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Lattice-location studies of cerium ions implanted into vanadium single crystals

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The substitutional fraction (f_s) of 0.1 at. % Ce in vanadium depends on the lattice temperature during implantation and is 0.73, 0.73, and 0.15 at 5, 77, and 300 K, respectively. Increasing the implanted Ce concentration at 300 K to 3.3 at. % leads to an increase of f_s from 0.15 to 0.66. Postirradiation of *V*Ce systems as produced at 300 K with He ions at 77 K leads to an increase of f_s. If the postirradiated systems are warmed up to room temperature f_s decreases. It is concluded that Ce-vacancy clusters are formed within the prompt cascade regime and by trapping mobile vacancies. Pre- and postimplantation experiments proved that the increase of f_s with Ce concentration is due to cluster dissolution accompanied by the formation of competing vacancy-trapping centers.

I. INTRODUCTION

Ion implantation into metals is a well-known technique used to produce supersaturated solid solutions for those binary systems whose components are immiscible in the melt.[1] Several basic mechanisms may govern the lattice site occupancy of implanted ions. The effectiveness of these mechanisms depends on the collision cascade density and the lattice temperature during implantation. In high-density collision cascades, where a collective motion of all atoms prevails, the lattice occupation mechanisms could be considered as an ultrafast quenching process of a thermal spike region.[2] In the linear-cascade regime the lattice site occupancy may be governed by replacement collisions.[3] Thermodynamic driving forces may play a role. Neighbor vacancies which are potential minima recombine with interstitial foreign atoms. Interactions of impurity atoms with point defects have been studied by applying the channeling technique in postirradiation and annealing experiments at temperatures where the point defects become mobile.[4] Undersized foreign atoms share substitutional lattice sites with host atoms forming mixed dumbbells, whereas oversized impurity atoms trap more than one vacancy to form impurity-vacancy clusters. Such interactions occur even in the cooling period of the cascade.[5,6]

Previous results on lattice site determinations of implanted metallic alloys have been summarized and discussed.[1] From this summary it is seen that heavy elements from groups IIIa to VIIa of the periodic systems usually reveal high substitutional fractions in Cu, Ni, Fe, and V, while those of groups Ia, IIa, and IIIb, and some rare-earth elements are almost nonsubstitutional. In a recent study[6] it was shown that in V, after implantation and channeling analysis at 5 K, f_s of the nonsoluble elements Cs, Ba, and La was 0.65, 0.4, and 0.58, respectively, whereas f_s was zero after implantation at 300 K. This behavior was exceptional compared to other elements with a low solid solubility, and it was attributed to the formation of impurity-vacancy clusters within the cascade regime. The present study was undertaken to obtain more information on the cluster formation and on the question of whether the trapping probability for vacancies does depend on the heat of solution. The system *V*Ce has been chosen because it has an intermediate positive value of ΔH_{sol} as estimated from Miedema's theory.[7]

II. EXPERIMENTAL METHODS AND ANALYSIS

Vanadium single crystals are cut 6° to 8° off the ⟨111⟩ or ⟨110⟩ axes in the form of 3-mm-thick disks. The disks are lapped and electrolytically polished in a solution of 14% H_2SO_4 in methanol, as described in detail elsewhere.[8] A 2-MeV He-ion beam is used to perform the backscattering analysis. The scattering chamber used for the low-temperature experiments is attached to a 350-keV ion implanter in order to perform *in situ* implantation and analysis. A liquid-helium-cooled two-axis cryostat goniometer described elsewhere[9] is used. The implantations and *in situ* analysis have been performed using an ion energy of 300 keV at 5, 77, and 300 K.

The application of channeling measurements for lattice location studies is well documented in the literature.[10] The angular yield curves are characterized by the critical angle $\psi_{1/2}$, i.e., the half-angle at half-height between the normalized random and minimum yield, and the normalized minimum yield $\chi_{\min}$. $\chi^s_{\min}$ and $\chi^h_{\min}$ are the ratios of the aligned to random scattering yields for the solute and for the host, respectively. The substitutional fraction f_s of the implanted species is defined by

$$f_s=(1-\chi^s_{\min})/(1-\chi^h_{\min}) . \quad (1)$$

The minimum yield of the host ($\chi^h_{\min}$) has to be determined at a depth corresponding to the projected range of the implanted species.

An important factor limiting the sensitivity of the channeling method for studying the lattice location of low concentration impurity is the rate-dependent background due to pulse pileup. Therefore, a commercial pulse pileup rejector and low beam currents of about 1 to 5 nA have been used during the measurements. The impurity peak areas in the aligned and random spectra have been corrected by subtracting the background, which is taken to be linear and is estimated by taking the mean value for the number of counts in 10 channels below and above the impurity peak. In order to perform reliable pulse pileup corrections in the angular scan measurements, four energy windows are set: in the bulk, at the impurity peak, and above and below the impurity peak. The averaged mean values for the number of counts in energy windows above and below the impurity peak are used for the corrections.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In the following the results on the lattice site occupation for the as-implanted samples are presented first, then the influence of postirradiation and annealing experiments on the lattice site occupation will be described.

A. Low-temperature implantation

Ce ions with a concentration of 0.08 at. % have been implanted at 5 K. Angular yield curves through the ⟨110⟩ axial direction of the vanadium single crystal are shown in Fig. 1(a). The critical angles for Ce and V are equal. From Eq. (1) it can be determined that 73% of Ce atoms are located on substitutional sites without relaxations. A similar f_s value was found for samples implanted with 0.04 or 0.2 at. % Ce and analyzed *in situ* at 77 K. The corresponding angular yield curves through the ⟨111⟩ axial direction show a slight narrowing for the impurity [Fig. 1(b)]. The nonsubstitutional component is independent of the crystal direction. This result excludes a possible precipitation of the nonsubstitutional Ce atoms on dislocation loops as was, for example, seen for the system *Fe*Bi.[11] The nonsubstitutional component could be due to Ce atoms trapped in vacancy-rich cores of the dense collision cascades. As will be shown below the interaction of Ce atoms with mobile vacancies will lead to a decrease of the substitutional fraction of Ce in V. For samples implanted at 5 and 77 K, f_s is about 0.73 ± 0.05 independent of the lattice temperature. As the main recovery stage for self-interstitial atoms (SIA) in vanadium is located at 47 K,[12] the results indicate that mobile SIA's do not affect the lattice site occupancy of Ce atoms. Warming up a sample implanted at 5 K to 300 K results in a decrease of f_s from 0.73 to 0.65.

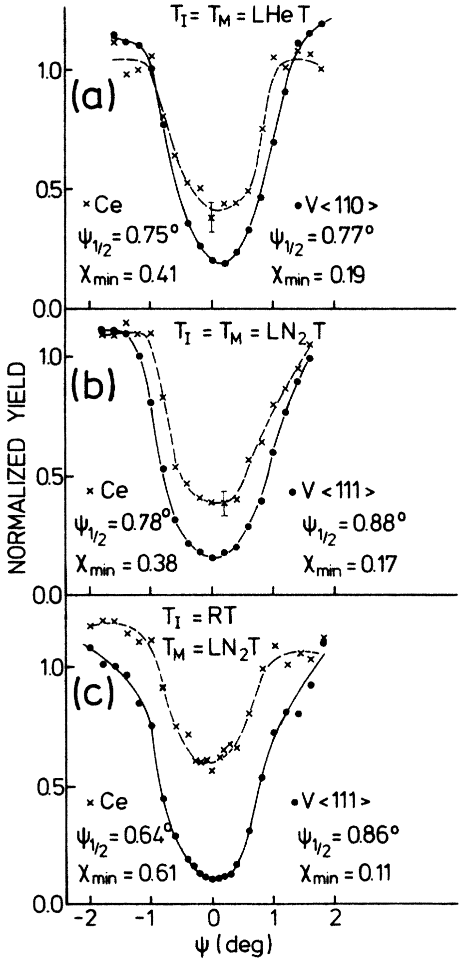

FIG. 1. Angular yield curves for Ce and V through high symmetry directions of Ce$^+$ implanted vanadium single crystals. Ce-concentration values are between 0.08 and 0.2 at. %. As-implanted (a) at 5 K, (b) at 77 K, (c) at 300 K.

B. Room-temperature implantation

Implantations of Ce ions into vanadium at 300 K reveal a quite different behavior. Firstly, the angular yield curves through the ⟨111⟩ axial direction of a vanadium single crystal implanted with 0.17 at. % Ce show that the critical angle for Ce atoms is smaller than that for V host atoms [Fig. 1(c)], indicating that the Ce atoms are displaced from the substitutional lattice site. Secondly, the substitutional fraction of Ce at low concentrations is much smaller than that reached for the same concentration after implantation at 77 K, and increases with increasing Ce concentration. Such an effect has been observed recently for the *Fe*Au system.[13] This unusual behavior is summarized in Fig. 2. It is seen that f_s increases steeply from 0.15 to 0.45 by increasing the Ce con-

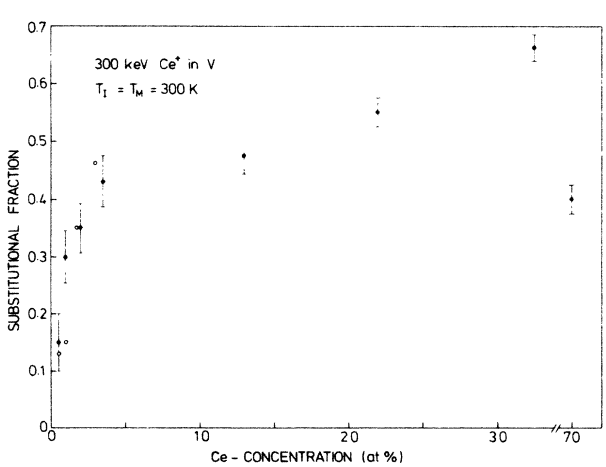

FIG. 2. The substitutional fraction of Ce$^+$ implanted into vanadium at 300 K as a function of the Ce concentration.

centration from 0.08 to 0.5 at. %. The substitutional fraction reaches a maximum value of 0.66 at 3.3 at. % Ce. At about 7 at. % Ce, f_s is seen to decrease presumably due to Ce precipitation. It may be noted that the maximum value of f_s is approximately equal to the value reached for samples implanted with low Ce concentration at temperatures below 100 K.

The critical angle of the Ce atoms increases with increasing Ce concentration and is equal to that of the V host atoms at about 0.45 at. % Ce, indicating the occupation of regular lattice sites by impurity atoms without relaxations. This effect is demonstrated by the angular yield curves through the ⟨110⟩ axial direction shown in Figs. 3(a), 3(b), and 3(c) for different Ce concentrations. It should be noted that the angular yield curve for 0.39 at. % Ce [Fig. 3(b)] indicates the existence of two components, a slightly displaced substitutional component [as in Fig. 3(a)] and a perfect one. While the perfect substitutional component increases with increasing Ce concentration the displaced component decreases.

The simplest explanation of the rather low substitutional fraction, and the narrowing of the angular yield curves for Ce after low dose implantation at 300 K, is the assumption that Ce multivacancy complexes have formed by trapping mobile vacancies. It should be noted that stage III for vacancy motion in vanadium lies between 200 and 300 K.[14]

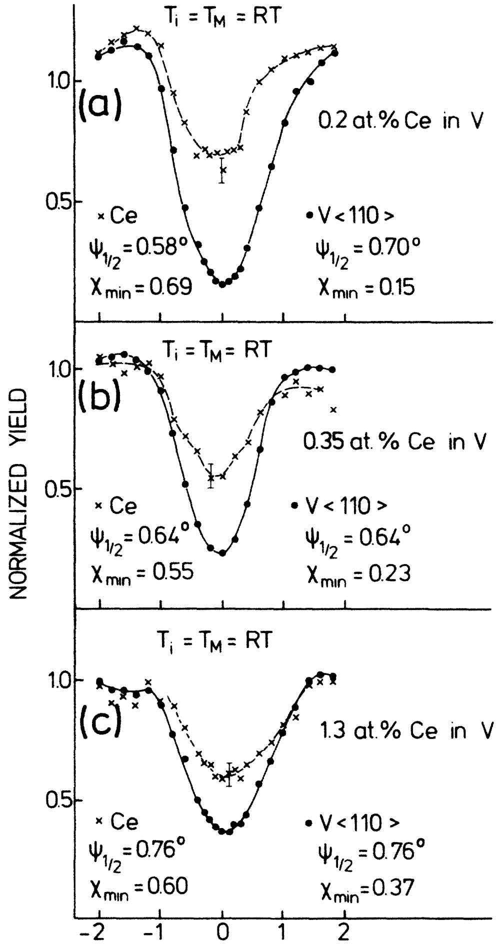

FIG. 3. Angular yield curves for Ce and V atoms through the ⟨110⟩ axial direction from vanadium single crystals implanted with Ce$^+$ at different concentrations: (a) 0.2 at. % Ce (b) 0.35 at. % Ce (c) 1.3 at. % Ce.

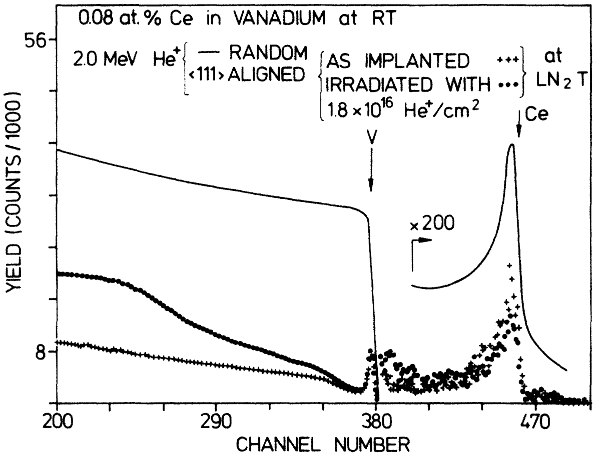

FIG. 4. Random and ⟨111⟩ aligned backscattering spectra from a vanadium single crystal implanted with 0.08 at. % Ce at 300 K. The ⟨111⟩ aligned spectra are shown before and after postirradiation with 1.8×10^{16} He$^+$/cm^2 (200 keV) at 77 K.

C. Postirradiation experiments

Impurity-vacancy associations should annihilate by absorbing mobile SIA's. In order to test this assumption samples implanted at 300 K were cooled to 77 K and were postirradiated with He ions. Figure 4 shows as an example aligned and random backscattering spectra taken at 77 K for a vanadium single crystal implanted with 0.08 at. % Ce at 300 K. After postirradiation with 1.8×10^{16} He$^+$/cm^2 (200 keV) at 77 K, the Ce peak area in the ⟨111⟩ aligned spectra is seen to decrease compared to the area before postirradiation. The results of these postirradiation experiments are summarized in Table I. With increasing He ion fluence, f_s is seen to increase and reaches a maximum saturation value of 0.75. This value is in

TABLE I. Influence of postirradiation with He ions at 77 K on the substitutional fraction of *V*Ce systems produced by Ce implantation at room temperature.

Ce (at. %)	Fluence (He/cm^2)	f_s($\pm$0.05)
0.08	0	0.38
	2×10^{15}	0.64
	5×10^{15}	0.71
	1.8×10^{16}	0.75
0.17	0	0.36
	2×10^{16}	0.56
0.3	0	0.46
	2×10^{16}	0.58

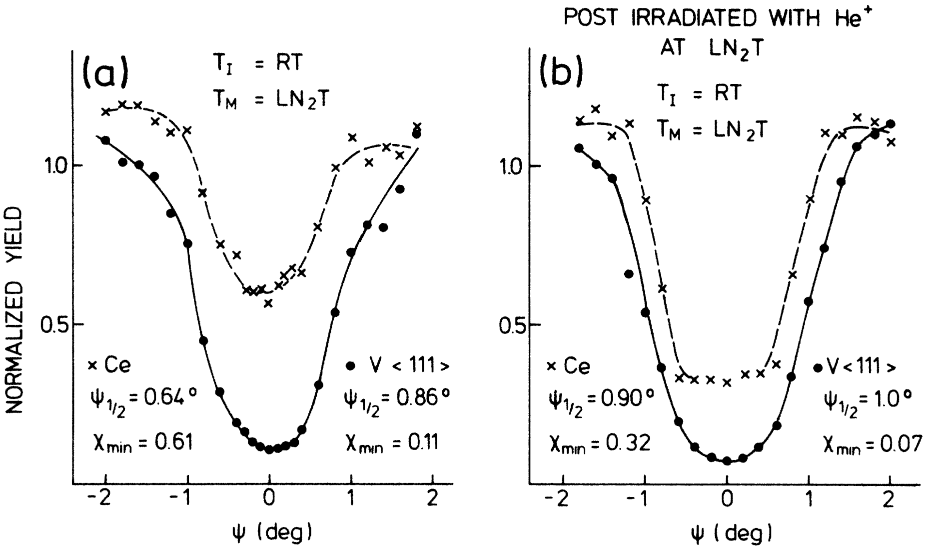

FIG. 5. Angular yield curves for Ce and V through a ⟨111⟩ axial direction from a Ce^+ implanted vanadium single crystal. (a) Implanted at 300 K and measured at 77 K; (b) implanted at 300 K, postirradiated with 1×10^{16} He^+/cm^2, and measured *in situ* at 77 K.

agreement with the highest f_s values obtained after implantation at 77 K. More information can be obtained by comparing the angular yield curves before [Fig. 5(a)] and after postirradiation with He ions at 77 K [Fig. 5(b)]. It is noted that both f_s and the critical angle of the Ce atoms increase after postirradiation. If the postirradiated samples are warmed up to 300 K, f_s decreases to 0.2, indicating that single vacancies become mobile and get trapped by Ce atoms. Postirradiation of a *V*Ce system produced at 77 K with 2×10^{16} He^+/cm^2 at 300 K results in a decrease of f_s from 0.67 to 0.38 which also indicates trapping of mobile vacancies.

D. Pre- and postimplantation experiments

The increase of both f_s and the critical angle for Ce with increasing Ce concentration can be attributed to the annealing of the existing Ce-vacancy complexes and the generation of additional sinks for vacancies. New Ce-vacancy complexes will be formed during further implantation; however, the equilibrium state between complex formation and annealing is shifted because vacancies generate their own sinks. In this way the concentration of mobile vacancies and thus the formation probability of Ce-vacancy complexes is reduced. In the following pre- and postimplantation experiments with Au ions are performed to prove the assumption discussed above. Au ions are implanted into vanadium single crystals at 300 K to a peak concentration of 0.1 at. %. The substitutional fraction for Au atoms is equal to one. Therefore the Au atoms themselves are not expected to influence the situation of the Ce atoms which are postimplanted within the same projected range to a peak concentration of 0.15 at. %. The measured substitutional fraction for the Ce atoms of 0.64 is larger than the value of 0.3 obtained without preimplantation (see Fig. 2). This result indicates that mobile vacancies which are produced during implantation of Ce ions are mainly trapped by competing vacancy trapping centers formed during the preceding Au-ion implantation. In this way the probability of Ce-vacancy complex formation is reduced. On the other hand, implantation of 0.46 at. % Ce in vanadium at 300 K followed by postimplanting Au ions to a peak concentration of about 0.37 at. %, results in an increase of the substitutional fraction of Ce from about 0.45 to 0.73. This result shows that Ce-vacancy complexes are dissolved during the postbombardment, accompanied by the formation of competing vacancy trapping centers.

E. Annealing experiments

Annealing experiments at temperatures above room temperature (RT) have been performed on some *V*Ce samples to study the influence of vacancy cluster annihilation on the lattice site occupation of Ce atoms. Figures 6(a) and 6(b) show the angular yield curves for the Ce and the V atoms before and after annealing to 525 K, respectively. By comparing the angular yield curves of the Ce atoms it is concluded that Ce-trivacancy complexes are formed, leading to a flux peak in the ⟨111⟩ axial direction [Fig. 6(b)]. The Ce position between three vacancies in the (110) plane lies within an isosceles triangle which after projection into the (111) plane, results in a position 10% displaced from the center. Thus a broadening of the flux peak is expected in agreement with the measurement. At 575 K the angular scan indicates a random position for the Ce atoms.

The annealing behavior of a high-dose Ce-implanted V sample (3.3 at. % Ce) is quite different. For annealing temperatures up to 800 K the angular yield curves for the Ce atoms have the same critical angle as the V host atoms [shown in Fig. 7(a) for the as-implanted sample]. Upon annealing up to 925 K, a narrowing in the Ce angular yield curve is observed [Fig. 7(b)] followed by a reduction

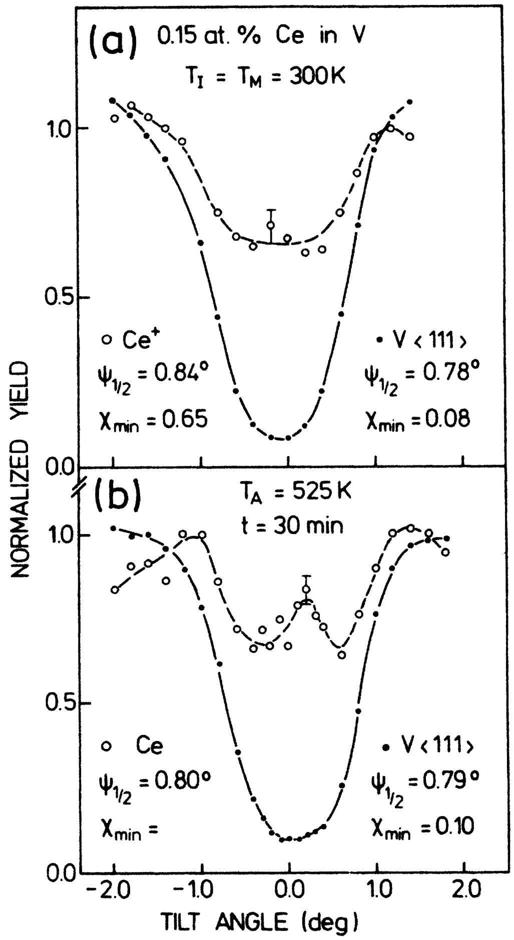

FIG. 6. Angular yield curves for Ce and V through a ⟨111⟩ axial direction of 0.15 at.% Ce^+ implanted vanadium single crystal: (a) As-implanted at 300 K, (b) annealed up 525 K and measured at 300 K.

of the f_s value from 0.66 to 0.47. After prolonged annealing at 925 K, f_s decreased to 0.14.

During high-temperature annealing a direct backscattering peak is formed in the implanted region of the aligned host spectrum indicating the displacement of V atoms. The displacement of Ce and V atoms during high-temperature annealing may be attributed to the formation of a V-Ce compound. Such an effect has been observed previously for the VGa system.[15] During the process of compound formation, the Ce atoms first precipitate coherently [Fig. 7(b)] and then occupy several distinct interstitial lattice sites as indicated by the complex structure of the angular yield curve shown in Fig. 7(c). A detailed structure analysis of the compound by x-ray diffraction has not yet been performed and is not the purpose of this study.

IV. SUMMARY AND CONCLUSIONS

About 30% of the Ce atoms implanted at temperatures below 100 K are nonsubstitutional. This component

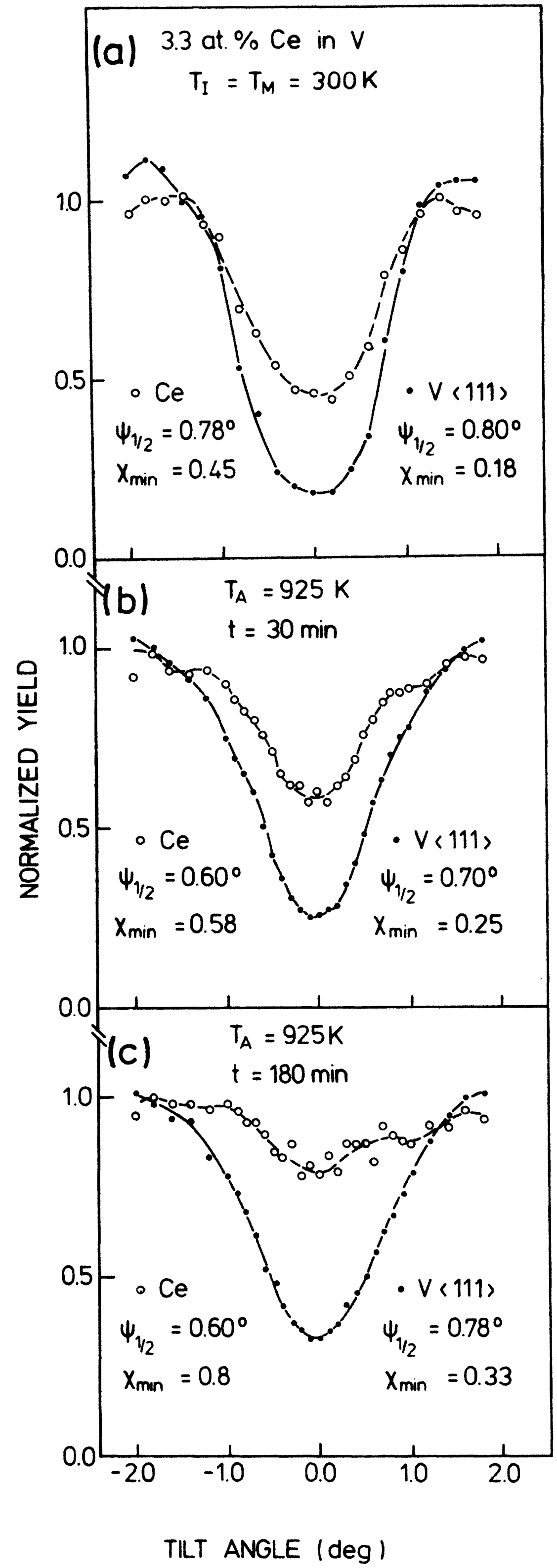

FIG. 7. Angular yield curves for Ce and V atoms through the ⟨111⟩ axial direction of 3.3 at.% Ce implanted V single crystal: (a) As-implanted at 300 K, (b) annealed at 925 K for 30 min, (c) annealed at 925 K for 180 min.

could be due to the formation of Ce precipitates or due to Ce atoms trapped in vacancy-rich cores of the collision cascades. The formation of Ce precipitates is thought to be highly improbable as the mean distance between Ce atoms is about 30 Å at 0.1 at. % and diffusion is negligible at 5 K. Thus the only explanation seems to be that there is a certain probability for Ce atoms to come to rest in depleted zones of the collision cascades. Also, there is a certain probability that Ce atoms are able to trap several vacancies in the cascade as point defects can perform some thermally activated jumps in the dynamic regime of the collision cascade.[16] These possibilities are further supported by the discussion given below.

The substitutional fraction of Ce after implantation into V at room temperature is smaller, at least for low Ce concentrations, than the f_s values observed after implantation at temperatures below 100 K. This result is attributed to the formation of Ce-vacancy clusters which cause the Ce atoms to be removed from the substitutional lattice sites. Postirradiation and annealing experiments support this assumption.

The comparatively small reduction of f_s by warming up the samples implanted at low temperatures indicates that only a few vacancies survive the recombination and agglomeration processes in the cooling period of the cascade.

The increase of f_s with increasing implanted Ce concentration could be attributed to the fact that existing Ce-vacancy complexes are dissolved and that mobile vacancies are trapped by an increasing number of competing vacancy trapping centers, presumably vacancy clusters and vacancy loops. In this way the concentration of mobile single vacancies and thus the formation of Ce-vacancy clusters is reduced. The observed increase of f_s by both pre- and postbombardment with Au ions confirms the interpretation which postulates a variable sink concentration for vacancies.

Annealing studies at temperatures above room temperature have provided information on the dissolution of vacancy clusters and on the vacancy-assisted motion of the Ce atoms. For V samples containing low Ce concentrations the formation of Ce-trivacancy clusters has been observed at temperatures above 500 K, followed by a decrease of f_s to zero at 600 K, probably due to the trapping of additional vacancies. At high Ce concentrations the lattice site of the Ce atoms does not change in this rather-low-temperature region, presumably because of a relatively low vacancy concentration. The reduction of f_s is observed after annealing to 925 K, where both V and Ce atoms are displaced. Two annealing stages for vacancy clusters above RT have also been observed using positron annihilation for cold-worked vanadium.[14] A similar type of enhanced impurity motion has been studied recently in more detail for the *Fe*Au system.[17]

The Darken-Gurry plots based on the Hume-Rothery limits for equilibrium solid solutions are usually used to separate the substitutional from the nonsubstitutional implanted species in a metallic host.[1] Elements from groups Ia, IIa, and IIIb, and some rare-earth elements are not substitutional in vanadium after implantation at 300 K, in accordance with the thermal equilibrium rules.[6] These elements, however, reveal high substitutional components if implanted at 5 and 77 K, which is at variance with all the rules mentioned before. It was speculated, that these elements having a rather positive heat of solution (ΔH_{sol}) would have a high trapping probability for vacancies in order to reduce ΔH_{sol}.[6] The heat of solution is calculated for the systems under consideration using Miedema's theory.[7] In Fig. 8 the substitutional fractions for these systems are correlated to the calculated heat of solution. The solid lines are only guides to the eye to connect the data measured at the same temperatures. It is noted that elements having a negative heat of solution in vanadium are 100% substitutional at 300 K. Other elements with small positive heat of solution (for example Bi) are 100% substitutional independent of the lattice temperature. Elements such as La, Xe, Ba, and Cs which have a rather high positive heat of solution (between 200 and 686 KJ/mole) reveal a temperature-dependent substitutional fraction. It can be seen from Fig. 8 that the results obtained here for the *V*Ce system fit nicely in this systematic study. The results are in agreement with a previous theoretical discussion,[18] which states that a positive heat of solution will enhance the solute-vacancy attraction. The results further support the previous statement[6] that replacement collisions are not responsible for the lattice site occupation of implanted ions in the first place. The main basic mechanism for lattice site occupation is the recombination of foreign atoms with vacancies in the cascade region and additional trapping of vacancies either in the cascade regime or in the delayed regime, a process governed by thermodynamical driving forces.

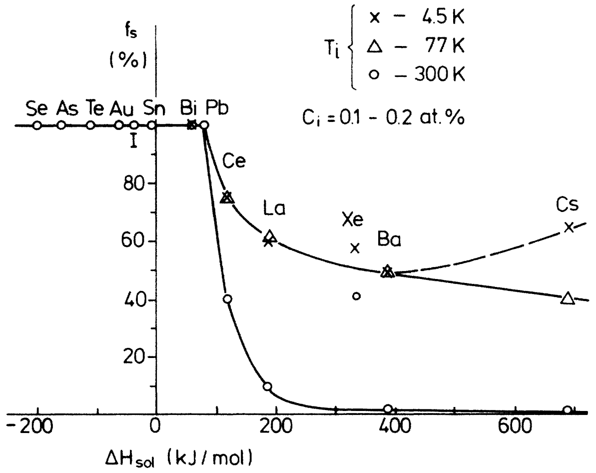

FIG. 8. Substitutional fraction of different ions implanted in V single crystals as a function of the heat of solution. The implantation and *in situ* measurements are performed at 4.5, 77, and 300 K.

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[1] J. M. Poate and A. G. Cullis, in *Treatise on Materials Science and Technology*, edited by J. K. Hirvonen (Academic, London, 1980), Vol. 18, p. 85.

[2] J. M. Poate, J. A. Borders, A. G. Cullis, and J. K. Hirvonen, Appl. Phys. Lett. **30**, 365 (1977).

[3] P. H. Dederichs, Chr. Lehmann, and H. Wegner, Phys. Status Solidi **8**, 213 (1965). W. W. Anderson, Solid State Electron. **11**, 481 (1968); D. K. Brice, *Application of Ion Beams to Materials*, IOP Conf. Ser. No. 28, edited by G. Carter, J. S. Colligon, and W. A. Grant (IOP, Bristol, 1976), p. 334.

[4] M. L. Swanson and L. M. Howe, Nucl. Instrum. Methods **218**, 613 (1983).

[5] G. Weyer, F. T. Pedersen, and H. Grann, Nucl. Instrum. Methods **B7/8**, 103 (1985).

[6] A. Azzam and O. Meyer, Nucl. Instrum. Methods **B7/8**, 113 (1985); Phys. Rev. B **33**, 3499 (1986).

[7] A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica **100B**, 1 (1980); and CALPHAD (to be published).

[8] M. Gettings, O. Meyer, and G. Linker, Radiat. Eff. **21**, 51 (1974)

[9] R. Kaufmann, J. Geerk, and F. Ratzel, Nucl. Instrum. Methods **205**, 293 (1983).

[10] D. E. Gemmell, Rev. Mod. Phys. **46**, 129 (1974); L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).

[11] P. T. Callaghan, P. Kittel, N. J. Stone, and P. D. Johanston, Phys. Rev. B **14**, 3722 (1976).

[12] C. E. Klabunde, J. K. Redmann, A. L. Southern, and R. R. Coltmann, Jr., Phys. Status Solidi A **21**, 303 (1974).

[13] A. Turos and O. Meyer, Phys. Rev. B **33**, 8829 (1986).

[14] S. Tanigawa, I. Shinta, and H. Iriyama, in *Point Defects and Defect Interactions in Metals*, edited by Jin-Ichi Takamuta *et al.* (North-Holland, Amsterdam, 1982), p. 736; H. Schulz, *ibid.*, p. 183.

[15] J. M. Lombaard, G. Linker, and O. Meyer, J. Less-Common Met. **96**, 191 (1984).

[16] M. W. Guinan and J. H. Kinney, J. Nucl. Mater. **103/104**, 1319 (1981).

[17] A. Turos and O. Meyer, Phys. Rev. B **31**, 5694 (1985).

[18] A. R. Miedema, Metallkunde **70**, 345 (1979).