta\langle r^2\rangle =+(6.6\pm 2.4)\times 10^{-3}$ fm^2. This calibration makes it possible to reasonably interpret the extremely high isomer shifts observed in some refractory metals implanted with ^{133}Xe, where we take into consideration an increase in *s*-electron density originated from a decrease in the shielding effect on the *s* electrons by a removal of the $5p$ electron from the Cs impurity atom, which is attributed to the broadening of the valence band with compression and the resulting increase in overlap between the host and the impurity valence bands.
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I. INTRODUCTION

^{133}Cs is one of two isotopes of alkali metals for which the Mössbauer effect has so far been observed and only ^{133}Cs has yielded a substantial amount of reliable isomer shift data; another is ^{40}K, whose $\Delta\langle r^2\rangle$ is, however, so small that its widespread application would be inhibited. Cesium generally forms highly ionic compounds by more or less completely losing a valence electron, which leaves behind a spherically symmetric and relatively inert core. At the same time, this makes us expect that the Mössbauer spectra are in a lack of variety. However, some measurable differences between the isomer shifts of different chemical compounds have so far been found.[1–3] The isomer shift, which directly measures the *s*-electron density at the nuclear origin, is a unique parameter specific to Mössbauer spectroscopy; it is influenced by the character of chemical bonding, ionicity, charge transfer, and so forth. Therefore, ^{133}Cs is an invaluable probe for the elucidation of the nature of chemical bondings in highly ionic compounds.

On the other hand, it is worthy of notice that in the case of an impurity in metallic hosts or in alloys of cesium the widespread values of the isomer shift have been observed; furthermore they are extremely large. Recent works[4] as well as early works[5,6] for the isomer shift of ^{133}Cs in some metallic lattices show that observed values are unusually large; these values are much larger than those observed in any cesium compounds. The larger isomer-shift values cannot be explained by the previous isomer-shift calibration constants of ^{133}Cs in terms of $6s$-electron density.[1–3] Generally speaking, although discussions of the electron densities at the nucleus (sometimes called *electron contact density*) have been started with the assumption of a $5s^2 5p^6 6s^n$ configuration for the cesium atom or ion, this is not to say that all shifts are in fact attributed to changes in the $6s$-electron population. In many cases it merely means that shifts are expressed in terms of an equivalent $6s$ population *n*. When these large isomer shifts are interpreted in terms of $6s$-electron densities near the Cs nucleus, an extremely high compression or an existence of high local pressure at the impurity sites should be considered. In that sense, as pointed out by Pattyn *et al.*,[7] it is highly possible that the volume contraction of the electronic orbitals of Cs in the host matrix will result in changes not only in the $6s$ and $5p$ electrons of Cs, but will also directly affect the $5s$ electrons. As an idea for the explanation of the large isomer-shift value of ^{133}Cs in their observations on ^{133}Xe implanted into iron, de Waard and Drentje[5] have already proposed the promotion of $5p$ electron to the conduction band and the resulting loss of screening, which are caused by the *lattice pressure* on the impurity atom. To understand these large shifts is still an open question; and there exist the possibility that this may include a revision of the isomer shift calibration schemes proposed to date.

Various schemes[1–3] have been employed to calibrate the isomer shift in terms of electron density changes at the nucleus, and the value of $\Delta R/R$ for the 81-keV transition of ^{133}Cs has been proposed by several authors on the basis of theoretical[8] or Mössbauer-measurement approaches.[1–3] Although the sign of $\Delta R/R$ is considered to be positive, which has not yet been experimentally proved, its magnitude is still controversial; the proposed value of $\Delta R/R$ ranges from 0.15×10^{-4} to 2.3×10^{-4}. These determinations, except for the nuclear-theory calculation[8] which is generally considered unreliable, however, are based mainly on Mössbauer measurements and theoretical calculations of electron contact densities for hypothetically defined cesium configurations or on the assumption of isoelectronic configurations. The theoretical calculations of electron contact densities for free atoms and ions are reasonably reliable for the inner shells, but they are of doubtful significance for the outermost shells of atoms in a solid from which the largest contributions to the isomer shift are expected to arise; therefore, it is important to obtain more direct experimental information about $\Delta\rho(0)$. During the last decade, determinations of the $\Delta R/R$ values for ^{119}Sn and ^{125}Te have been carried out by the present authors using the internal conversion method,[9,10] which is a unique method that combines the isomer shifts obtained from Mössbauer measurements with measurements of the influence of the chemical environment on internal conversion probabilities for the same sample. Thus, the present paper describes a determination of $\Delta R/R$ in the 81-keV $(M1+2.8\%E2)$ transition of ^{133}Cs by the internal conversion method, and also using the calibration constant thus obtained, a quantitative interpretation of the isomer shift of ^{133}Cs focusing on the large shifts observed in metallic matrices.

II. EXPERIMENTAL DETAILS

Samples in this work were prepared by the implantation of ^{133}Xe $(T_{1/2}=5.25d)$, which decays to the 81-keV Mössbauer level in ^{133}Cs. The ^{133}Xe gas was purchased from Amersham International (U.K.) with a small amount of fission xenon. Ion implantation of ^{133}Xe was carried out at a terminal voltage of 20 kV at room temperature by means of the electromagnetic isotope separator of the Japan Atomic Energy Research Institute (JAERI, located at Takasaki). The integrated dose of ^{133}Xe atoms was estimated to be $\sim10^{13}$ atoms/cm^2 based on the radioactivity of the implanted samples. Host materials, into which ^{133}Xe was implanted, were polycrystalline foils of Al, V, Cr, Mo, and Rh with the purity of 99.0–99.99% and the thickness of 3–12 μm (purchased from Goodfellow Metal). These metallic foils were polished mechanically and washed with acetone before implantation.

The ^{133}Cs Mössbauer spectra were measured using a single-line absorber of CsCl with 360 mg/cm^2 Cs thickness while keeping both the source and absorber at liquid-helium temperature. In some cases an additional measurement in which the source was set at higher temperatures and the absorber at liquid-helium temperature was performed in order to estimate recoilless fraction. The 81-keV γ rays of ^{133}Cs from the implanted source were detected with a thin NaI(Tl) scintillation detector. A constant acceleration drive with a triangular velocity shape was used at ±6 mm/s.

The internal conversion electron spectra from the same samples used for Mössbauer measurements were observed by using the $\pi\sqrt{2}$ iron-free β-ray spectrometer with $\rho=75$ cm at the Institute for Nuclear Study, the University of Tokyo. For measurements of the internal conversion electrons in the region of the K line, L lines, and M, N, O, and P lines of the 81-keV transition, a single-wire proportional counter (SWPC) with a multislit (10-49 slits, 0.5 mm slit-width) was used as a focal-plane detector. In some cases, the same type of SWPC was placed just behind the main counter in order to reduce the counter background by using a position-coincidence technique. The gas pressure was controlled using an automatic gas-flow and pressure-control system; isobutane was used as a counter gas. The sample source was covered with an aluminum slit for defining the source dimension to 0.5×20 mm^2. A momentum range of about 4% could be measured simultaneously. The conversion lines was scanned with momentum steps of $\Delta P/P=10^{-4}$ over a 1% momentum region. These scans were repeated several times; the final momentum spectrum was then obtained by summing the counts, which are the number of electrons passing through a slit corresponding to the same momentum window.

III. EXPERIMENTAL RESULTS AND DATA ANALYSIS

For the new determination of $\Delta R/R$ of ^{133}Cs by the internal conversion method, we have especially taken care of the following points; considerations about these points are essential in works such as the present one, where various systematic as well as statistical errors tend to affect the final results to a rather large degree. (i) Six kinds of samples were made by implantation ^{133}Xe into host matrices of Al, V, Cr, Rh, and Mo, in contrast to only two calibration points in previous Mössbauer-measurement approaches.[1–3] (ii) The Mössbauer spectrum and conversion electron spectrum of the outer shells $(6s$, $5p$, and $5s)$ and $4s$ shell were observed for the same sample; this has an advantage that it takes into account such a pressure-induced effect on the inner electron shells. (iii) The *population average* isomer shift (δ) for the source sample was estimated when the observed spectrum indicated more than one different chemical sites for the implanted atoms. (iv) The errors of δ as well as of the observed ratio of the conversion electron intensities, $(\alpha_0+\alpha_P)/\alpha_{N_1}$ or $(O+P)/N_1$ and various sources of errors were consistently taken into account in the final evaluation of $\Delta R/R$.

The Mössbauer spectra for the sources of ^{133}Xe implanted into Al, V, Cr, Rh, and Mo observed with a CsCl absorber

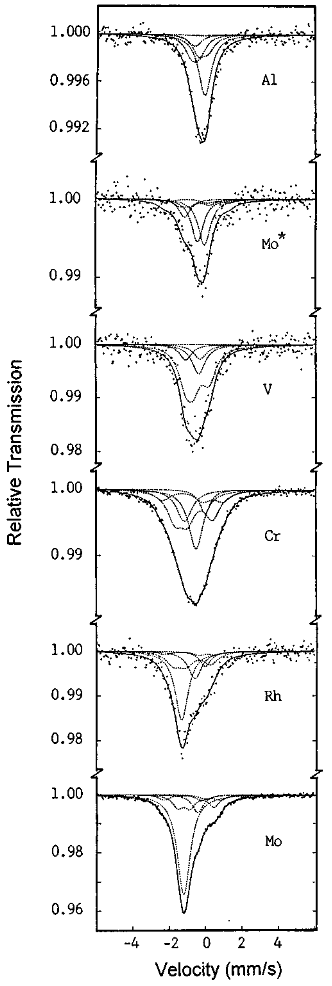

FIG. 1. Mössbauer spectra for the sources ^{133}Xe implanted into Al, V, Cr, Rh, and Mo observed with a CsCl absorber. Mo* denotes a source sample of Mo, which may include an appreciable amount of stable xenon coimplanted during ^{133}Xe implantations. The spectra were measured at liquid-helium temperature.

are shown in Fig. 1. All the spectra obtained in this work showed complex shapes caused by the implanted atoms occupying different sites in the host lattices. The spectra were analyzed by decomposition into several components. Such a decomposition procedure is often problematic if no additional information on the number of lines is obtainable. In the least-squares fitting of such spectra with single lines only, one of the single line is found in the large positive isomer-shift region with respect to a CsCl absorber. From the systematic isomer-shift studies on ^{133}Cs, it is unlikely to find isomer shifts larger than +0.1 mm/s with respect to a CsCl absorber.[1–3,11] Moreover, Campbell, Montet, and Perlow[12] have shown that the quadrupole splitting $e^2qQ_{\mathrm{ex}}(Q_{\mathrm{ex}}=-0.22$ barn) of the 81 keV ($5/2^+$) state in ^{133}Cs is not negligible; it can be measured by Mössbauer spectroscopy for sufficiently large field gradients. Thus, the line at positive velocity in the spectrum belongs to a quadrupole triplet which has a reasonable isomer shift. In reference to early works by de Waard *et al.*[5,6] and the systematic isomer-shift studies on ^{133}Cs implanted into metals by Pattyn and his co-workers,[4] and by taking into considerations the quadrupole splitting of the 81-keV ($5/2^+$) state, the complex experimental spectra were analyzed by the least-squares method under the assumption that three single lines and two quadrupole triplets exist in the spectrum.

For the purpose of the present study, the *average isomer shift* (δ) for a source sample was estimated by using the site population of the implanted atoms deduced from recoilless fractions for different sites, according to the method described in Ref. 9. The latter were estimated from the previous data[4] as well as the results from temperature dependence of the Mössbauer spectrum. It is to be noted that the δ value should correspond to the measured internal-conversion intensity, which is indeed the *population average* of the conversion intensities from different chemical sites.

Figure 2 shows typical conversion-electron spectra in the region of the *L* lines, *M* lines, and *N*, *O*+*P* lines of the 81-keV transition in ^{133}Cs. The momentum resolution was about 0.05%, although the spectrometer resolution was set at 0.03%. The conversion spectra were analyzed by a least-squares fitting using the computer code ACSEMP,[13] which employs numerical line shapes, and adjusts them in the process of peak fitting following the rule of constant tail fraction,[14] in addition to the adjustment of line positions. The *L*-conversion lines were completely resolved into subshells, but not the *M*, *N*, *O*, and *P* shells. The initial shape of the

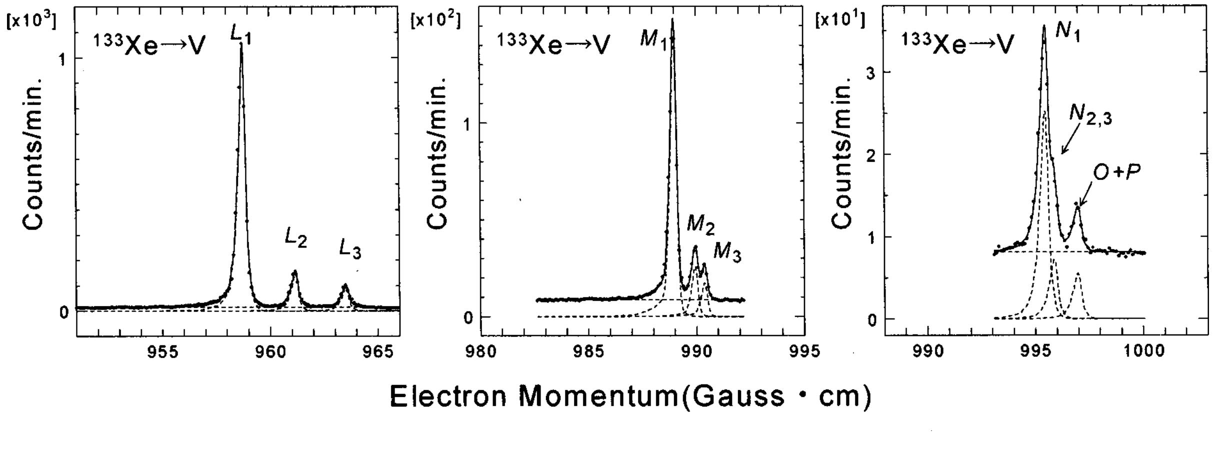

FIG. 2. The *L*-, *M*- and *N*,$O+P$-conversion lines of the 81-keV transition in ^{133}Cs observed for the source of ^{133}Xe implanted into V. The solid curves indicate the result of least-squares fittings using the conversion line shapes shown by the broken curves.

TABLE I. The outer-shell conversion electron intensities relative to the N_1-shell, and N-subshell ratios for the 81-keV transition in ^{133}Cs, together with the average isomer shifts.

Host	$(O+P)/N_1$	$N_{2,3}/N_1$	$\overline{\delta}$ (mm/s)[a]
Al	0.202(11)	0.289(16)	0.15(2)
Mo*	0.206(21)	0.283(44)	0.32(5)
V	0.220(10)	0.287(15)	0.41(4)
Cr	0.211(7)	0.282(9)	0.55(1)
Rh	0.226(16)	0.287(27)	0.77(3)
Mo	0.222(13)	0.290(20)	0.84(4)
Theor.[b]	0.212	0.287	

[a] Values at $T=4.2$ K.

[b] Theoretical values (Ref. 19) when the multipole mixing ratio of $\delta^2(E2/M1)=2.8\times10^{-2}$ (Ref. 21) is taken into account.

N_1-conversion line was determined from the N_1 line itself by a rough subtraction of the continuum from the higher-energy region of the line, namely, the contribution from the β continuum and the background. Since the intensity of the $N_{2,3}$ line was small and the line could not be clearly separated from the N_1 line, the initial position of the $N_{2,3}$ line was fixed in the spectral analysis by the electron binding energies for $Z=55$.[15] The O and P lines could not be resolved due to a limit of the experimental momentum resolution. The O lines including a small contribution of P lines ($O+P$ lines) were assumed to have the same shape as that of the N_1 line.

The results of the conversion electron spectra analyses are summarized in Table I, where the $(O+P)/N_1$-conversion ratios, as well as the $N_{2,3}/N_1$-subshell ratios, are given for the six samples, together with the average isomer shifts obtained from the Mössbauer-spectrum analysis. The $N_{2,3}/N_1$-subshell ratios are given to show the consistency of the present analysis.

IV. DERIVATION OF $\Delta R/R$

The Mössbauer isomer shift arises from the Coulomb interaction between the nuclear and electronic charge distributions. If it is assumed that a nucleus is a charged sphere of with radius R in the ground state and the electron density over the nuclear volume is constant $[\rho(0)]$, the isomer shift (δ) an be written as

$$\delta=(4/5)\pi Ze^2R^2(\Delta R/R)\Delta\rho(0), \tag{1}$$

where Z is the nuclear charge, e the electronic charge, $\Delta R/R$ the relative difference of the nuclear charge radius between the excited and the ground state, $\Delta\rho(0)$ the difference in the total electron density at the nucleus between the absorber and the source material, respectively. In spite of the situation that the valence-shell conversion, which is normally considered to be the most sensitive to the change in the chemical environments, could not be separately measured in contrast to previous works done by the present authors,[9,10] the following argument concerning the derivation of $\Delta R/R$ is considered to be still valid; namely, using the proportionality of $M1$ conversion coefficient to the electron density,[16–18] $\alpha_{nlj}=C_{lj}\rho_{nlj}(0)$, the outer-shell electron density, including the valence and next-inner shell electrons, $\rho_{\text{o.s.}}(0)=\rho_{5s}(0)+\rho_{5p}(0)+\rho_{6s}(0)$, is expressed as[9]

$$\rho_{\text{o.s.}}(0)/\rho_{4s}(0)=(\alpha_o+\alpha_p)/\alpha_{N_1}-(C_p/C_s-1)\times\rho_{5p}(0)/\rho_{4s}(0). \tag{2}$$

It is to be noted that the proportionality factor (C) depends only on the quantum numbers of l and j, not on the principal quantum number n, for a given transition. Since the $O_1(5s)$, $O_2(5p_{1/2})$, and $O_3(5p_{3/2})$ are not resolved, the second term introduces an error in obtaining $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$ from the first term. From the theoretical internal conversion coefficients[19] and electron densities,[20] (C_p/C_s-1) is calculated to be 8.2 when the multipole mixing ratio of $\delta^2(E2/M1)=2.8\times10^{-2}$ (Ref. 21) is taken into account. From Ref. 20, $\rho_{5p}(0)$ ranges from 4.79 to 4.75 a.u., corresponding to configurations of $6s^0$ and $6s^1$. Therefore, the second term in Eq. (2), if neglected, introduces a constant error of 0.029 in $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$, which is comparable to the experimental errors associated with the observed ratio of the conversion electron intensities, $(\alpha_o+\alpha_p)/\alpha_{N_1}$ or $(O+P)/N_1$. Thus the observed $(\alpha_o+\alpha_p)/\alpha_{N_1}$ values were reduced by a constant of 0.029 in order to estimate $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$. This estimation introduces small errors of $\pm1\times10^{-4}$ in $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$. Consequently, the general equation for the isomer shift [Eq. (1)] can be rewritten with the correlation between the averaged isomer shift (δ) and the change in $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$ as

$$\overline{\delta}=(4/5)\pi Ze^2R^2(\Delta R/R)\rho_{4s}(0)_{\text{theor}}\Delta[\rho_{\text{o.s.}}(0)/\rho_{4s}(0)]. \tag{3}$$

It is to be reminded that the change of the core electron density $\Delta\rho_{\text{core}}(0)$ $(n\leqslant4)$ due to the different chemical states is negligible as seen from the relativistic Dirac-Fock calculations[20] for free atoms and ions, and, thus, $\Delta\rho_{\text{o.s.}}(0)$ can be substituted for $\Delta\rho(0)$ in Eq. (1). In this method of deriving $\Delta R/R$, however, it is obvious that a use of $(\alpha_o+\alpha_P)/\alpha_{N_1}$ instead of α_P/α_o is less sensitive to the change in the chemical environments. On the other hand, Pattyn and his co-workers[4] have reported that in some cases the isomer shift values of Cs impurity introduced by implantation into various metallic as well as metalloid host matrices are unusually large, suggesting the possibility of very high local pressure at the impurity atom sites. From their observations, it has been pointed out that such a volume contraction of the electronic orbitals will result in changes not only in the $6s$ and $5p$ electrons of Cs, but also directly in the $5s$ electrons. The analytical method mentioned above has an advantage that it takes into account such an effect on the inner-electron shells.

In Fig. 3 the ratios $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$ obtained from conversion measurements are plotted against the average isomer shifts δ determined by Mössbauer experiments. The data of the present work were fitted to a solid straight line by a weighted least-squares analysis. The errors of δ, as well as errors of $\rho_{\text{o.s.}}(0)/\rho_{4s}(0)$, were taken into account in this fitting using an *iteration* procedure. The slope of this straight line includes the information of $\Delta R/R$. In Eq. (3) a relativistic value of $\rho_{4s}(0)_{\text{theor}}=1344.7$ a.u. calculated by Band

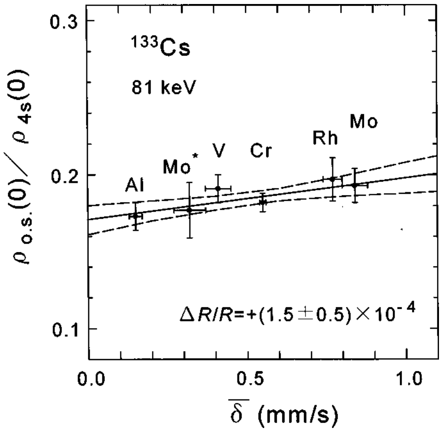

FIG. 3. Correlation of the electron-density ratio $\rho_{\rm o.s.}(0)/\rho_{4s}(0)$ obtained by the conversion electron measurements with the average isomer shifts $\bar{\delta}$ (relative to a CsCl absorber) measured for the samples of ^{133}Xe implanted into five kinds of host materials. The solid line indicates the result of a weighted least-squares fitting. The region in between the two dashed lines shows the region of $\rho_{\rm o.s.}(0)/\rho_{4s}(0)$ allowed for the variation of one standard deviation of $\Delta R/R$ if a theoretical value of $\rho_{4s}(0)_{\rm theor}=1344.7$ a.u. (Ref. 20) is used in Eq. (3).

et al.[20] was used for an isolated neutral Cs atom with the following result for the change of nuclear charge radius:

$$\Delta R/R=+(1.5\pm0.5)\times10^{-4},\quad\text{or}$$
$$\Delta\langle r^2\rangle=+(6.6\pm2.4)\times10^{-3}\ \ \text{fm}^2, \tag{4}$$

where $R=1.2\times A^{1/3}$ fm was used for the former expression.

V. DISCUSSION

A. Calibration constant of the isomer shift

As mentioned before, the interpretation of the isomer shift in terms of electron densities at the nucleus generally requires the knowledge of $\Delta R/R$, which is essential for correlating measured isomer shifts with the corresponding changes in the number of s electrons in a given system. Several values of $\Delta R/R$ for ^{133}Cs have been reported previously, most of which have been deduced from the correlation between the isomer-shift data and the estimated values of $6s$-electron population for several compounds.

Boyle and Perlow[3] analyzed their isomer-shift data assuming a general electron configuration for the cesium ion as $5p^66s^n$, where n is the number of $6s$ electron, and have obtained a *calibration value* of 0.121(46) mm/s, which corresponds to the change of the isomer shift due to a change of one $6s$ electron; i.e., $d\delta/dn$. In their calibration, this value was obtained from the difference of the measured isomer shifts between metallic cesium, $\delta(\text{Cs})=-0.164(57)$ mm/s with respect to ^{133}BaAl$_4$ source, assuming a configuration for the Cs ion as $5p^66s^n$ with $n=1.23$ and the most ionic compound of CsMnF$_3$, $\delta=-0.313(6)$ mm/s with $n=0$. This calibration value, $d\delta/dn=0.121$ mm/s, should correspond to the value $\Delta R/R=0.89\times10^{-4}$, if a theoretical $6s$-electron density of $\rho_{6s}(0)_{\rm theor}=5.4\times10^{25}\ \ \text{cm}^{-3}$ is used. On the other hand, Henning *et al.*[2] also derived a relative change of the mean square charge radius, $\Delta\langle r^2\rangle/\langle r^2\rangle=+2\times10^{-4}$, which was obtained from their Mössbauer measurements in three different ways using eight ionic compounds and an intermetallic compound CsBi$_2$. This value corresponds to $\Delta R/R=+1\times10^{-4}$.

Recently, Pattyn *et al.*[7,22] obtained an isomer-shift value of 0.222(45) mm/s for metallic cesium with respect to CsCl at ambient pressure in their high-pressure Mössbauer-effect experiments, which is considerably larger than the value of 0.105(57) mm/s reported by Perlow *et al.*[3] They also obtained a calibration value of $d\delta/dn=0.216(46)$ mm/s in the same manner as that of Perlow *et al.* by replacing the isomer-shift value for Cs metal by the new one. This value would change Perlow's calibration constant ($\Delta R/R=0.89\times10^{-4}$) to the value of $\Delta R/R=1.59\times10^{-4}$ which is in good agreement with the value reported here. In the derivation of the calibration constant, however, both Perlow *et al.* and Pattyn *et al.*, as well as Henning *et al.* have used the theoretical electron density of $\rho_{6s}(0)_{\rm theor}=5.4\times10^{25}\ \ \text{cm}^{-3}$ (8.08 a.u.) after correction of the nonrelativistic value of $\rho_{6s}(0)_{\rm theor}=2.0\times10^{25}\ \ \text{cm}^{-3}$ using the relativity factor of $S'(Z=55)=2.68$ as given by Shirley;[23] this value differs from a recent relativistic value of $\rho_{6s}(0)_{\rm theor}=3.38\times10^{25}\ \ \text{cm}^{-3}$ (5.01 a.u.) calculated by Band and Fomichev[20] by a factor of 1.6. If one uses the latter value instead of the former, the calibration constants will be changed to 1.4×10^{-4} for Perlow's, 2.5×10^{-4} for Pattyn's, and 1.6×10^{-4} for Henning's, respectively. This means that the calibration constants obtained from the methods discussed above strongly depend on the theoretical estimates of the valence electrons density at the nucleus $\rho_{6s}(0)_{\rm theor}$, as well as the estimation of $6s$-electron population n. In the internal conversion method adopted in the present work, on the other hand, the theoretical value of the inner-shell electrons $\rho_{4s}(0)_{\rm theor}=1344.7$ a.u. is used, which is supposed to be in general much more reliable than that of valence electrons, and also less affected not only by the difference of electronic configuration assumed in the theoretical calculation but also by the method of the calculation itself.[18,20] Thus the new value of $\Delta R/R=+(1.5\pm0.5)\times10^{-4}$ in the present work can be considered more reliable than those derived by former methods.

B. Interpretation of the isomer shifts

From Fig. 3, and by use of a relativistic value of $\rho_{4s}(0)_{\rm theor}=1344.7$ a.u. calculated by Band and Fomichev[20] for an isolated neutral Cs atom, we obtain the following relation between $\rho_{\rm o.s.}(0)$ and δ (hereafter we use δ instead of $\bar{\delta}$):

$$\rho_{\rm o.s.}(0)=230+36.4\delta\pm24\sqrt{(\delta-0.49)^2+0.045}\ \ \text{a.u.}, \tag{5}$$

where δ is the isomer shift in mm/s relative to CsCl. Equation (5) is very important because it converts the measured isomer shift, which is no more than a relative value, to an absolute value of the contact density. It will be possible not only to compare the contact density evaluated from the observed isomer shift using Eq. (5) with the theoretical calculations, but also to compare contact densities among Mössbauer elements; e.g., other nuclei in typical elements of fifth period such as ^{119}Sn, ^{121}Sb, ^{125}Te, ^{129}I, ^{131}Xe, and so on. In this case, however, only the outer-shell electron density at the nucleus (sum of $5s$, $5p$, and $6s$ electron contact densities) is evaluated instead of that of the valence-shell contact density in contrast to previous work done by the present authors.[9,10] This does not reduce its usefulness and importance; indeed this calibration, together with the isomer shift values reported by Boyle and Perlow[3] for cesium halides and metallic cesium, leads to a good agreement with electron density calculations.

The present value of $\Delta R/R$ corresponds to $d\delta/dn = 0.137(49)$ mm/s as a calibration value in another expression by Boyle and Perlow,[3] where it should be noted that this calibration value is based on the hypothetical configuration $5p^6 6s^n$ whose n is a function of δ, $n(\delta)$, and on the assumption that a change of n is equivalent to a change in $\rho(0)$ which determines δ. Using the isomer shifts as measured by Perlow *et al.* for $CsMnF_3$ and Cs metal, outer-shell electron densities at the nucleus $\rho_{\text{o.s.}}(0)$ in Cs atom included in these materials are estimated to be 228 and 234 a.u., respectively. The theoretical evaluations for the $\rho_{\text{o.s.}}(0)$ have been given as 194.7 a.u. for $6s^0$ and 199.9 a.u. for $6s^1$ by Band and Fomichev,[20] which are about 17% smaller than the estimated values from our experimental result. This discrepancy may be explained by the following argument: The electronic wave function of free cesium atoms should be modified for those in solids, this modification being called the *solid state effect*.[24,25] A simple approach for evaluation of this effect is to renormalize the electronic wave functions by a factor ξ_{nl} within the Wigner-Seitz sphere, as described by Friedman *et al.*;[26] they obtained $\xi_{5s} = \sqrt{1.09}$ and $\xi_{5p} = \sqrt{1.38}$ for $5s$ and $5p$ electrons in β-Sn, respectively. With the same manner, if ξ_{nl} data were available for cesium atoms in solids, we might be able to explain the discrepancy between the experimental and the theoretical contact densities, multiplying the theoretical values by appropriate factors for $5s$ and $5p$ electrons of cesium atoms.

On the other hand, the $\rho_{\text{o.s.}}(0)$ difference of 6 a.u. evaluated from Eq. (5) between $CsMnF_3$ and Cs metal, whose configurations for the Cs ion as $5p^6 6s^n$ have been assumed by Perlow *et al.* with $n = 0$ and $n = 1.23$, respectively, reasonably agrees with the theoretical estimation of 5.2 a.u. (199.9 a.u. for $6s^1$ minus 194.7 a.u. for $6s^0$) by Band and Fomichev,[20] which should correspond to the $6s$ electron contact density; in fact, 5.01 a.u. is a theoretical estimate of the $6s$ electron contact density for an isolated Cs atom with the configuration of $6s^1$. Using the value of $d\delta/dn = 0.137$ mm/s together with the difference between the isomer-shift values for $CsMnF_3$ and Cs metal, we can estimate Δn which is the difference of $6s$ electrons residing on the Cs atom between $CsMnF_3$ and Cs metal; it becomes $\Delta n = 1.1$, which is a little bit smaller than 1.23. With the same manner we observe $\Delta n = 9.2$ from the difference between the isomer shift of $CsMnF_3$ and the isomer-shift value of 1.22 mm/s which is measured for the Cs atom sitting on the substitutional site of Mo matrix in this work. What is especially surprising is that the Cs atom in the Mo host matrix has about nine times as much s character as in metallic cesium, and this corresponds to the apparent occupation number of $6s$ electron of about 9. As is pointed out by Perlow *et al.* that n may be greater than 2 if the atomic volume is reduced, the large isomer shifts which have been observed in refractory metals implanted with ^{133}Xe (Ref. 4) imply extremely high compression when the isomer shift is interpreted in terms of $6s$ electron densities of Cs.

The volume dependence of the isomer shifts of ^{133}Cs has been studied by Pattyn and his co-workers through the microscopic observation of the $s \rightarrow d$ transition in metallic cesium under high pressure[22] and also the observation of pressure effects on electron densities in CsCl and CsI.[7] In their analyses, since the large enhancements in the s-electron density seemed to contradict theoretical expectations[27] of a pressure-induced $s \rightarrow d$ transition in CsI and CsCl and a corresponding relative decrease in the $6s$-electrons values, they have proposed other mechanisms which enhance the s-electron density in order to explain their experimental results by such a transition. The first mechanism which may cause such an s-electron density enhancement is the charge-transfer mechanism, namely a back transfer from the halogen ion toward the Cs ion. From a theoretical estimation, however, they have concluded that this mechanism alone cannot be responsible for the large pressure-induced increase of the isomer shift. A second mechanism which can cause this additional increase in s-electron density with decreasing volume originates indirectly from the modified shielding effect of the $5p$ orbitals in CsI and CsCl. Judging that the band-structure calculations already predict some mixing in of the $5p$ cesium valence band into the iodine $5p$ band at normal pressure, a gradual shift and broadening of the $5p$ band of cesium and an increased overlap with the iodine $5p$ band shown by calculations of the pressure changes in the band structure[28] are equivalent to a partial removal of $5p$ electrons from the Cs ion, and result in a decrease of the shielding effect of these $5p$ electrons and thereby in an increase in $5s$-electron density at the Cs nucleus. We consider that the latter mechanism mentioned above is favorable to interpret or explain the extremely high isomer shifts observed in some metals implanted with ^{133}Xe, because a large increase of the isomer

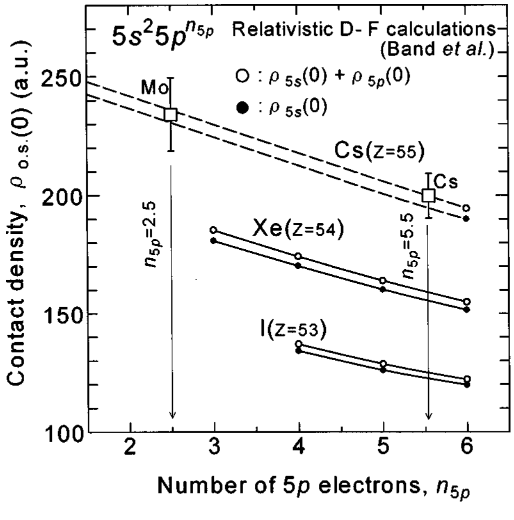

FIG. 4. Theoretical contact densities of the atoms or ions with the electronic configurations of $5s^2 5p^n$ in terms of number of $5p$ electrons, n_{5p}. Theoretical values were calculated by Band and Fomichev (Ref. 20) using the relativistic Dirac-Fock equations. Open squares with error bars and arrows are depicted as typical examples of the analyses for the estimation of the number of $5p$ electrons.

TABLE II. Estimated values of the outer-shell electron contact density and occupation numbers of $5p$ electrons for the Cs in the lattices of metallic hosts as well as in some cesium compounds. It was assumed that $CsMnF_3$ has an electronic configuration of $5s^2 5p^6$.

Host	δ[a] (mm/s)	Estimated values of $\rho_{\text{o.s.}}(0)$ (a.u.) This work[b]	Theory[c]	Occupation numbers expected: n_{6s}[d] if no $5p$ electron removal	n_{5p}[e]
$CsMnF_3$	−0.044(6)[f]	228(14)	194.7	0	6
Cs metal	0.105(57)[f]	234(11)		1.1	5.5
$BaAl_4$[g]	0.269(3)[f]	240(7)		(2.3)	5.0
Fe	1.1[h]	270(15)		(8.4)	2.8
Al	0.54(7)[i]	250(5)		(4.3)	4.3
V	1.04(6)[i]	268(14)		(7.9)	3.0
Cr	1.10(1)[i]	270(15)		(8.4)	2.8
Mo	1.22(1)[i]	274(18)		(9.2)	2.5
Rh	1.31(1)[i]	278(20)		(9.9)	2.2
CsCl (4.2 GPa)	0.084(12)[j]	233(11)		0.9	5.6
CsI (5.5 GPa)	0.140(10)[j]	235(10)		1.3	5.4

[a] Isomer shifts with respect to CsCl.

[b] Estimated values from Eq. (5).

[c] Theoretical contact density calculated by Band and Fomichev (Ref. 20).

[d] According to Boyle and Perlow (Ref. 3), this denotes the n in the hypothetical configuration of $5p^6 6s^n$ whose n is a function of δ, under the assumption that a change of n is equivalent to a change in $\rho(0)$ which determines δ. The values exceeding 2 are in parentheses.

[e] Evaluated values by using Fig. 4. See the text in detail.

[f] Taken from Ref. 3.

[g] $^{133}BaAl_4$ was used as a source in the Mössbauer experiment by Boyle and Perlow (Ref. 3).

[h] The isomer shift for the high field sites in Fe taken from Ref. 5.

[i] The isomer shift for the substitutional sites obtained from the present work.

[j] Taken from Ref. 7.

shift cannot be expected from the former mechanism and the addition of $6s$ electrons seems unable to account for the very large isomer shifts. It should be noticed that this mechanism including the $5p$-electron removal and the loss of screening has already been pointed out by de Waard and Drentje[5] in their observations on implanted ^{133}Xe sources; they explained the isomer shift for the high field sites in Fe by a promotion of about two $5p$ electrons to the conduction band of the host.

Since there exists no empirical relationship between the $5p$-electron removal and the resulting increase in $6s$ electron or in $5s$ and $5p$ electron density, we try to compare our experimental values of outer-shell electron densities with the theoretical estimates by Band *et al.* for the outer-shell electron densities, where since the electron densities evaluated from Eq. (5) using isomer-shift values do not coincide with the theoretical values in the absolute value and nobody knows what is the true value, as the first-order approximation the experimental ones are tentatively normalized to the theoretical value in the electronic configuration of $5s^2 5p^6$ (corresponding to the isomer shift of $CsMnF_3$, −0.044 mm/s with respect to CsCl). In Fig. 4, theoretical contact densities of the outer-shell electrons for the atoms or ions with the electronic configuration of $5s^2 5p^n$ in terms of number of $5p$ electrons (n_{5p}) are shown together with those of Xe and I, where since in the case of Cs no theoretical estimate is available except for the configuration of $5s^2 5p^6$ (Cs^+), the values corresponding to other configurations are estimated as shown by the dashed line under the assumption that they have a similar dependence systematically changing with Z on n_{5p} to those of Xe and I. It can be seen that the contact densities of $5s$ and $5p$ electrons increase with decreasing the number of the $5p$ electron and the dependence of $\rho_{5s}(0)+\rho_{5p}(0)$ on the number of $5p$ electron is almost the same as that of $\rho_{5s}(0)$; however, the increase of $\rho_{5p}(0)$ is more rapid (not shown in the figure). Using this relationship, for example, we can estimate the numbers of 0.5 and 3.5 $5p$ electrons that have to be removed from the Cs in the lattices in metallic cesium and Mo in order to account for the isomer shifts of 0.105 and 1.22 mm/s, respectively, as is shown in Fig. 4. Thus, the ion cores left by $5p$ electrons would be described approximately as $Cs^{1.5+}$ and $Cs^{4.5+}$ in the lattices of metallic cesium and Mo, respectively, which are, of course, surrounded by a screening charge to preserve electric neutrality. See Table II.

As another example of the application of this relationship, we consider the Cs in $BaAl_4$ which was used as a source in the Mössbauer experiment by Boyle and Perlow.[3] In Cs metal one usually takes the conduction band to contain one electron and describe the ion cores by Cs^+. Perlow *et al.* treated an impurity introduced into the aluminum structure as

Cs^+ ion, taking into account the problem of shielding the two extra charges of the Cs^+ ion, because $BaAl_4$ possesses a band structure not unlike pure aluminum, which contains three conduction electrons, two with *s* character and one with *p* character. They suggested then that the energy of the holes in the aluminum conduction band is lower than that of some of the $5p$ electrons in the Cs^+ ion; thus the cesium impurity in $BaAl_4$ fills these holes with two $5p$ electrons as well as the $6s$ electron leaving a core described approximately by Cs^{3+}. From the isomer shift of $BaAl_4$ with respect to CsCl, 0.269(3) mm/s,[3] we can estimate the number of $5p$ electrons that have to be removed from the Cs^+ ions in $BaAl_4$ to be 1.0, using our relationship with the same manner mentioned above. This result is equivalent to the ions being Cs^{2+}, which is in reasonable agreement with the estimation by Perlow *et al.* as for the tendency. This agreement seems to be good support for the idea that these large isomer shifts arise from the conduction electrons which scatter from the impurity and surround it as a screening charge.

Pattyn *et al.*[7] have also estimated an additional increase in *s*-electron density originating from the shielding effect of the $5p$ electrons in CsI and CsCl by applying the relationship extracted from the Iodine Mössbauer isomer-shift data. The relationship translated into the ^{133}Cs isomer shift scale is that the removal of 0.24 and 0.23 $5p$ electrons corresponds to increases equivalent to 0.37 and 0.35 $6s$ electrons in CsI having an isomer-shift value of 0.140 mm/s, and CsCl having an isomer-shift value of 0.084 mm/s, respectively. This relationship for the experiments at high pressure, when applied to the case of the Cs in the lattices of metallic cesium and Mo, yields the estimated values of 0.45 and 3.8 $5p$ electrons that have to be removed from the Cs in order to account for the isomer shifts of 0.105 and 1.22 mm/s, respectively. These values are in good agreement with our estimations, 0.5 and 3.5 $5p$ electrons. We are not sure, however, whether or not such an effect expected in Cs halides as the broadening of the valence band with compression and the resulting increase in overlap exists also in metallic cesium and impurity atoms of Cs in metallic hosts; in fact, no calculation is not available for the changes in the impurity electron energy levels of the Cs impurity atom and its overlap with the host electron bands.

As a concluding remark, the present results conclusively show that the volume contraction of the electronic orbitals of Cs impurity in the metallic host results in changes in not only the outermost shell electrons ($6s$ electrons) but also next-inner shell electrons ($5p$ and $5s$ electrons) of Cs, and that an additional increase in *s*-electron density with decreasing volume, which originates from such changes as the $5p$-electron removal and the loss of the shielding effect by them, determines the extremely high isomer shifts observed in some refractory metals implanted with ^{133}Xe. Theoretical calculations dealing with this subject are desired in order to test them with the present results.

VI. CONCLUSIONS

An additional determination of $\Delta R/R$ in the 81-keV $(M1+2.5\%E2)$ transition of ^{133}Cs has been achieved by the internal conversion method that obtain more direct experimental information about $\Delta\rho(0)$. Radioactive ^{133}Xe was implanted into five host materials (Al, V, Cr, Rh, Mo) by means of an isotope separator. Internal conversion electron spectra of the 81-keV transition in ^{133}Cs were measured with an iron-free magnetic spectrometer and Mössbauer spectra were recorded independently. From the correlation between the weighted mean Mössbauer isomer shifts and the intensity ratios of $(O+P)$-shell to N_1-shell conversion electrons, the change of the nuclear charge radius of the 81-keV transition in ^{133}Cs was deduced to be $\Delta R/R=+(1.5\pm0.5)\times10^{-4}$ for a uniform charge distribution of $R=1.2\times A^{1/3}$ fm or, equivalently, $\Delta\langle r^2\rangle=+(6.6\pm2.4)\times10^{-3}$ fm^2. This value is somewhat higher but more reliable and accurate than those obtained previously.

Using the calibration constant thus obtained, a quantitative interpretation of the isomer shift of ^{133}Cs has also been performed focusing on the large shifts observed in metallic matrices. The calibration factor yields a useful equation for the outer-shell electron densities as a function of the isomer shift by using the results in conversion-electron measurements in outer shells and Mössbauer isomer-shift measurements. This equation is very important not only because it converts the measured isomer shift to an absolute value of the contact density, but also because it will be possible to compare the contact density evaluated from the observed isomer shift with the theoretical calculations. In the present work, this equation is uniquely utilized to explain an increase in *s*-electron density at the nucleus when the atomic volume is reduced. Since there exists no empirical relationship between the $5p$-electron removal and the resulting increase in $6s$-electron or in $5s$- and $5p$-electron density, we try to compare our values for the outer-shell electron densities evaluated from the equation with the theoretical estimates by Band *et al.* for the outer-shell electron densities of free atoms or ions with various electronic configurations. These analyses make it possible to reasonably interpret the extremely high isomer shifts observed in some refractory metals implanted with ^{133}Xe, where we take into consideration an increase in *s*-electron density originated from a decrease in the shielding effect on the *s* electrons by a removal of the $5p$ electron from the Cs impurity atom, which is attributed to the broadening of the valence band with compression and the resulting increase in overlap between the host and the impurity valence bands.

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