Isomer shift of ^{133}Cs implanted in various elements

I. Dézsi,* H. Pattyn, E. Verbiest, and M. Van Rossum

Instituut voor Kern- en Stralingsfysika, University of Leuven, B-3030 Leuven, Belgium

(Received 26 August 1988)

The isomer shift (δ) values of ^{133}Cs, the daughter isotope of ^{133}Xe, implanted in Al, Be, Cr, Ge, Si, Te, Zn, diamond, graphite, Fe, Ir, Lu, Mo, Pt, Re, Rh, Ta, Ti, V, and W, were measured. Some of the values were unusually large and suggested very high local pressure at the impurity atomic sites. The formation of vacancy impurity complexes tended to decrease the δ values. A correlation between the rigidity of the host lattice and the δ values was found.

I. INTRODUCTION

Unusually large isomer shift (δ) values of ^{133}Cs, the daughter element of ^{133}Xe, implanted in some metallic lattices were already reported.[1,2] These values were much larger than could be observed in any Cs compounds. The large δ values were attributed to the existence of high local pressures at the impurity sites. Some spectra were complex and suggested locations for Cs atoms not only in the substitutional atomic positions, but also in vacancy-impurity complexes.[3] Extremely large δ values are observed in diamond[4] which has the most rigid lattice and the smallest lattice constant among the solids.

In order to obtain more data and possibly find systematics of the isomer shift values of Cs impurity introduced by implantation into various lattices, further metallic as well as metalloid host matrices were implanted with ^{133}Xe and their Mössbauer spectra studied. An attempt was made to find a correlation between the δ values of ^{133}Cs and the bulk moduli characterizing the rigidity of the solids in which the Cs was introduced.

II. EXPERIMENT

The ^{133}Xe implantations were carried out at 85 keV with doses between 5×10^{13} and 1×10^{14} atoms/cm^2 in the Leuven isotope separator. The target materials were in most cases single crystals except diamond and graphite

TABLE I. The Mössbauer parameters of the implanted samples. δ is the isomer shift, Δ the quadrupole splitting, and Γ the linewidth. These values are given in mm/s.

Host	δ	Δ	Γ	Relative fraction (%)
Al	−0.55(2)	≤1.5	1.25(2)	100
Be	−0.28(1)	≤1.7	1.28(2)	100
Cr	−1.00(4)	≤1.4	1.22(3)	100
Ge	−0.16(2)		0.98(2)	100
Si	−0.18(2)		0.92(2)	100
Te	−0.11(2)	≤1.0	1.00(2)	100
Zn	−0.16(2)	≤0.6	0.90(2)	100
graphite	0.05(1)	≤0.84	0.95(2)	100
diamond	−3.44(2)		0.94(3)	33(5)
	−1.31(2)		0.94(3)	33(5)
	−0.33(2)	−5.1(2)[b]	0.94(3)	
	−0.20(2)[a]		0.94(3)	
Fe	−1.10(5)		0.78(7)	
Ir	−1.72(2)		0.84(8)	43(3)
Lu	−0.85(10)		0.84(8)	22(4)
Mo	−1.28(4)		0.84(8)	85(2)
Pt	−1.37(3)		0.84(8)	34(3)
Re	−1.54(2)		0.84(8)	52(4)
Rh	−1.37(2)		0.84(8)	66(3)
Ta	−1.25(10)		0.84(8)	25(5)
Ti	−0.80(10)		0.84(8)	12(4)
V	−0.97(10)		0.84(8)	26(4)
W	−1.56(7)		0.84(8)	17(4)

[a]This component appeared only above 5×10^{13} atoms/cm^2.
[b]For group 2 quadrupole split components appeared for vacancy associated sites; $\eta = 0$ was imposed.

where the former was with the mosaic of natural crystals and the latter pyrolitic graphite. Some implantations were made at 77 K in order to keep the target below its characteristic vacancy migration temperature. The Mössbauer spectra were measured in a liquid-He cryostat where both the implanted source and the single line absorber were kept at 4.2 K. Single line absorber CsCl with 360 mg/cm^2 Cs thickness was used. The δ values are given relative to this absorber.

III. RESULTS

Two types of Mössbauer spectra appeared in the various implanted solids. In one group of elements (Al, Be, Cr, Ge, Si, Te, Zn, graphite, called group 1) the spectra showed a broadened single line (the natural line width for ^{133}Cs transition is $2\Gamma = 0.5$ mm/s). In group 2 (diamond, Ir, Lu, Mo, Pt, Re, Rh, Ta, Ti, V, and W) the spectra were complex and contained more than one spectral component.

The analysis of the spectra of group 1 was first made by assuming a single line. Since the quadrupole moment at the first excited state of ^{133}Cs is -0.22 b and the Sternheimer factor is large, -121.3 (Ref. 5), a broadening can be caused by a quadrupole splitting. Therefore, in group 1 the spectra were analyzed also in terms of quadrupole splitting. The δ values, however, obtained by assuming a single line or a quadrupole split multiplet, were within ± 0.01 mm/s value. The parameters obtained are compiled in Table I. The maximum possible $\Delta = eQV_{zz}/20$ quadrupole split values (Q is the nuclear quadrupole moment, V_{zz} is the electric field gradient) are also shown.

The analysis of the spectra of group 2 was more complex. Some spectra undoubtedly showed a single line component which could be recognized by its large intensity. This component appeared with the largest negative δ value in most cases. As a representative the ^{133}Cs spectra in Mo are shown in Fig. 1. In other cases where this recognition could not be made easily the thermal evolution of the spectra helped to resolve the single line with the largest negative δ value. The details of this analysis procedure have been described in more detail elsewhere.[6,7] It was assumed that some spectral components belong to impurity-vacancy complexes containing two to five vacancies. The spectral component, a single line, with the most negative δ value was always chosen as characteristic of the substitutional Cs.

The lattice location of Xe after implantation has not been determined by independent (e.g., channeling) methods; only for iron was it found that the substitutional fraction is at least 40%.[10] Some spectra (in Lu, Ta, Ti and V) showed large broadening with fewer details. Their δ values are obtained by using the same analyzing principle as for other hosts in group 2. In the latter case, however, the δ values have the largest uncertainty.

IV. DISCUSSION

For Cs the valence electron is 6s and the isomer shift can be expressed (assuming that core electrons are not delocalized) as

$$\delta = K \frac{\Delta R}{R} \Delta |[\psi(0)]_{6s}|^2 \ . \tag{1}$$

K is a constant depending on the nucleus, $\Delta R/R$ is the nuclear radii difference, $[\psi(0)]_{6s}$ is the 6s electron density at the nucleus.

Various schemes have been employed to calibrate the isomer shift of ^{133}Cs in terms of electron density (expressed in terms of 6s population) changes at the Cs nucleus.[8,9] The most plausible seems to be that proposed by Boyle and Perlow.[8] The δ value of CsMnF$_3$ was found to be the smallest among the Cs compounds and accepted, as the δ value corresponds to $6s^0$ electron configuration. A calibration line was obtained by connecting the δ value of this compound with the δ value of metallic Cs in the δ-6s-electron density scale. This line (dashed line) is shown in Fig. 2 where some of the δ values of implanted samples are also shown. The figure demonstrates that δ values are well outside the limit represented by two 6s electrons. These large negative δ values indicate large s electron densities at the Cs nuclei which are caused by a large compression of the s electronic shell of the oversized Cs sites. Some δ values (mostly of implanted metal-
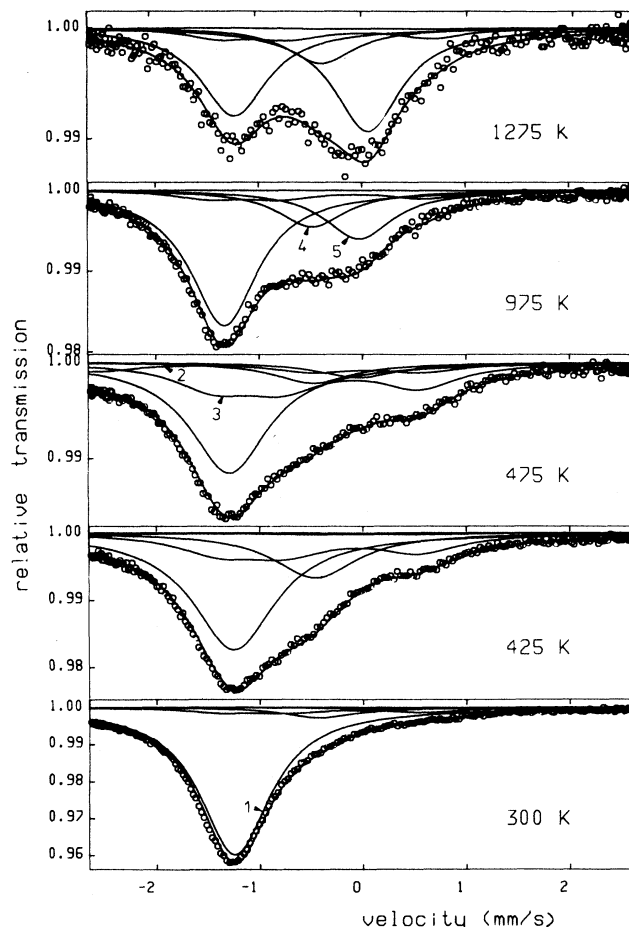

FIG. 1. The ^{133}Cs Mössbauer spectra measured in Mo annealed at various temperatures. Spectral components: 1, substitutional; 2–5, XeV$_2$, XeV$_3$, XeV$_4$, and XeV$_6$ vacancy complexes, respectively.
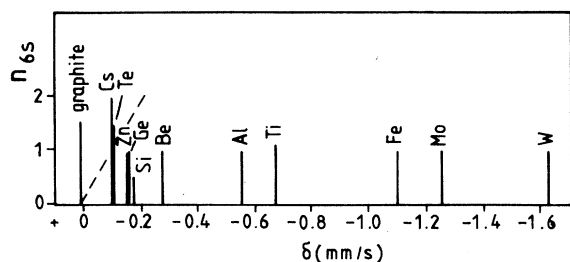
FIG. 2. The δ values of ^{333}Cs in some lattices. The dashed line shows an approximate calibration curve for δ depending on the number of 6s electrons. The δ values are negative because the source moved.
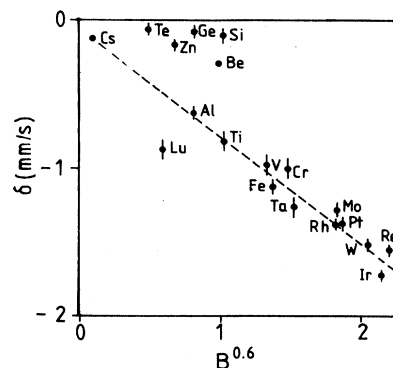

FIG. 3. The δ values vs the bulk moduli of the various matrices. The bars indicate statistical errors. The δ value in Cs metal is taken from Ref. 8.

loids) are close to or even larger than the δ value of Cs metal as if no 6s electrons were transferred to the metalloid atoms. However, because of the large electronegativity differences between the Cs and these host atoms, this is not the case. Instead, the large negative δ values indicate also electronic shell compression because of the small volume available for the Cs atom.

The δ values measured in various hosts do not correlate with the reciprocal volume of the host atom vacancies. Various processes may modify the volume at the impurity Cs atom. The result of these processes is the decrease of the stress created by the oversized Cs atom via e.g., lattice relaxation, vacancy-impurity complex formation, electron delocalization. Calculation of lattice relaxation for alloys was attempted by the application of the continuous elastic model[11,12] but it failed in this case, probably because of the very large size differences between the Cs and the host atoms. The calculated reciprocal equilibrium volumes exhibited some correlation with the δ values only for small groups (3–4 elements) of hosts, but it did not reveal general correlation. In another attempt we plotted the δ values against the bulk modulus (B) of the hosts (Fig. 3). The values were taken from Ref. 13. For most of the δ and B values of the metallic hosts a correlation was found by a least-squares fit and could be expressed as

$$\delta = -0.74B^{0.60(5)} - 0.05(2) , \qquad (2)$$

B is given in 10^{11} N/m^2.

The 0.6 exponent can be understood if the 6s electrons have a free-electron-like behavior because $\delta \sim 6s$ electron/volume and the volume of the free-electron gas scales as $B^{-3/5}$.[14] For simple metals the free-electron gas model in numerous cases reproduces well some physical

parameters (e.g., the B values).

An electron delocalization of the impurity Cs atoms was not justified. It was attempted (1) to attribute the large s electron density to 5p electron delocalization and a subsequent decrease of the screening, but too many (~ 3–4) 5p electrons should be removed, which seemed unrealistic. Also, no independent experiments were done, which might confirm such a high degree of delocalization.

For a group of hosts there is a strong deviation from the dotted straight line shown in Fig. 3. This upward deviation can be attributed to the formation of impurity-vacancy complexes, where the local pressure is lower than at the substitutional sites. Vacancy-impurity complexes may be formed by the vacancies created in the collision cascade and by trapping them above the vacancy migration stages. These complexes were readily observed in many implanted metallic systems. Such a complex formation of Xe implanted in Be has been concluded[15] and can also be expected for Zn where the annealing stage III is below room temperature. In Ge, Si, and Te such complexes may also form.

Recently high-pressure values for Xe implanted in Al have been published.[16–18] Xe atoms were implanted at 10^{15} atoms/cm^2 dose and a pressure value of 2.8–5.7 GPa was obtained for the small solid Xe particles precipitated in the bubbles in the metallic lattice. We obtained $\delta = -0.02\pm0.01$ mm/s for ^{133}Cs in Al implanted with Xe under the same condition.[19] This relatively low δ value indicates that in the ^{133}Cs impurity sites in the Al matrix ($\delta = -0.55$ mm/s) much higher-pressure values exist than in the bubbles.

---

[1]H. De Waard, P. Schurer, P. Inia, L. Niesen, and Y. K. Agarwal, in Hyperfine Interactions of Excited Nuclei, edited by G. Goldring and K. Kalish (Gordon and Breach, London, 1970), Vol. I, p. 89.

[2]I. Dézsi, R. Coussement, G. Langouche, H. Pattyn, S. Reintsema, M. Van Rossum, and J. De bruyn, J. Phys. (Paris) 40, 573 (1979).

[3]S. R. Reintsema, E. Verbiest, J. Odeurs, and H. Pattyn, J. Phys. F 9, 1511 (1979).

[4]M. Van Rossum, J. De bruyn, I. Dézsi, G. Langouche, and R. Coussement, Phys. Status Solidi B 52, 31 (1979).

[5]F. D. Feiock and W. R. Johnson, Phys. Rev. 187, 39 (1969).

[6]E. Verbiest, H. Pattyn, and J. Odeurs, Nucl. Instrum. Methods **182&183**, 815 (1981).

[7]E. Verbiest, Ph.D. thesis, University of Leuven, 1983.

[8]A. J. F. Boyle and G. L. Perlow, Phys. Rev. **149**, 165 (1966).

[9]L. E. Campbell, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 777.

[10]H. De Waard, S. R. Reintsema and L. C. Feldman, Hyperfine Interact. **4**, 720 (1978).

[11]F. D. Eshelby, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 3, p. 79.

[12]F. Friedel, *Dislocations* (Pergamon, New York, 1964), p. 360.

[13]K. A. Gschneider, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 275.

[14]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Sounders College, Philadelphia, 1976), p. 39.

[15]R. Vianden, E. N. Kaufmann, and J. W. Rodgers, Phys. Rev. B **22**, 63 (1980).

[16]A. von Felde, F. Fink, Th. Müller-Heizerling, F. Pfüger, B. Scheerer, G. Linker, and D. Kaletta, Phys. Rev. Lett. **53**, 922 (1984).

[17]F. G. Evans, Nucl. Instrum. Methods D **18**, 16 (1986).

[18]C. Templier, H. Garem, F. P. Riviere, and J. Delafond, Nucl. Instrum. Methods B **18**, 24 (1986).

[19]H. Pattyn *et al.* (unpublished).