Lattice-location studies of argon, potassium, and calcium in iron

Jack R. MacDonald and R. A. Boie
Bell Laboratories, Murray Hill, New Jersey 07974

W. Darcey* and R. Hensler†
Physics Department, Rutgers University, New Brunswick, New Jersey 08903
(Received 16 April 1975)

The lattice locations of argon, potassium, and calcium implanted into iron single crystals have been studied using a particle-channeling technique. Yields of K x-rays and backscattered $^4He^+$ ions were monitored as a function of crystal-incident beam orientation. Substitutional fractions of 0.55 ± 0.05, 0.11 ± 0.05, and ≤ 0.05 were deduced for calcium, potassium, and argon, respectively; the remaining atoms reside in undetermined sites.

I. INTRODUCTION

The phenomenon of charged-particle channeling in single crystals has recently been applied in a variety of systems to study the lattice location of dilute impurities in single-crystal hosts (Ref. 1 and references contained therein). In particular, the lattice sites of foreign atoms in ferromagnetic hosts[2] are of obvious interest and importance in the interpretation of measurements of hyperfine magnetic fields and of perturbed-angular-correlation experiments which utilize these fields to measure nuclear magnetic moments. This paper presents the results of experiments designed to determine the lattice sites of argon, potassium, and calcium implanted into iron in an attempt to correlate lattice-site and hyperfine-field data.

II. EXPERIMENTAL TECHNIQUE

Application of the charged-particle channeling technique to the determination of lattice locations of impurity atoms in single-crystal hosts is well described elsewhere.[1] In the present cases, we observed the channeling dependence of the yield of K x rays induced by bombardment with 1.5-MeV $^4He^+$ ions, since for light impurities in a heavier host the Rutherford scattering technique is not easily applicable.

Single crystals of iron, cut such that the ⟨110⟩ axis was normal to the crystal surface, were lapped, polished, and ion implanted. The implants were effected at room temperature and with the incident-ion beam in a nonchanneling (random) direction. A series of implant doses and energies was chosen according to range theory[3] to result in an approximately uniform impurity concentration of 3.4×10^{20} cm^{-3} to a depth of 0.08 μm.

Samples were mounted on a two-axis goniometer and analyzed using suitably collimated $^4He^+$-ion beams from a 2-MV Van de Graaff accelerator. X rays were detected at 90° to the beam direction in a 25-mm^2 Si(Li) detector. A titanium foil, 6.3×10^{-4} cm thick, was placed between the target and detector to selectively absorb K x rays from the iron host crystal and thus improve the impurity/host x ray intensity ratio in the detector. Backscattered $^4He^+$ ions were simultaneously detected in a Si surface barrier counter to provide an accurate measure of relative crystal-beam orientation and to monitor, in a sensitive fashion, the details of the host-beam interaction.

The energy dependence of cross sections for x-ray production by $^4He^+$ ions was measured for target

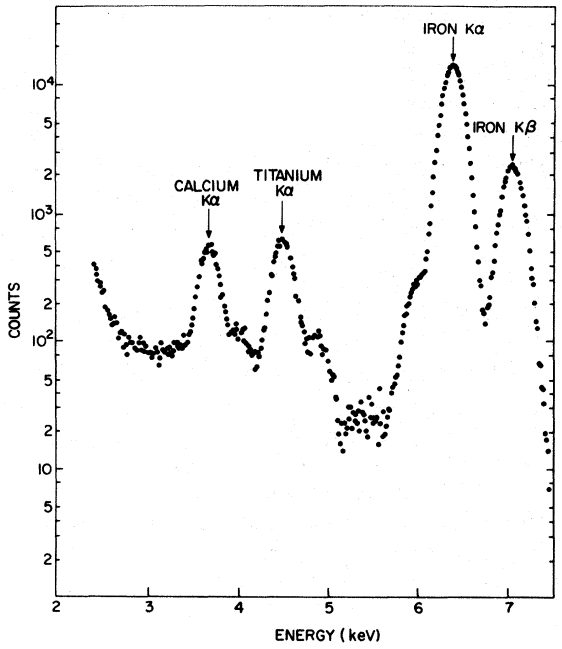

FIG. 1. X-ray spectrum obtained by bombardment of a calcium-implanted iron single crystal with 1.5-MeV $^4He^+$ ions incident in a ⟨111⟩ axial channeling direction. The total implant dose was approximately 3×10^{15} cm^{-2}.

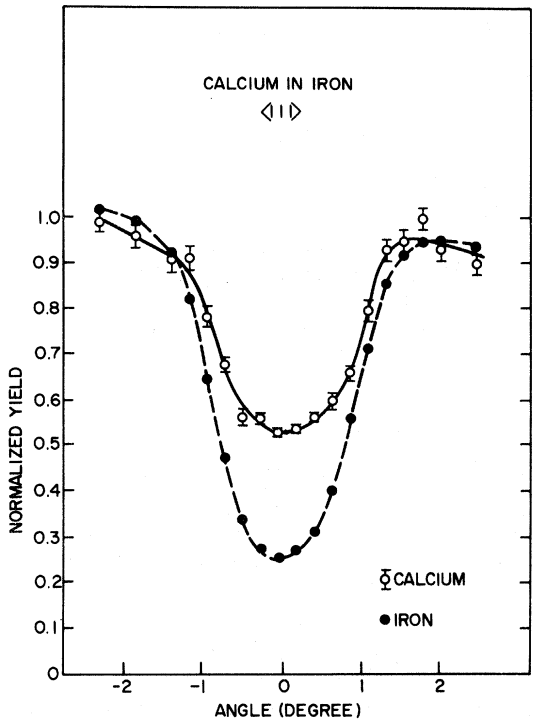

FIG. 2. Angular scan across the ⟨111⟩ axis in a calcium-implanted iron single crystal.

species of interest in order to estimate the effect on x-ray yields of differing energy loss in channeled and random cases and to attempt to maximize impurity/host x-ray yields by choosing an optimum bombarding energy. From these results, we calculate that for normal incidence at 1.5 MeV on samples implanted with the depth distribution previously described, the impurity x-ray yield would increase by 4% in going from a random to channeled orientation. This effect is in addition to any lattice-location contribution to the angular dependence of the yield and is due entirely to changes in the energy-depth distribution resulting from an assumed 50% difference in stopping power in random and channeled orientations. At lower incident energies the change in x-ray yields is much larger while at higher energies the ratio of impurity to host x-ray yields decreases. A bombarding energy of 1.5 MeV was chosen as a compromise between these conditions and the x-ray production cross section was assumed to be constant in all analyses.

III. RESULTS

Figure 1 shows an x-ray spectrum obtained by bombarding a calcuim-implanted iron single crystal with 24 μC of 1.5-MeV $^4He^+$ ions incident in a ⟨111⟩ axial channeling direction. In clear evidence are peaks due to the iron host, the titanium absorber, and the calcium implant. The results of peak area analysis for similar spectra taken in a ⟨111⟩ angular scan are shown in Fig. 2. The dashed curve represents the yield of $^4He^+$ ions backscattered from depths corresponding to the implant range distribution. The angular widths of impurity and host dips are equal and

$$S=\frac{1-\chi_{\min}^{\text{impurity}}}{1-\chi_{\min}^{\text{host}}}=0.59\pm0.03.$$

Figure 3 shows ⟨100⟩ axial scans for which $S=0.49\pm0.05$. In this case the angular width of the calcium dip is approximately 90% of the host dip. A similar situation obtains for the {100} planar scan of Fig. 4, where the impurity angular width appears considerably narrower than that of the host. A ratio $S=0.45\pm0.15$ is indicated. In all cases, the errors quoted included statistical uncertainty and possible systematic error associated with uncertainties in implant depth distributions.

Figure 5 summarizes the results of x-ray and $^4He^+$-ion angular scans for potassium in iron. These data give $S=0.13\pm0.05$ and 0.09 ± 0.05 for the ⟨111⟩ and ⟨100⟩ channeling directions. Figure 6 is an angular scan typical of those observed for argon in iron. There is no evidence for reduced yield in any channeling direction for this system.

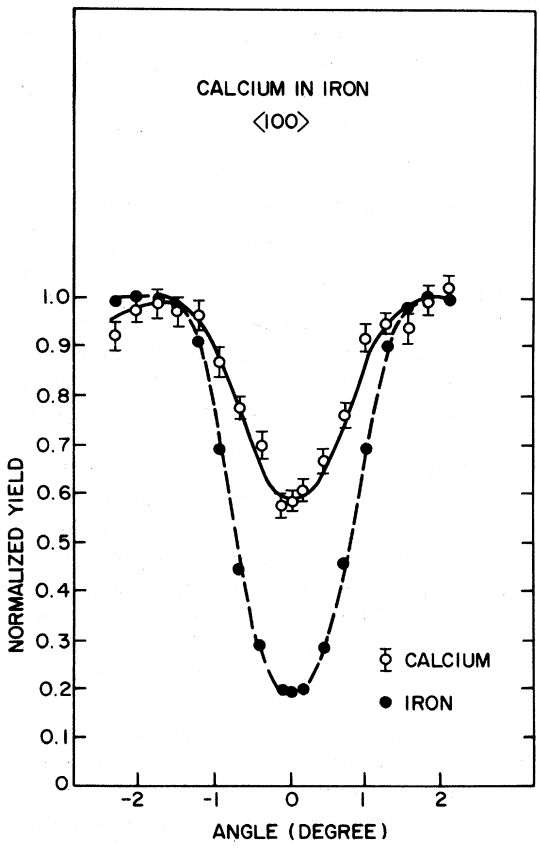

FIG. 3. Calcium in iron ⟨100⟩ angular scan.

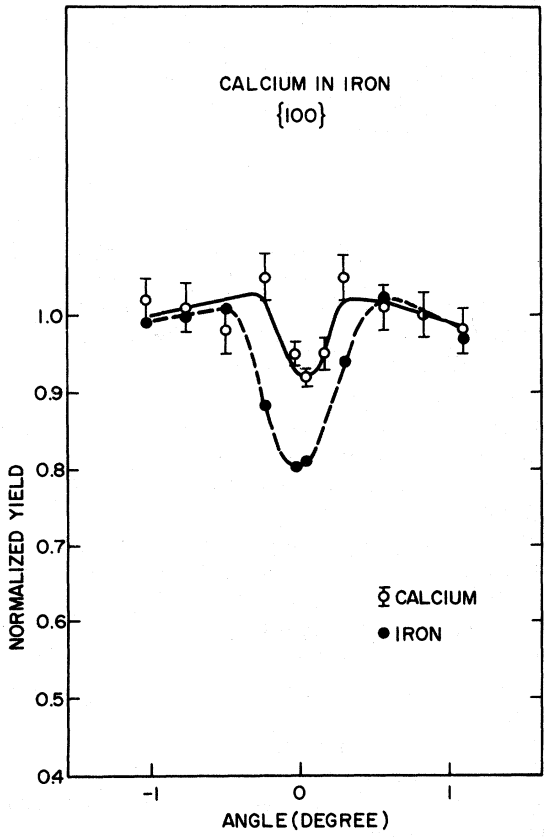

FIG. 4. Calcium in iron {100} angular scan.

IV. DISCUSSION

The combination of ⟨111⟩, ⟨100⟩, and {100} channeling measurements should be capable of detecting significant fractions of implanted atoms in substitutional sites and/or octahedral or tetrahedral interstitial sties in the bcc iron lattice. Occupation of the octahedral site would be manifested by flux peaks in the ⟨100⟩ and ⟨111⟩ axial channels and apparent substitutionality in the {100} planar channel, for which all octahedral sites are shadowed. Similarly, of the 12 equivalent tetrahedral interstitial sites, one-half are shadowed in {100} planar channeling, while all are visible in the ⟨111⟩ and ⟨100⟩ axial directions. The observed implant and host minimum yields are summarized in Table I. In no case was there evidence for flux peaking; neither

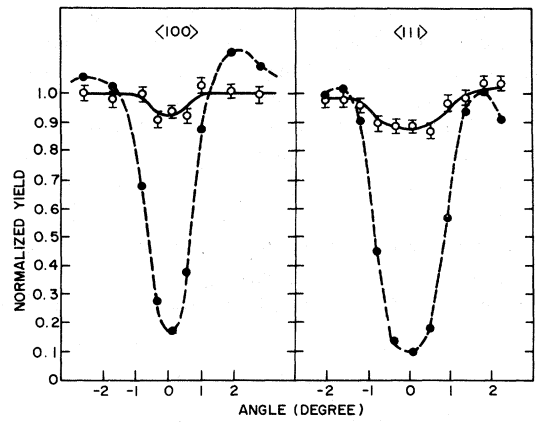

FIG. 5. Potassium in iron angular scans.

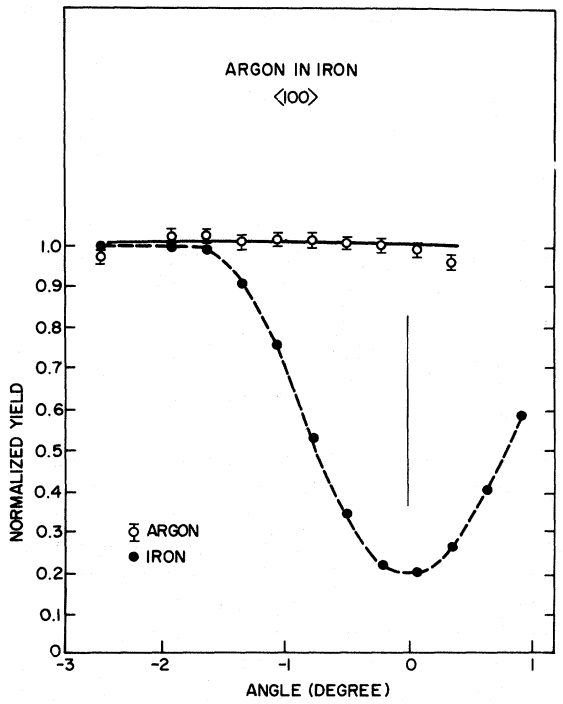

FIG. 6. Argon in iron ⟨100⟩ angular scan.

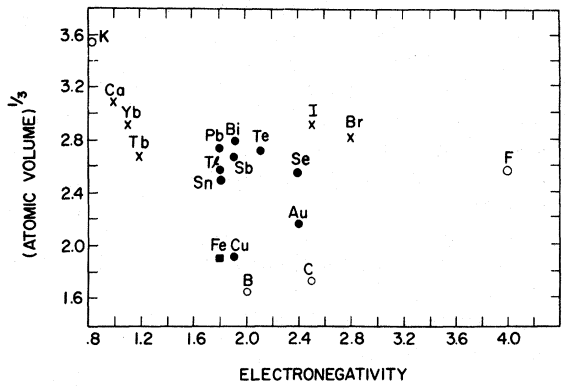

FIG. 7. Darken-Gurry plot for impurities implanted into Fe at room temperature. The atomic volume is in arbitrary units and the electronegativity follows Pauling's scale. ●, > 80% substitutional; ×, 50–80% substitutional; o, < 50% substitutional.

TABLE I. Summary of host and impurity minimum yields.

Impurity	Channel	Minimum yields χ_{host}	χ_{imp}	$S=\frac{1-\chi_{imp}}{1-\chi_{host}}$
Calcium	⟨111⟩	0.25	0.56	0.59 ± 0.04
	⟨100⟩	0.19	0.60	0.49 ± 0.05
	{100}	0.81	0.91	0.45 ± 0.15
Potassium	⟨111⟩	0.10	0.88	0.13 ± 0.05
	⟨100⟩	0.17	0.92	0.09 ± 0.05
Argon	⟨111⟩	0.13	1.00	≤ 0.05
	⟨100⟩	0.20	1.00	≤ 0.05

were there significant differences in minimum yields for the three channeling directions. A consistent but not unique interpretation of the data would indicate substitutional fractions of 0.55 ± 0.05 for calcium, 0.11 ± 0.05 for potassium, and ≤ 0.05 for argon, the nonsubstitutional components being in undetermined sites with significant occupation of regular octahedral or tetrahedral interstitial sites specifically excluded. In the case of calcium, the differing angular widths for implant and host scans may indicate a displacement of calcium from a regular substitutional location.

De Waard and Feldman[2] have recently reviewed systems for which lattice-location and hyperfine-field data are available. In the case of calcium in iron, a unique field of -100 ± 6 kG has been measured by Marmor, Cochavi, and Fossan[4] in a time-differential-implantation perturbed-angular-correlation experiment utilizing the 3.19-MeV (6^+) state of ^{42}Ca ($g=-0.415\pm0.015$, $\tau_m=7.7$ nsec). The experiment would have detected other field components of magnitude between 30 and 500 kG but could not establish the fraction of implanted calcium nuclei experiencing the -100-kG field. They further observed that the correlation for implantation into iron was attenuated by a factor of approximately 5 relative to that for implantation into platinum. On the other hand, Hensler *et al.*,[5] in a time-*integral*-implantation perturbed-angular-correlation experiment, utilized the 4.49-MeV (5^-) state of ^{40}Ca as a probe ($g=0.52\pm0.08$, $\tau_m=0.39$ nsec). In this case an *average* hyperfine field of -45 ± 14 kG was found and no attenuation of the angular correlation was observed. A consistent accomodation of these sets of data with the lattice-location results is possible but somewhat implausible. It is the case that a field of -100 kG acting on 50% of the implanted atoms results in an average field of roughly -50 kG providing the remaining atoms experience a low field ($\lesssim 20$ kG). The significant attenuation observed by Marmor *et al.* would then require explanation in terms of a relaxation mechanism acting on a time scale lying conveniently between 0.39 and 7.7 nsec. These conclusions must be tempered by the realization that the hyperfine measurements were done on the order of 1 nsec after implantation, whereas the lattice-location measurements were carried out days after implantation. Furthermore, the hyperfine experiments dealt with impurity concentrations of approximately 1% those of the channeling experiments. There is no explicit evidence which would suggest these differences in time or concentration should jeopardize meaningful comparison between experiments; nonetheless, different diffusion, radiation damage, or annealing phenomena could be operative in the two cases.

The magnetic hyperfine field of potassium in iron has been measured to be -157 ± 20 kG by Marmor and Fossan.[6] In this case, the observed correlation was not severely attenuated but rather exhibited at least $\frac{2}{3}$ of the expected anisotropy. This result implies that at least $\frac{2}{3}$ of the implanted potassium atoms experienced the measured field. If the present channeling results are applicable to this situation, the conclusion would be that the site corresponding to the observed field is not substitutional, nor either the octahedral or tetrahedral interstitial sites.

There are no hyperfine-field measurements for the argon-iron system. There are, however, both hyperfine-field and lattice-location measurements for xenon in iron (see Ref. 2). These data indicate a multiplicity of fields and lattice sites. The hyperfine field on argon in nickel has been measured[7] in a time-differential experiment exhibiting a severe attenuation. A lattice-location measurement of this system is difficult because of the severe radiation damage attendant to ion implantation in nickel.

De Waard and Feldman[2] have correlated the degree of substitutionality for impurities in iron with atomic size and electronegativity of impurity, in a fashion similar to Darken and Gurry.[8] The present results have been added to their compilation and are illustrated in Fig. 7. In this scheme, potassium fails on both counts to qualify for substitutional behavior. Calcium, not approaching values of size and electronegativity typical of substitutional impurities in iron, lies very close to ytterbium in a Darken-Gurry plot. Alexander *et al.*[9] and Able *et al.*[10] have measured the lattice sites of ytterbium in iron and find 55% substitutional with the remainder in undefined sites, in substantial accord with the calcium case. Indeed, there is evidence[9] that these fractions correspond to magnetic and nonmagnetic sites. Argon, having no well-defined electronegativity, cannot be included on a Darken-Gurry plot.

ACKNOWLEDGMENTS

The authors thank W. L. Brown and L. C. Feldman for many enlightening discussions. We are

indebted to W. F. Flood for his expert crystal preparation and J. W. Rodgers for performing the ion implantation.

---

*Present address: Victoria University of Wellington, Wellington, New Zealand.
†Present address: Ebasco Services, Inc., New York, N. Y.

[1]R. B. Alexander, P. T. Callaghan, and J. M. Poate, Phys. Rev. B 9, 3022 (1974).
[2]H. *International Conference on Applications of Ion Beams to Metals, Albuquerque*, 1973, edited by S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum, New York, 1973).
[3]J. Lindhard, M. Scharff and H. E. Schiøtt, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. 33, No. 14 (1963).
[4]M. Marmor, S. Cochavi, and D. B. Fossan, Phys. Rev. Lett. 25, 1033 (1970).
[5]R. Hensler, J. W. Tape, J. Matthews, N. Benczer-Koller, and J. R. MacDonald, Phys. Rev. C 10, 919 (1974).
[6]M. Marmor and D. B. Fossan, Bull. Am. Phys. Soc. 17, 87 (1972), and private communication.
[7]H. G. Devare and H. de Waard, Phys. Rev. B 5, 134 (1972).
[8]L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill, New York, 1953).
[9]R. B. Alexander, E. J. Ansaldo, B. I. Deutch, J. Gellert, and L. C. Feldman, in Ref. 2.
[10]F. Abel, M. Bruneaux, C. Cohen, H. Bernas, J. Chaumont, and L. Thome, Solid State Commun. 13, 113 (1973).