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Watanabe

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THE CONTACT CHARGE DENSITIES OF 4s ELECTRONS OF Fe IMPURITY ATOM IN SOME TRANSITION AND NOBLE METALS

T. SHINOHARA, M. FUJIOKA (*) (**), H. ONODERA, K. HISATAKE (*)
H. YAMAMOTO and H. WATANABE

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan

Résumé. — Les électrons de conversion interne des couches M et N de la transition de 14,4 keV de ^{57}Fe diffusé dans des matrices de Cr, Ni, Cu, Pt et Au ont été mesurés à l'aide d'un spectromètre β de haute résolution.

La densité de charge des électrons 4s ($\rho_{4s}(0)$) de l'impureté de ^{57}Fe dans ces matrices métalliques a été déduite à partir des intensités relatives des électrons de conversion analysées à l'aide d'une méthode de déconvolution. On a trouvé que les densités de charge au contact 4s de ^{57}Fe dans ces diverses matrices métalliques, ainsi que dans Fe et Co métalliques, sont pratiquement égales. Ceci indique que la densité de charge au contact 3s ($\rho_{3s}(0)$) joue un rôle important dans la variation du déplacement isomérique de ^{57}Fe dans ces alliages.

Abstract. — The internal conversion electrons from M and N shells of the 14.4 keV transition of ^{57}Fe diffused into Cr, Ni, Cu, Pt and Au substrates were measured using a high-resolution β -ray spectrometer.

From relative intensities of conversion electrons analyzed using a deconvolution method, we deduced the contact charge density of 4s electrons $\rho_{4s}(0)$ of ^{57}Fe impurity atom in these host metals. The 4s contact charge density of ^{57}Fe embedded in these host metals, as well as Fe and Co metals, is found to be nearly equal. This fact indicates that the 3s contact charge density $\rho_{3s}(0)$ plays an important role in the variation of the isomer shift of ^{57}Fe in these alloys.

1. **Introduction.** — The Mössbauer isomer shift may be written as [1]

$$\delta = C[\rho_a(0) - \rho_s(0)] \frac{\Delta R}{R} = C \cdot \Delta\rho \cdot \frac{\Delta R}{R} \quad (1)$$

where $\Delta R/R$ is the fractional change of the nuclear charge radius (R) between the excited and ground states, and $\rho_s(0)$ and $\rho_a(0)$ are the total s electron densities at the nuclei for source and absorber, respectively [1]. The notation C is the calibration constant consisting of purely nuclear factors except the relativistic correction factor [1].

The isomer shift has provided valuable information in many branches of studying the atomic state. Concerning only with ^{57}Fe , the value of $\Delta R/R$ has been deduced by many authors but it is far from agreement [2]. Therefore, it has been considered that in those analyses inaccurate wave functions were used [2]. Recently, Rügsegger *et al.* has determined $\Delta R/R$ to be $-(3.1 \pm 0.6) \times 10^{-4}$ by measuring the nuclear life time of ^{57}Fe in different atomic environments [3]. At present this method is considered to be the most reliable, since it is free from the assumption that only

$\rho_{4s}(0)$ is sensitive to the atomic environment [3]. However, this value of $\Delta R/R$ demands $\Delta\rho$ to be much larger than that has ever been estimated.

To the elucidation of such a problem internal conversion measurement is very useful [4]. For the M_1 transitions, the s electron conversion is dominant: $\alpha_s \sim 10$, $\alpha_{p_{1/2}} \sim 10^2$, $\alpha_{p_{3/2}}$ and with the accuracy of a few percents, the following relation holds [4-9]:

$$\alpha_i = \text{const } \rho_i(0), \quad (2)$$

where the index i denotes the different s shells involved in internal conversion. Then, assuming the atomic environment to have an influence only on the valence electrons, we can obtain the relation:

$$\delta = C \cdot \frac{\Delta R}{R} \cdot \rho_{ncs} \cdot \frac{\Delta\alpha_{nvs}}{\alpha_{ncs}}. \quad (3)$$

In this equation n_v is the principal quantum number of the valence s electrons and n_c that of the core s electrons nearest to the valence shell. If one uses the theoretical value of $\rho_{ncs}(0)$, one can deduce $\Delta R/R$ from a measurement of $\alpha_{nvs}/\alpha_{ncs}$ versus the isomer shift; a recent successful example was given for ^{125}Te [10].

Previously, we deduced $\rho_{4s}(0)$ of ^{57}Fe in Fe and Co metals from measurement of conversion spectra of the 14.4 keV transition of ^{57}Fe diffused in these metals

(*) Department of Applied Physics, Tokyo Institute of Technology, Meguro, Tokyo, Japan.

(**) Present address: Department of Physics, Tohoku University.

using a high-resolution β -ray spectrometer [11-12]. We have further extended this method to the measurement of $\rho_{4s}(0)$ of an Fe impurity atom in some transition and noble metals.

The results give the first experimental indication that the 3s contact charge density plays an important role in the isomer shift of these alloy systems.

2. Experiment and analysis. — **2.1 PREPARATION OF THE SAMPLES.** — The method of sample preparation was similar to that described earlier [12]. Prior to the following procedure, $^{57}\text{CoCl}_2$ in dilute HCl was purified with an ion exchange method using anion-exchange resin in HCl media. The radioactive ^{57}Co was electroplated onto the surface of various host metals in the form of foil or crystal piece, at a current density of $\sim 100 \text{ mA/cm}^2$. The electrolyte was similar to those described previously [12]. The dimension of the electroplated region was $1 \text{ mm} \times 10\text{-}15 \text{ mm}$. The source intensity was $100\text{-}300 \mu\text{Ci}$.

Before the plating of ^{57}Co the metal samples of Ni, Cu, Pt and Au were annealed for recrystallization and degassing in vacuum. After the plating most of the samples were put into a furnace with a temperature of $400\text{-}500^\circ\text{C}$ under hydrogen atmosphere and were slowly cooled after 10 min. Then they were annealed at the same temperature in vacuum for a few minutes and were subjected to quenching. In this stage, we measured the Mössbauer spectrum to check whether they were the desired ones or not. If they were not the desired

ones, the treatment in vacuum was repeated at a higher temperature until we obtained the desired samples.

The temperatures and the Mössbauer spectra in the last stage for these samples are given in table I and figure 1, respectively. The hydrogen atmosphere was not used for the sample of ^{57}Co in Cr. The samples treated thermally after plating are denoted as ^{57}Co in Pt, etc. whereas those not treated as ^{57}Co on Cr, etc.

2.2 MEASUREMENT AND ANALYSIS OF THE MÖSSBAUER SPECTRA. — The Mössbauer spectrometer used to obtain figure 1 was a standard one from Elron. The Mössbauer spectra of the standard source of ^{57}Co in stainless steel and in Cu are also shown in figure 1. The measurements were made at room temperature in a transmission geometry with a stationary source and a moving absorber. The source-absorber distance was $20\text{-}30 \text{ mm}$. The absorbers were a 0.001 inch stainless steel (SS) foil or a potassium nitroprusside polycrystal sample of 0.63 mg/cm^2 in ^{57}Fe .

In the analysis of the Mössbauer spectra, the center of an absorption dip (here after denoted as CD) was defined as the center of the full width at half maximum. For ^{57}Co in Ni, the center of the spectrum (CS) was determined as a simple average of six CD's. For ^{57}Co on Cr and on Au, CS was defined as the center of gravity of the absorption spectrum. The sample of ^{57}Co in Cu exhibited a satellite besides the main dip, and from the latter the CS was determined. Every measurement was sandwiched with two measurements with

TABLE I

Thermal treatments, the Mössbauer data, intensity ratios of conversion lines and 4s contact charge densities for various samples of ^{57}Co

	^{57}Fe in metals					^{57}Fe on metals	
	(Cr) ^(a)	Ni	Cu ^(e)	Pt	Au	Cr	Au ^(f)
Thermal treatment ^(a) in vacuum	$600^\circ\text{C} \times 30 \text{ min}$	$670^\circ\text{C} \times 1 \text{ min}$	$620^\circ\text{C} \times 1 \text{ min}$	$705^\circ\text{C} \times 2 \text{ min}$	$625^\circ\text{C} \times 1 \text{ min}$	no	no
Isomer shift ^(b) rel. to Fe	$+0.01 \pm 0.05$	-0.01 ± 0.05	-0.23 ± 0.05	-0.34 ± 0.02	-0.65 ± 0.02	-0.185 ± 0.015	-0.700 ± 0.078
$I_{M_{2,3}}/I_{M_1}$	0.0687 ± 0.0054	0.0800 ± 0.0077	0.0991 ± 0.0076	0.0898 ± 0.0092	0.0875 ± 0.0098	0.0844 ± 0.0053	0.0775 ± 0.0053
I_{N_1}/I_{M_1}	0.0425 ± 0.0037	0.0468 ± 0.0052	0.0433 ± 0.0042	0.0420 ± 0.0058	0.0497 ± 0.0065	0.0341 ± 0.0019	0.0327 ± 0.0025
$\rho_{4s}(0)$ in a_0^{-3} ^(c)	5.55 ± 0.50	6.11 ± 0.71	5.65 ± 0.57	5.48 ± 0.78	6.49 ± 0.88	4.45 ± 0.26	4.27 ± 0.34

^(a) See the text.

^(b) Source isomer shift relative to Fe metal.

^(c) Contributions from 3d and 4p electrons were connected by subtracting 4 % of the N_1 intensity and corrected to $\rho_{4s}(0)$ using $\rho_{3s}(0)_{\text{theor}} = 136.0 + 2.0 a_0^{-3}$ (ref. 12).

^(d) Isomer shift of this sample did not agree with the literature value.

^(e) Estimated contribution from FeO impurity was corrected for.

^(f) Analyzed by itself.

FIG. 1. — Mössbauer spectra of ^{57}Co diffused into or deposited onto several metals taken at room temperature in an absorber driving mode. a) Mössbauer spectra of the samples of ^{57}Co on Cr, in Cr, and in Cu together with the spectrum of a standard source of ^{57}Co in stainless steel. b) Mössbauer spectra of the samples of ^{57}Co in Ni and on Au together with the spectrum of a standard source of ^{57}Co in Cu. The absorber was $0.001''$ stainless steel. c) Mössbauer spectra of the samples of ^{57}Co in Pt and in Au together with the spectrum of a standard source of ^{57}Co in Cu. The absorber was $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ powder with a thickness of 0.63 mg/cm^2 ^{57}Fe .

the standard source and from the difference of the CD's of the latter was estimated the experimental error of the CS of the former. The isomer shifts obtained are given in table I, where they have been converted into those relative to Fe metal using

$$\delta(^{57}\text{Fe in Cu}) - \delta(^{57}\text{Fe in Fe}) = -0.233 \text{ mm/s}$$

and

$$\delta(^{57}\text{Fe in Cu}) - \delta(^{57}\text{Fe in SS}) = -0.323 \text{ mm/s}.$$

The isomer shift thus obtained for most of the samples is consistent with the literature value [13]. For the case of ^{57}Co in Cu, we can attribute a weak satellite to ^{57}Co in FeO from the isomers shift [14]. Since the recoilless fraction of FeO is unknown, we use

the Debye model. Using $\theta = 372 \text{ K}$ and 324 K as the Debye temperature for Cu metal and Fe_3O_4 [15, 16] respectively, we get an estimation that about 4.3 % of the source intensity is due to ^{57}Co in FeO. This fact is taken into account in the analysis of conversion spectrum. The isomer shift for ^{57}Co in Cr is definitely different from the previous value [13]. ^{57}Co must have diffused into a complex surface layer of Cr substrate because of no preheating before the plating. ^{57}Co on Au and on Cr is revealed to be in complex physical states from the spectra.

2.3 MEASUREMENT AND ANALYSIS OF CONVERSION SPECTRA. — The conversion electrons of the 14.4 keV transition of ^{57}Fe emitted from the samples of ^{57}Co in and on various substrates described in the previous section were measured with a high-resolution β -ray spectrometer of the Institute for Nuclear Study, University of Tokyo [17].

The momentum resolution of the spectrometer was set to 0.05 %. The conversion electrons were detected after momentum analysis by a small-volume gas-flow-type proportional counter. Because the window was a thin film of VYNS with a cut off energy for electrons $E_c \sim 1.5 \text{ keV}$, the electron detection efficiency of the detector was expected to be practically constant over the energy range covered by the present experiment.

The M_1 - N_1 part of the spectra are shown in figure 2. As seen from this figure, the conversion lines

FIG. 2. — The M and N shell conversion spectra of the same samples which were used in the Mössbauer measurement. Solid curves are the results of least squares fitting. Each line profile for ^{57}Co in Ni and in Au is shown in broken curve as examples. The M_1 and $M_{2,3}$ profiles are assumed to be the same. The counting time was 25 min per point for all the samples but for the samples of ^{57}Co in and on Cr it was 15 min per point.

are best resolved for the samples of ^{57}Co on Cr and on Au. For the analysis of the spectra, the conversion line profiles were constructed with the deconvolution method combined with the rule of constant tail-to-total ratios [21]. The samples of ^{57}Co on Cr and on Au were intended as the reference source, but it was found that the spectrum of ^{57}Co on Au could not be used as a reference for the reason of the very long tail of the line profile. On the other hand, the spectrum of ^{57}Co on Cr worked well as a reference. We reanalyzed the previous spectra of ^{57}Co in Fe and in Co using the new reference of ^{57}Co on Cr and obtained essentially the same results as the previous ones obtained with the reference of ^{57}Co on Co. The spectrum of ^{57}Co on Au was analyzed by itself.

Using the line profiles obtained by the present procedure and a constant background, the observed spectrum was decomposed and intensity ratios, $\alpha_{M_{2,3}}/\alpha_{M_1}$, $\alpha_{N_1}/\alpha_{M_1}$ were determined by a least squares method, where a chi square test was performed and statistical errors were calculated. The tail part of the line intensity which was not covered by the measurement was approximated by an extrapolation with an exponential function.

Besides the statistical errors, we included the errors which were caused by other origins as follows. The extrapolation part for M_1 and $M_{2,3}$ lines were expected to have errors of 10 %. For N_1 line we took an error of 10 % on the lower energy side than the channel where $M_{2,3}$ and N_1 lines cross each other. On the higher energy side, errors of counts for M_1 and $M_{2,3}$ lines were expected to be within 20 % in those channels where the count became to be lower than the half of the peak value.

So far we have not considered the effect of the conversion electrons due to 3d and 4p electrons, which is small but can not completely be neglected. We assumed that the contribution to the N_1 line amounted to a fraction of 4 % similarly as for Fe metal [12].

For the sample of ^{57}Co in Cu, the contribution from ^{57}Co in FeO was corrected, assuming that $\rho_{4s}(0)$ is zero for ^{57}Fe in FeO. We deduced the value of $\rho_{4s}(0)$ using a theoretical value of $\rho_{3s}(0) = 136.0 \pm 2.0$ a. u. [12]; $\rho_{4s}(0) = (\alpha_{N_1}/\alpha_{M_1})_{\text{exp}} \cdot \rho_{3s}(0)_{\text{theor}}$. The final result is shown in table I. It is to be noted that the present values of $\rho_{4s}(0)$ are the non-relativistic ones as is $\rho_{3s}(0)_{\text{theor}}$.

3. Discussion. — Let us consider the 4s contact charge density, $\rho_{4s}(0)$, deduced from the present experiment. Initially, we intended to find out a variation of $\rho_{4s}(0)$ on a naive assumption that the isomer shift of ^{57}Fe in various host metals reflects directly the variation of $\rho_{4s}(0)$; use of $\Delta R/R \sim -4 \times 10^{-4}$ predicts $\Delta\rho_{4s}(0) \sim -4.5$ a. u. between ^{57}Fe in Fe and in Au metals [3, 18]. Contrary to this expectation, we could not find such a variation as shown in table I and figure 3. In figure 3 is also plotted the relation between $\rho_{4s}(0)$ and δ obtainable if the value of Rügsegger

FIG. 3. — Contact charge densities obtained from the conversion measurement versus the isomer shift obtained from the Mössbauer measurement; see the text for details.

et al. [3] for $\Delta R/R$ is used and the core contribution is neglected; the constant term was so adjusted that it passed through an ideal (not experimental) point of ^{57}Fe in Fe. Discrepancy between the present result of $\rho_{4s}(0)$ and the value of $\Delta R/R$ is apparent, and it should be attributed to a core contribution $\Delta\rho_{3s}(0)$. This conclusion is not consistent with the recent interpretations of the isomer shift for these alloys [2], [19]. If we use an estimated value of β under the assumption [20] of $\Delta\rho_{3s}(0) = \beta \cdot n_d$, we can convert $\Delta\rho_{3s}(0)$ into the variation of 3d population, Δn_d .

We now consider the value of $\alpha_{M_{2,3}}/\alpha_{M_1}$. Since the 3s and 3p electrons should be relatively insensitive to the atomic environment, this ratio is expected to be constant within the experimental error. But as seen in table I, there is a scatter of this value, which can not be explained physically. Since the $M_{2,3}$ line is sandwiched between the M_1 and N_1 lines, we could not determine a reliable profile of this and the M_1 profile was employed instead, which might be a cause of such scatter. Indeed, from our preliminary measurement of L conversion spectra, the shape of the $L_{2,3}$ line was found to be different from that of the L_1 line, and an analysis taking this difference into account gave values of $\alpha_{L_{2,3}}/\alpha_{L_1}$, which were constant for all the samples within the experimental error. However, as seen in table I, such an uncertainty of the $M_{2,3}$ line profile could not effect so much on the above conclusion.

At present we can not draw too detailed a conclusion concerning each of the host metal investigated, and it seems desirable to extend the scope of such an experi-

ment and to reduce the experimental error as far as possible. At the same time, a reliable determination of $\Delta R/R$ for ^{57}Fe is very important. To do so, very accurate determination of $(\alpha_{M_1} + \alpha_{N_1})/\alpha_{L_1}$ is required.

Accuracy of 1 a. u. for $\Delta\rho(0)$ requires a relative accuracy of 0.7 %. With all this difficulty, however, such an experiment seems to be highly desirable.

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