

Impurity displacement by vacancy trapping in gold-implanted iron single crystals at low dose

A. Turos* and O. Meyer

Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik,
P.O.B. 3640, D-7500 Karlsruhe, Federal Republic of Germany

(Received 26 March 1986)

The substitutional fraction (f_s) of Au atoms implanted into Fe single crystals at room temperature increases with increasing dose from $f_s=0.6$ for 0.1 at.% Au to $f_s=1.0$ for Au concentrations exceeding 1 at.%. This concentration dependence of f_s is attributed to the formation of Au-vacancy complexes. The number of the complexes decreases with increasing Au concentration due to complex dissolution accompanied by the formation of an increasing number of competing vacancy-trapping centers.

Recent interest in the environment of implanted atoms in metallic hosts¹ arose from the search for the factors determining the substitutionality of implanted species. The guidelines provided by the Hume-Rothery² and Miedema³ rules are found to be not always adequate for metal-in-metal implanted systems: Some of the implants which are unsoluble in the host matrix are found to be largely substitutional,⁴ others which are supposed to be substitutional exhibit nonsubstitutional behavior after room-temperature implantation. The later effect disappears when the implantations are performed at temperatures below stage-III recovery (free migration of vacancies) thus indicating the association of implanted atoms with one or more vacancies.⁵

In this Rapid Communication we present the results of a study where the lattice location of Au implanted into Fe single crystals was determined by means of ion channeling and backscattering techniques,⁶ and where, to our knowledge, for the first time an increase of the substitutional component with increasing impurity concentration has been observed.

Iron single crystals were cut perpendicular to the $\langle 100 \rangle$,

$\langle 110 \rangle$, and $\langle 111 \rangle$ directions and lapped and etched as described elsewhere.⁷ Au was implanted along random directions at an energy of 600 keV and at fluences ranging from 1×10^{15} to 1×10^{17} cm⁻². The analyses were performed *in situ*, using a 2-MeV ⁴He⁺ beam. Figure 1 shows the random and the $\langle 110 \rangle$ -aligned backscattering spectra for an Fe single crystal implanted with Au to a fluence of 2×10^{15} cm⁻². The maximum Au concentration amounted in this case to 0.25 at.%. The substitutional fraction (f_s) of Au was determined in the conventional manner:⁶

$$f_s = (1 - \chi_i^{\min}) / (1 - \chi_h^{\min}) ,$$

where χ_i^{\min} and χ_h^{\min} are the normalized minimum yields for the impurity and the host, respectively. The yields were measured in the energy windows as indicated in Fig. 1.

Although Au in Fe does not satisfy the Hume-Rothery rules very well, a limited solubility of Au in Fe has been reported.^{7,8} Therefore, one can expect the substitutional fraction to be close to 1 at low Au concentrations, and to decrease eventually at high concentrations when precipitation

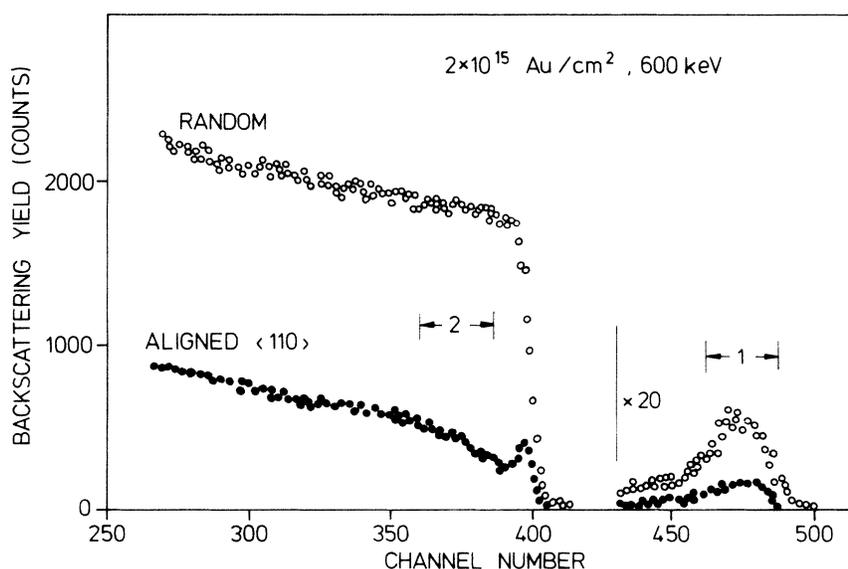


FIG. 1. Random and aligned backscattering spectra for 2-MeV ⁴He ions from a Au-implanted Fe single crystal.

occurs. In agreement with this expectation *in situ* analyses after the implantation of Au into Fe at 77 K yield a substitutional fraction of 1.0 independent of the implanted Au concentration in the range 0.1–2 at.%. The experimental results after implantation of Au into Fe at 295 K, however, show the opposite trend. As presented in Fig. 2 f_s is 0.6 at 0.1 at.% Au and increases monotonically up to 1.0 for Au concentrations above 1.0 at.%. This value does not change even at the highest implanted concentration of 7 at.%, although the solubility limit was exceeded by a factor of more than 70.

The angular dependence of the normalized yields in the energy windows 1 and 2 (see Fig. 1) are shown in Fig. 3. They provide more detailed information on the lattice location of the implanted species than the f_s value alone. For small Au doses [Fig. 3(a)] the angular scans for the impurity are not only shallower, but also narrower with respect to the scan for the host lattice. With increasing implantation dose the impurity scan becomes broader and deeper and finally matches perfectly that of the host, as shown in Fig. 3(b). The detailed analysis of the shape of angular scans⁹ has shown that there are two fractions of Au atoms: The first one is composed of Au atoms which are slightly (~0.01 nm) displaced from the regular lattice sites, and the second one consists of Au atoms randomly distributed on interstitial lattice sites.

To understand the behavior of Au implanted at room temperature two questions are to be answered: (a) Why are the Au atoms displaced from the regular lattice sites after low dose implantation and (b) what is the mechanism for improving the Au substitutionality with increasing Au concentration?

The first question could be answered by assuming the formation of Au-vacancy associations during implantation at room temperature. Because of the positive heat of solution of Au in Fe (36 kJ/mole) the Au atoms are expected to capture freely migrating vacancies¹⁰ forming mono- or multivacancy-impurity complexes.¹¹ The formation of such complexes leads to the displacement of impurity atoms.¹² The formation of Au-divacancy complexes could lead to a relaxation of the impurity towards the vacancy which would produce a narrowing of the angular-scan curve. The forma-

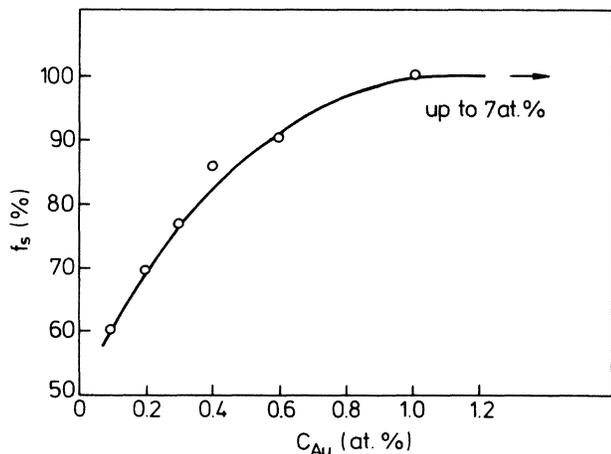


FIG. 2. Variation of the substitutional fraction with the dose of Au implanted into Fe single crystal at room temperature.

tion of Au–multiple-vacancy associations with various possible interstitial sites of the Au atoms would provide a component of apparent randomly distributed impurity atoms. Stage-III recovery for the Fe starts at temperatures above 200 K (Ref. 13) and thus vacancies are immobile at 77 K. In contrast to room temperature implantations, no displacements of impurity atoms after implantation at 77 K were observed. This provides a strong argument in favor of the hypothesis that this effect is due to the formation of Au-atom–vacancy complexes.

A further cross checking of this hypothesis was performed by irradiating a sample implanted at 77 K with 1×10^{16} (He ions)/cm² at 200 keV without changing the temperature. No change of the angular scan was noticed after irradiation [Fig. 4(a)], however, as can be seen in Fig. 4(b), the impurity scan became shallower when the sample was warmed up to room temperature. Rehn, Okamoto, and Averbach¹⁴ showed that swift light ions produce few collision cascades with high defect densities and create mostly isolated Frenkel pairs. Upon warming up above the temperature of stage-III recovery, vacancies become mobile and can be trapped by impurity atoms.

To answer the second question concerning the mechanism of the dose dependence of the substitutional fraction, further postirradiation experiments were performed. A sample implanted at room temperature with Au ions to the maximum concentration of 0.2 at.% ($f_s = 0.75$) was bombarded

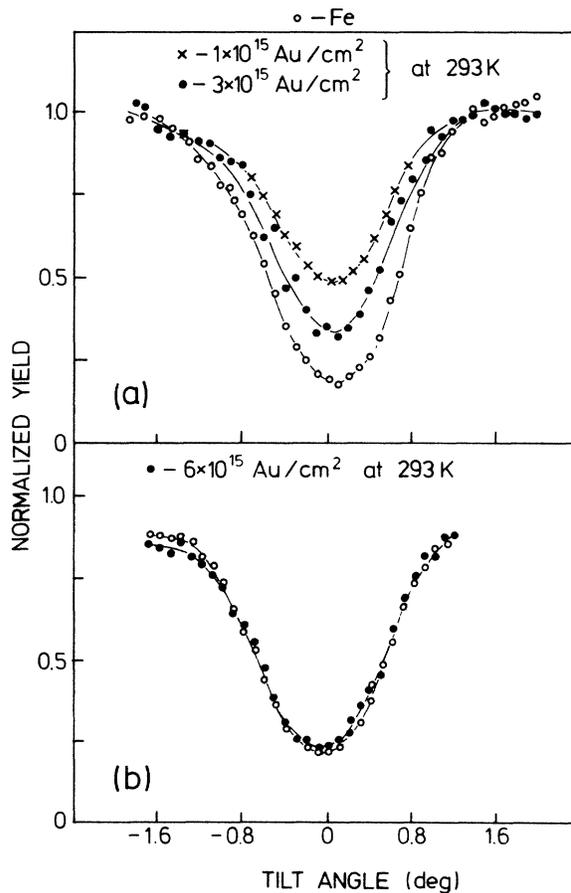


FIG. 3. Angular scans through the $\langle 110 \rangle$ axial direction of Fe single crystals implanted with different doses of Au.

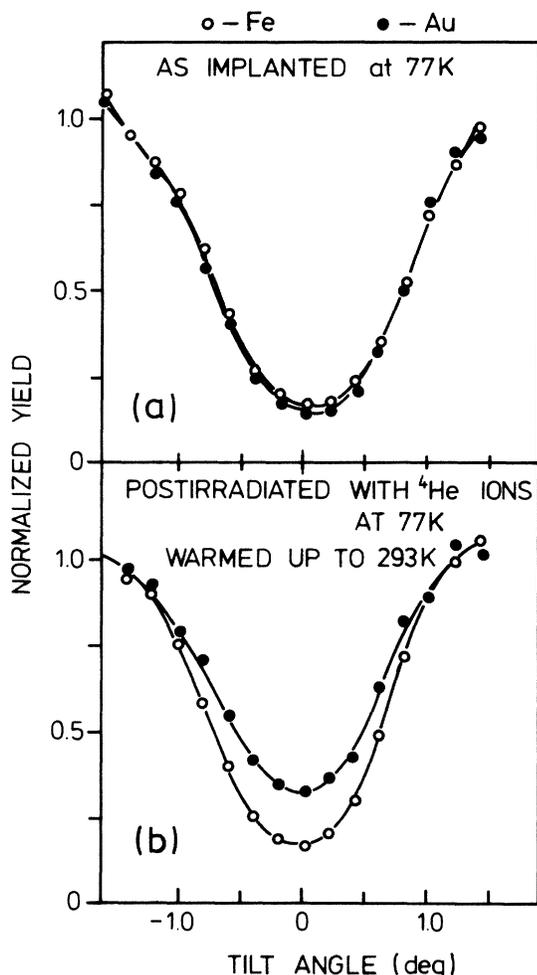


FIG. 4 (a) Angular scans through the $\langle 110 \rangle$ axial direction of Fe single crystal implanted with 1×10^{15} (Au atoms)/ cm^2 at 77 K and (b) after postirradiation with 2×10^{16} (^4He ions)/ cm^2 at 200 keV and subsequent warming up to room temperature.

with Xe ions at 600 keV. The variation of f_s with the Xe dose was very similar to that shown in Fig. 2. For doses exceeding 6×10^{15} (Xe ions)/ cm^2 , f_s amounted to 1.0. It is worth pointing out that a postirradiation experiment performed at room temperature using ^4He ions did not result in a noticeable change of the Au substitutional fraction. From these results it is concluded that the vacancy-Au associations can be annealed by applying high-density collision cascades at room temperature.

These results indicate that together with high-density cascades an increasing number of competing trapping centers for vacancies are introduced in the implanted region. In the dynamic development of the collision cascade, vacancy-rich regions surrounded by a halo of interstitial atoms are

formed. During the relaxation phase, local vacancy supersaturation causes a transformation of the cascade region into dislocation loops or small voids.¹⁵ In Fe the cascade collapse in dislocation loops is enhanced by overlapping of the subsequent cascades.¹⁶ The binding energy of a vacancy in a dislocation loop amounts to about 1.2 eV (Ref. 17) and is substantially higher than the estimated binding energy of a Au-atom-vacancy pair of 0.24 eV.¹¹ Thus, the capture of vacancies by planar defects is energetically favorable and should be considered as a stronger vacancy sink than an impurity atom.

The vacancy-impurity complexes formed during ion implantation at room temperature decompose due to the overlap of cascades produced by the successively impinging Au ions. If the competing sink density is high enough, the vacancies will preferentially migrate towards them, and the decomposed complexes will not be restored. The decomposition of vacancy-impurity complexes enables Au atoms to return to the regular lattice sites. Such competing trapping centers can be formed in the region to be implanted before the Au ions are introduced. Therefore, 5×10^{15} (Xe ions)/ cm^2 have been implanted prior to the Au implantation. After implanting 0.2 at. % Au into the preirradiated region, an f_s value of ~ 1 was observed. This result confirms the assumption made above that competing trapping centers for vacancies are introduced by high-density collision cascades. This result is further supported by the fact that postirradiation with He ions at room temperature did not influence the equilibrium between complex dissolution and formation. The production of competing sinks is obviously small, while the production of mobile vacancies is high for this case. The dissolution of the complexes by postirradiation with He ions at 77 K as well as with Xe ions does, however, occur. This result has two consequences: First, complex formation at 77 K is not possible because vacancies are immobile. Second, the dissolution of complexes occurs within the lifetime of the cascade, while the cascade density does not play an important role. This dissolution mechanism will be the subject of an additional study.

In summary, a new implantation effect has been observed, where the substitutional fraction of Au implanted in Fe at room temperature increases with increasing dose. It was found that the displacements of impurity atoms at low concentrations are due to the formation of Au-atom-vacancy complexes. The mobile vacancies are captured after the Au atoms have come to rest on substitutional lattice sites. With increasing heavy-ion dose in as-implanted as well as in pre- and postirradiated samples, different types of vacancy sinks (dislocation loops, vacancy clusters, etc.) are formed which compete with the impurity atoms in capturing vacancies. The Au-vacancy clusters which form in as-implanted samples at low Au concentrations dissociate during irradiation and do not form if the density of the competing sinks is high enough. This effect is thermally activated and was not observed after implantation at low temperatures when the vacancies are immobile.

*Permanent address: Institute for Nuclear Studies, Hoza 69, 00-681 Warsaw, Poland.

¹A. Azzam and O. Meyer, Phys. Rev. B 33, 3499 (1986).

²W. Hume-Rothery, R. E. Smallman, and C. W. Haworth, *The*

Structure of Metals and Alloys (Institute of Metals, London, 1969).

³A. R. Miedema, Philips Tech. Rev. 36, 217 (1976).

⁴A. Turos, O. Meyer, and H. Alberts, Nucl. Instrum. Methods Phys. Res. 209-210, 1041 (1983).

- ⁵A. Azzam and O. Meyer, Nucl. Instrum. Methods Phys. Res. Sect. B **7-8**, 113 (1985); M. K. Kloska and O. Meyer, *ibid.* **14**, 268 (1986).
- ⁶L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).
- ⁷A. Turos and O. Meyer, Phys. Rev. B **31**, 5694 (1985).
- ⁸E. Raub and P. Walter, Z. Metallkd. **41**, 234 (1950).
- ⁹A. Turos, O. Meyer, and Hj. Matzke, Appl. Phys. Lett. **38**, 910 (1981).
- ¹⁰M. Doyama, J. Nucl. Mater. **69-70**, 350 (1978).
- ¹¹A. Weidiger, Hyperfine Interact. **17-19**, 153 (1984).
- ¹²A. Turos, Phys. Status Solidi (a) (to be published).
- ¹³A. Vehanen, P. Hautojärvi, J. Johannson, J. Yli-Kaupila, and P. Moser, Phys. Rev. B **25**, 762 (1982).
- ¹⁴L. E. Rehn, P. R. Okamoto, and R. S. Averback, Phys. Rev. B **30**, 3073 (1984).
- ¹⁵M. L. Jenkins, C. A. English, and B. L. Eyre, Philos. Mag. A **38**, 97 (1978).
- ¹⁶I. M. Robertson, M. A. Kirk, and W. E. King, Scr. Metall. **18**, 317 (1984).
- ¹⁷L. Thome, H. Bernas, and C. Cohen, Phys. Rev. B **20**, 1789 (1979).