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Lattice Location and Hyperfine Fields of Rare-Earth Ions Implanted into Iron

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We show that the implantation and anneal behavior of Gd implanted into iron is strongly affected by the process of "internal oxidation." This result is used to clear up discrepancies in earlier measurements on rare-earth ions implanted into iron.

Since the advent of the channeling technique[1] for determining the location of impurities in single crystals, a great deal of research has been performed to study the location in the lattice, and change of that location under annealing,[2] of implanted ions. Recently, such measurements have been combined with studies of the hyperfine (hf) structure of implanted ions.

Lattice location, hf fields, and annealing behavior of rare-earth (RE) ions implanted into iron have been extensively studied.[3-6] We report here new experimental results, based on the Mössbauer spectroscopy of *Fe*:Eu^{151} (Gd^{151} is the implanted species) which show that internal oxidation of the implanted Gd ions dominates the observed behavior. The chemical and metallurgical properties of the RE ions are rather similar; thus these findings can be extended to explain the results of many previous measurements performed on RE ions implanted into iron.

The conclusions from previous work on *Fe*:RE systems can be summarized as follows: (1) Channeling lattice-location measurements[3-5] show that about 60% of implanted Yb ions are substitutional in Fe, but the remaining 40% do not occupy well-defined interstitial sites. (2) Off-line time-integral perturbed angular correlation (PAC) measurements[3,4] (using radioactive Yb implanted into Fe, with the hf field measured for the Tm daughter) indicate an "average" hf field which is substantially less than would be expected for *Fe*:Tm. (3) Both the substitutional fraction (measured by backscatter experiments) and the average hf field go to essentially zero after a brief anneal at 500°C.[3,4] After the anneal, the Yb ions do not occupy well-defined sites. (4) On-line implantation PAC (IMPAC) measurements, in which hf fields of the implanted RE ions are measured within 10^{-9} sec after the ions stop, suggest that one hf field is produced by the RE ions of a given species,[6] and that the observed fields are consistent with expectations. (5) The electron relaxation rate for Tm PAC measurements (implanted *Fe*:Yb) for an annealed (500°C) source is the same as that for Yb_2O_3:Tm, and one-third that for an unannealed source.[3]

We present here the result of Mössbauer measurements on sources of Gd^{151} implanted (4×10^{14}/

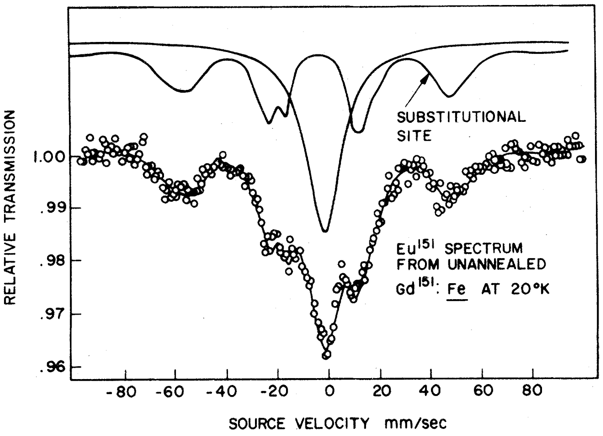

FIG. 1. Mössbauer spectrum of Eu^{151} from *Fe*:Gd implanted source. A least-squares fit (line through the data points) was made using the known ground- and excited-state magnetic and electric quadrupole moment ratios, known transition probability ratios for the eighteen lines in the hf spectrum, and assuming that there was one split and one unsplit component. The hf field is 4 times larger than normally observed in Eu^{151} spectra; the four groups of lines at ±20 and ±60 mm/sec correspond to the four strong lines normally observed in Eu Mössbauer spectra.

cm^2, 50 keV energy) into polycrystalline iron foils.[7] The Gd^{151} decays to Eu^{151}, and the hfs of the 21.7-keV γ rays emitted by the Eu^{151} has been studied using the Mössbauer effect. The chemical and metallurgical properties of Ge^{3+} and Yb^{3+} should be similar enough for results of our measurements on the *Fe*:Gd system to be applicable to phenomena observed in *Fe*:Yb.[8]

A sample spectrum is shown in Fig. 1, and the results can be briefly described as follows: (1) Measurements of the isomer shift show that all the Eu ions are Eu^{3+} ($4f^6$ configuration). Since Eu^{2+} would appear ~14 mm/sec to the right of Eu^{3+}, divalent Eu would be easily distinguished. (2) The unannealed source spectrum (Fig. 1) can be resolved into two components, corresponding to two sites for the Eu ions. One component is split [hf field $B_{\rm hf}=1.31$ MG, isomer shift (IS) 3.5 mm/sec versus EuF$_3$]; the other is a broadened but essentially unsplit line ($B_{\rm hf}<50$ kG, IS 1 mm/sec versus EuF$_3$). The split hfs comprises about 60% of the total intensity of the spectrum.[9] (3) A 15-min anneal (in H$_2$) at 430°C decreases, and a 15-min anneal at 480°C completely eliminates (see Fig. 2), the split component of the spectrum. (4) Further annealing (including 30 min at 500°C in air, which results in massive oxidation of the source) does not significantly alter the spectrum (see Fig. 3).

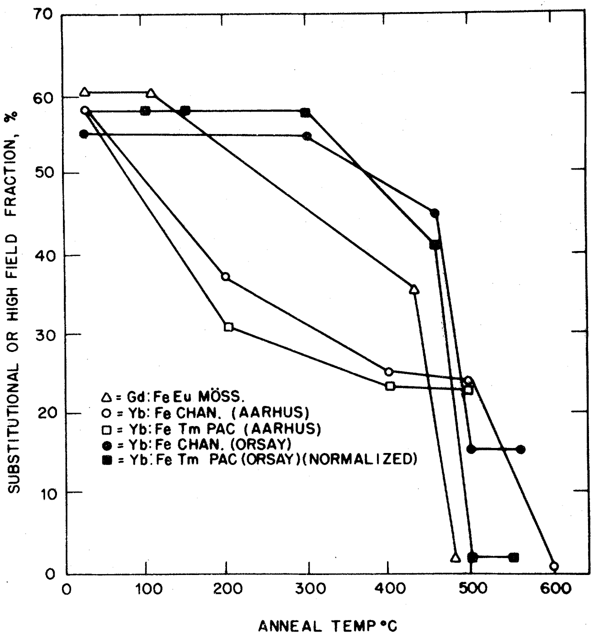

FIG. 2. Composite plot of Mössbauer, location, and hf field results versus anneal temperature, from Ref. 3 (open points) and Ref. 4 (filled points). Some of the original data points have been averaged or smoothed to make the plot legible. The lines have been drawn only to connect the data points. Implantation energies were 50–80 keV (Mössbauer and Ref. 3) and 400 keV (Refs. 4, 5), corresponding to depths of 130 and 530 Å for the implanted RE ions. Anneals for all experiments were 15 min long. PAC measurements have been plotted implicitly assuming that there is one site with a large hf field and one site with a negligible hf field, and that only the relative fraction of atoms between these two sites changes under anneal. Thus, the high-field fraction equals the ratio of the average hf field to the hf field expected for substitutional ion.

The large hf field and the isomer shift of 3.5 mm/sec are exactly what would be expected[10] for Eu in an Fe metal matrix. (In metallic surroundings, conduction-electron density normally increases the IS for Eu^{151} by 2–5 mm/sec over that in ionic compounds.[10]) The relative intensity[9] of the split spectrum, 60%, is the same as that of the substitutional site population seen by lattice location studies of *Fe*:Yb, suggesting that this spectrum arises from substitutional Eu ions, and that the unsplit spectrum arises from the ions observed (by lattice-location measurements) to be nonsubstitutional. The anneal behavior (Fig. 2) of the split component of the Mössbauer spectrum is the same as that observed for substitutional ions in the location experiments, confirm-

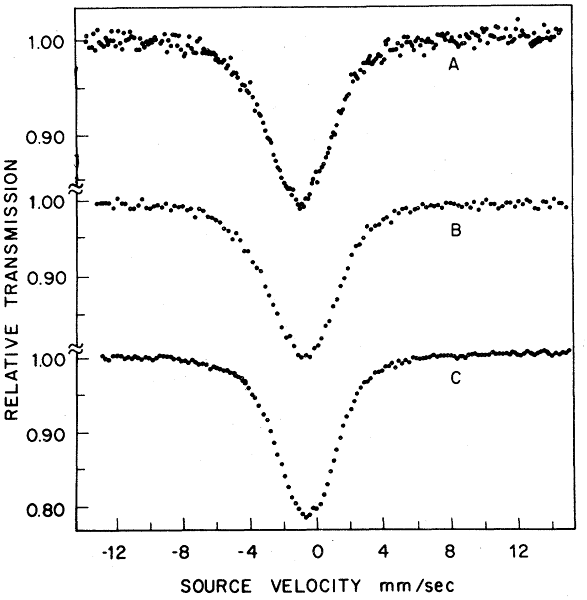

FIG. 3. Spectrum of source of Fig. 1, curve *A*, after anneal at 480°C in H_2; *B*, after anneal in air (500°C, 30 min) to assure complete oxidation. Curve *C*, comparison spectrum of Eu^{151} from Sm_2O_3 source, which is chemically similar to other trivalent-rare-earth oxides. The spectrum of the annealed *Fe*:Gd source is the same as that obtained from Eu^{3+} in an oxide environment.

ing this hypothesis.

The evidence is also very strong that the Eu ions producing the unsplit line are not in an interstitial or defect-associated site, but are internally oxidized: (1) Both the isomer shift and the lack of hf field are exactly what would be expected for Eu in an oxide environment [IS(Eu_2O_3 versus EuF_3) = 0.6–0.8 mm/sec]. Other ionic Eu^{3+} compounds with similar IS values are composed of elements which are not present in this system. (2) Interstitial ions should have even greater conduction-electron IS contributions than substitutional ions. Although defects associated with the implanted ion might slightly reduce the size of the conduction-electron contribution to the isomer shifts, they should not completely eliminate it. (3) The complete lack of hf field would not be expected for an interstitial site[11]; even accidental cancellation of different contributions to the hf field (for a dissolved Eu ion) could not lead to the observed behavior, since the various contributions would have different temperature dependence, and the observed hf field is zero (within the limit of measurement) from 20 to 400 K.

The analysis of the Mössbauer data suggests the following picture: When RE ions are implanted into iron, the vast majority of them initially stop at substitutional sites. (Thus, the IMPAC experiments measure a hf field corresponding to a high substitutional fraction.) During the course of the implantation, which may take several hours, some of the stopped RE ions are internally oxidized and removed from the regular lattice sites on which they stopped.

Recently, Moline, Reutlinger, and North[12] have observed and measured the "driving in" of surface oxygen into silicon by incident Ne, Ar, and Kr ions in the 3–48-keV range. They showed that the operative mechanism was recoil implantation, in which relatively large amounts of recoil energy were given to oxygen ions in the surface oxide layer, and the oxygen ions recoiled into the substrate with a range approximately the same as that of the incident heavy ions. This process is dependent on nuclear kinematics and cross sections only, and should be completely insensitive to the details of host-properties chemistry.

Extrapolating from the conditions studied by Moline, Reutlinger, and North to those present in our implantation, we would expect approximately one oxygen atom to be implanted into the iron for each incident RE ion. Within the accuracy to which the surface-oxide-layer thickness and recoil-implantation efficiencies are known, we consider this adequate quantitative confirmation of oxygen recoil implantation as the primary contributor to the internal oxidation. Anneals after the implantation, then, do not simply drive RE ions off the substitutional sites into interstitial sites (as happens in other systems[13]), but mobilize additional oxygen, which oxidizes the remaining substitutional RE ions.

This analysis is fully supported by the relevant systematics. The basic requirements for internal oxidation[14]—that the dopant (RE) oxide is thermodynamically more stable than the host (Fe) oxide, that the oxide is insoluble in the host, and that a source of oxygen is present—are strongly fulfilled, and this process would be expected to occur.

The new results we are reporting here using the Mössbauer hf spectra of Eu^{151} in Fe show directly that both oxidized and unoxidized sites exist, and that the "anneal" process actually oxidizes formerly substitutional RE ions. This analysis appears to explain the apparent contradictions among a number of RE lattice-location and hf-field measurements which have been published in recent years, and can be extended to results obtained with other highly oxidizible (e.g., Hf and Ta) ions.

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[7] Less than 5% of RE ions implanted at this energy stop within the first 40 Å of the target. The foils used in Ref. 3 and this work have an oxide layer known to be 20–30 Å thick.

[8] Lattice location measurements use Fe single crystals as a host. IMPAC and PAC measurements have used both single crystals and polycrystalline foil. The relatively good agreement between the measurements suggests that this difference is not significant.

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Thermoreflectance of Tetrathiafulvalinium Tetracyanoquinodimethanide (TTF-TCNQ)

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We report the first observation of a marked temperature dependence in the optical properties of TTF-TCNQ, based on thermoreflectance spectroscopy. The structure just above the plasma edge exhibits an abrupt 25% drop with $\vec{e}\parallel\vec{b}$ as the temperature is lowered past 45–50 K; simultaneously, a strong response for this transition with $\vec{e}\perp\vec{b}$ emerges. This supports the suggestion that a librational distortion of the TCNQ ion may be responsible for a Peierls transition in the complex.

The molecular charge-transfer salt TTF-TCNQ behaves electrically[1] and optically[2] like a one-dimensional metal at room temperature, with perhaps a tendency toward Fröhlich superconductivity which is frustrated by a Peierls transition.[1] Physical measurements as functions of temperature have been employed to study this hypothesis, although the mean-field T_c may be much higher than 60 K, the temperature of maximum conductivity.[3] Bright, Garito, and Heeger[2] and Grant *et al.*[4] report reflectivity spectra spanning the range 0.1–4.0 eV. The major structure is associated with a screened plasma resonance at 1.2–1.3 eV,[2] with additional weak structure at higher energies arising from interband[2] or molecular[4] effects. The temperature dependence of the di-