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Determination of the Contact Charge Density of 4*s* Electrons in Fe Metal from an Internal-Conversion Experiment

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A clearly resolved spectrum of the outer-shell conversion was obtained for the 14.4-keV nuclear transition in ^{57}Fe with sources consisting of ^{57}Co diffused into Fe metal. From the ratio of the 4*s*-conversion-electron intensity to that of the 3*s*, the contact charge density of 4*s* electrons of Fe metal was uniquely determined to be $\rho_{4s}(0)=5.53\pm0.46\,a_0^{-3}$, which is compared with various theoretical values. Although these are generally smaller than the experimental value, the calculation of Wakoh and Yamashita gives the closest value of $5.18 a_0^{-3}$. The 3*p*-to-3*s* conversion-intensity ratio was also obtained, as 0.0828 ± 0.0038.

The recent study by Pleiter and Kolk[1] on the internal conversion spectrum of the 14.4-keV transition in ^{57}Fe diffused in Fe metal shows the possibility that electron configurations in the outer shells of transition metals may be determined by internal conversion. The energy spectrum measured by them, however, exhibits too much broadening, so that it is rather difficult to analyze the data in order to determine the contribution to the contact charge density at the Fe nuclear site from the *s*-like electrons of each shell. The purpose of the present paper is to show that careful sample preparation can lead to a successful measurement of the electron energy spectrum with such a high resolution that one can obtain clear profiles of the contributions from 4*s*, 3*s*, and even 3*p* electrons. With such a technique, there is no reason why further information on other transition metals and their dilute alloys cannot be investigated. As pointed out by Watson *et al.*,[2] the measurement of internal-conversion electrons probes the contact charge density associated with the Bloch orbitals of band electrons below the Fermi energy, and it should serve as a crucial test for the existing band calculations of the metal, since the conversion experiment can select energetically the valence electrons; and, specifically, for nuclear magnetic dipole (*M*1) transitions effectively only the *s*-like electrons are ejected.[3] The latter selection rule gives to (*M*1) internal conversion a unique superiority in obtaining the contact charge density of *s* electrons in each shell.

Although internal-conversion electrons from the outermost shells of the atom, or from the valence band of the crystal, have been measured for some nuclear transitions and the so-called chemical effects have been detected,[4] the data of Pleiter and Kolk[1] for the 4*s*-electron conversion of the 14.4-keV *M*1 transition in ^{57}Fe diffused into Fe metal are the first to have been subject to comparison[2] with the band calculation of the metal. According to Watson *et al.*,[2] however, the value of the contact charge density of the valence band of Fe metal obtained by Pleiter and Kolk is too large to be explained by the existing band theory of Fe metal. Recently a similar experiment[5] gives for ^{57}Fe in Co metal a smaller value, but direct comparison with theory is impossible, since there is no calculation available of the contact charge density for the dilute alloy of Fe in Co metal.

We observed the outer-shell conversion of the nuclear transition in question at a higher resolution and statistics by using a high-precision iron-free $\pi\sqrt{2}$ spectrometer[6] (from the Institute for Nuclear Study, University of Tokyo) having a mean radius of 75 cm. Activity of ^{57}Co of about 200 μCi was electroplated from a 4-N ammonium chloride solution through a slit of 1×8 mm onto an iron foil of about 20-μ thickness at a current of 2 mA. The sample was reduced and annealed for 10 min at 600 °C and 2 h from 600 to 500 °C under 1 atm of hydrogen. The chemical state of the activity atoms was checked by measuring the Mössbauer spectrum [see Fig. 1(a)]. The isomer shift relative to a stainless-steel absorber and the internal field strength, $\delta = -0.19 \pm 0.09$ mm/sec and $H_{\text{int}} = -334 \pm 4$ kOe, are consistent with the bulk values for Fe metal.[7] The conversion spectrum was measured at an instrumental momentum resolution of 5×10^{-4}. As is seen from Fig. 1(b), the conversion peak corresponding to the band electrons can be clearly resolved even for an annealed sample by a suitable choice of the annealing conditions as mentioned above.

It has been reported by Porter and Freedman[4] that the $M_1(3s)$ and $N_1(4s)$ conversions have different spectrum profiles owing to the electron shakeoff during conversion, presenting some difficulty in the analysis of conversion spectra. This difficulty was avoided by a deconvolution-recon-

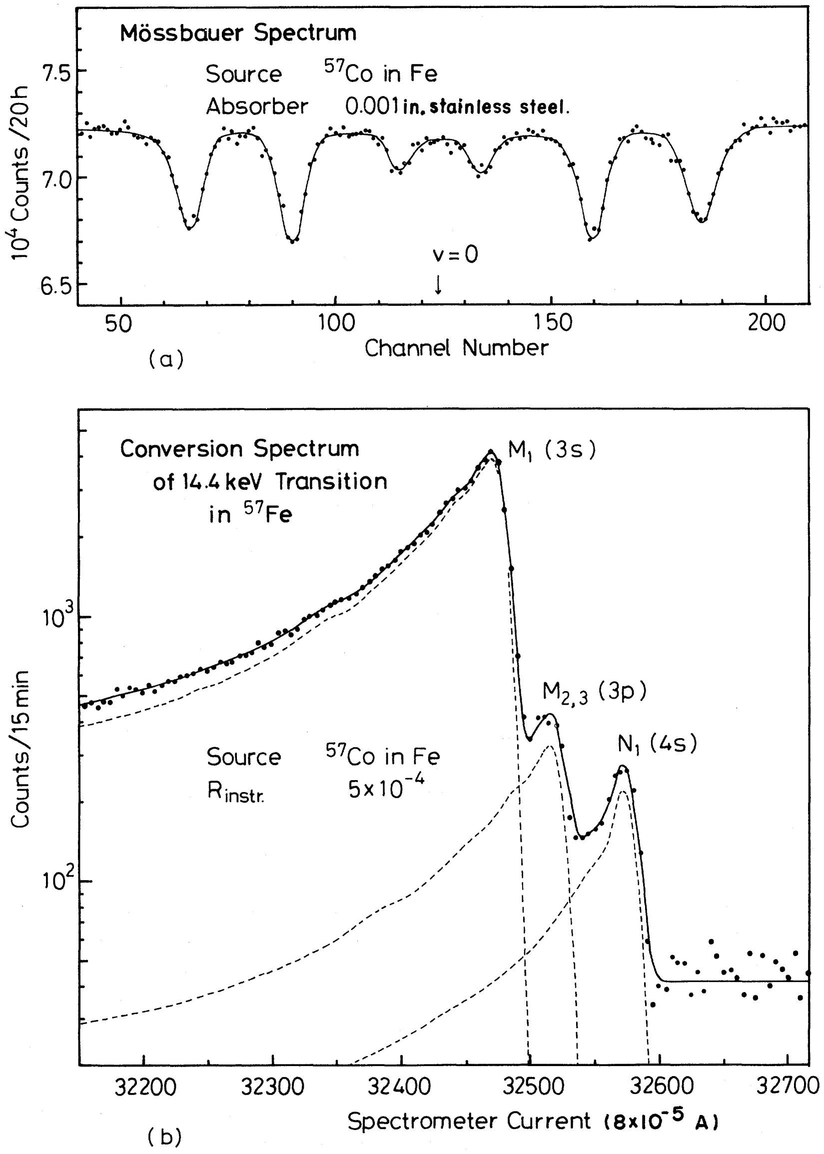

FIG. 1. (a) Mössbauer spectrum of the ^{57}Co source ($\simeq$200 μCi) diffused into Fe metal taken at room temperature in the absorber-driving mode. The source was located at 2 cm from an aperture of 8-mm diameter in a lead shield in front of the counter. Larger channel number corresponds to negative Doppler velocity. (b) Conversion spectrum of the same source as in (a). The indicated counting time is per point of measurement. The broken curves represent the individual line profiles employed in a least-squares analysis of the spectrum. The profile of N_1 conversion was constructed by the deconvolution-reconvolution procedure (see Ref. 5). R_{instr} designates an instrumental momentum resolution.

TABLE I. Relative conversion probabilities and the contact charge density $\rho_{4s}(0)$ of band electrons of Fe metal obtained from the internal-conversion measurement of the 14.4-keV transition of ^{57}Fe embedded in Fe metal, in comparison with various band-theoretical calculations.

	Present result	Result of Ref. 1	Theoretical value of Ref. 12	Ref. 10	Ref. 2	Ref. 13
M_{2+3}/M_1	0.0828 ± 0.0038	...				
N_1/M_1	0.0407 ± 0.0033	0.066 ± 0.007				
$\rho_{4s}(0)$ (a_0^{-3})	5.53 ± 0.46	8.9 ± 0.9	5.18	3.8 ± 0.4	$\simeq 4.5$	4.82

volution procedure[5] in the analysis of the conversion spectrum of ^{57}Fe in Co metal. We also employ this method in the present analysis of the spectrum, as shown in Fig. 1(b). The spectrum of ^{57}Co deposited on Co metal without further treatment was used as the reference, and the errors arising from the inaccuracy of the line shapes employed were considered.[5] The line shapes of the M_1 and $M_{2+3}(3p)$ conversion were taken to be the same. Although the conversion probabilities for p and d electrons are relatively small, the contributions to the region of the N_1 peak from the M_{4+5} $(3d)$ and N_{2+3} $(4p)$ conversion cannot completely be neglected. The theoretical conversion coefficients of the 14.4-keV $M1$ transition for ^{57}Fe neutral atoms obtained by using the program of Pauli[8] and the screening function of Herman and Skillman[9] give as the intensity of the $3d$ electrons relative to the $3s$ electrons $M_{4+5}/M_1 = 4.9 \times 10^{-4}$, leading to a small correction of the N_1 intensity by −1%. It is more difficult to compute the contribution from $4p$ electrons, but a rough estimate can be made by using the calculated electron configuration $4s^{0.5}\,4p^{0.5}$ for Fe metal[10] and the approximate constancy of subshell ratios (calculation[8,9] shows $L_{2+3}/L_1 = 0.0842 \simeq M_{2+3}/M_1 = 0.0824$). This correction leads to a reduction of the N_1 intensity by $(N_{2+3}/N_1)_{4s^{0.5}4p^{0.5}} \simeq \frac{1}{3}(M_{2+3}/M_1)_{3s^23p^6} \simeq 3\%$, where the experimental value of M_{2+3}/M_1 was used. The relative intensities thus obtained are shown in Table I.

Since the internal conversion measures only the relative contact charge densities for s electrons, it is necessary to use some theoretical estimate of the contact charge density of $3s$ electrons $\rho_{3s}(0)$ in order to obtain that of the band electrons from relative conversion probabilities.[11] From two extreme values[10,12] we adopt $\rho_{3s}(0) = (135.95 \pm 1.95)a_0^{-3}$, which, multiplied by the experimental N_1/M_1 ratio, gives the *nonrelativistic point-nucleus* value of the contact charge density of band electrons of Fe metal, as shown in Table I. The present value is considerably smaller than that obtained by Pleiter and Kolk[1] (Table I); part of the discrepancy may be explained in terms of the electron shakeoff effect, which was not considered in their analysis. Band-theoretical values for Fe metal have been obtained under several approximations as follows: the Korringa-Kohn-Rostoker (KKR) method by Wakoh and Yamashita,[12] the modified tight-binding approximation by Ingalls,[10] and the modified orthogonal-plane-wave (OPW) approximation by Watson *et al.*[2] and by Duff and Das.[13] They are cited in Table I. As is seen from Table I, the theoretical values are generally smaller than the experimental ones, but the value of Wakoh and Yamashita, which is the largest, agrees well with the present result within the experimental error. It is to be noted that band calculations have been compared with other experimental information, e.g., the x-ray and neutron-diffraction experiments, where the *total* charge and spin densities around the nucleus can be measured, whereas in the conversion experiment the charge density *only* at the nuclear site can be obtained but the band s electrons can be separated. The present result shows that further information on other metals and their dilute alloys can be obtained with a similar method, and that the internal-conversion measurement will add a new, though somewhat limited, experimental method to the conventional ones. Analysis of the data of internal-conversion electrons of the dilute alloy of ^{57}Fe in Cu and Ni host metals is now in progress. From such data the information on the charge-screening mechanism around the Fe atom in these alloys can be obtained.

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Magnetic Anisotropy and Conduction-Electron Exchange Polarization in Ferromagnetic (Rare-Earth)Al_2 Compounds

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^{27}Al NMR in ferromagnetic $R\mathrm{Al}_2$ (R = Pr, Nd, Sm, Gd, Tb, Dy, Ho) has been studied. The easy direction of magnetization has been observed experimentally for the first time and a theoretical calculation, in accord with the observation, has been developed. The s-f exchange parameters have been examined and in addition to the isotropic exchange parameter Γ_{sf}, the existence of a small but significant anisotropic s-f exchange term is verified experimentally for the first time. The accurately determined (±1%) isotropic exchange parameters are compared with presently available theoretical predictions.

I. INTRODUCTION

Magnetic properties of the $R\mathrm{Al}_2$ (R = rare earth) intermetallic compounds[1] were studied extensively during the last ten years. Magnetization[2] and neutron-diffraction[3,4] measurements verified that the compounds order magnetically below a transition temperature and form, in most cases, ferromagnets. Studies of magnetic transition temperature,[2–5] paramagnetic ^{27}Al Knight shifts,[6–10] and more recently, susceptibility[11] and resistivity[5,12] have been conducted in attempts to illuminate various aspects of the interactions between the presumably localized R spins and the electronic conduction band. Several groups[9,13–16] have studied the ^{27}Al hyperfine interactions in the *ferromagnetic* phase of GdAl_2, and it was demonstrated[14(a),16] that a slightly modified Ruderman-Kittel-Kasuya-Yosida (RKKY) model can adequately account for the relevant experimental observations.

The present report describes an extension of the ^{27}Al hyperfine field study to the ferromagnetic phases of compounds with non-S-state ions, ranging from PrAl_2 up to HoAl_2, with the exception of EuAl_2. The investigation was aimed at studying two phenomena: (a) the magnetic anisotropy and its variation across the group and (b) the variation of the s-f exchange across the series. Very