Iron on Substitutional and Interstitial Lattice Sites in Alkali Metals and Isomer Shift Systematics for Interstitial Iron in Elemental Metals

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In-beam Mössbauer spectroscopy is applied to study implanted Fe atoms in the alkali metals Li, Na, and K. From the Mössbauer parameters we infer that the Fe implants take up substitutional as well as interstitial sites. The interstitial Fe experiences a strongly increased *s*-electron density which is shown to hold quite generally in elemental metals and can be explained by the resulting lattice pressure. It is concluded that recently reported local moment formation in the alkali metals has contributions from both substitutional and interstitial Fe.

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If one inspects a Darken-Gurry plot [1] or more sophisticated schemes like Miedema's coordinates [2] to estimate the solubility of a certain impurity in a host metal it is hard to find alloy partners more incompatible than Fe as a solute in alkali metals. Strong disparity in atomic volume, electronegativity, and electron density clearly displays the experimentally born out fact that Fe is practically not soluble in these metals. On the other hand, the wide range of free-electron densities and atomic volumes accessible in the alkali metals represent an attractive environment for the small 3d impurity Fe to study its local electronic and magnetic structure. In a series of experiments [3–5] the perturbed angular distribution (PAD) technique has revealed the formation of magnetic moments on Fe implants which the authors explained mainly by the small hybridization with the host matrix. First-principles calculations have illuminated this interpretation in more detail [6–8].

The important question of the implant's lattice position was not touched in the initial publication [3]; in subsequent work the authors try to deduce a substitutional lattice site mainly from the impurity's magnetic behavior itself [4,5]. However, from the exotic character of these systems one might be tempted to expect that implantation would not necessarily lead to substitutional Fe. Recent implantation experiments of ^{57}Fe using in-beam Mössbauer spectroscopy (IBMS) have revealed that under certain conditions a sizable fraction of Fe may end up in interstitial sites, and that lack of solubility is an important parameter which governs this behavior [9–11].

In the present Letter we apply IBMS on ^{57}Fe to the alkali metals Li, Na, and K. We obtain information on the local electronic structure and can draw conclusions on the lattice position and the nearest neighborhood of the Fe probe. Our experiments can be compared directly to the PAD experiments since Fe is the probe atom in both methods.

IBMS is a combination of Mössbauer spectroscopy with Coulomb excitation and implantation to study single, isolated Fe atoms in high dilution (10^{15} cm^{-3}) [9–11]. ^{57}Fe nuclei are Coulomb excited to the 14.4 keV Mössbauer level by a pulsed ^{40}Ar beam of 100 MeV hitting a ^{57}Fe target foil. The ^{57}Fe nuclei are ejected from the target and implanted into the specimens whose temperatures can be varied between 10 and 500 K. The unscattered primary Ar beam does not hit the sample. The 14.4 keV γ quanta of the decaying ^{57}Fe are detected between the beam pulses (separation 200 ns) by parallel-plate avalanche counters. The specimens, metallic foils of 5 to 20 mg/cm^2, were prepared in an argon glove box and transferred to the experiment using a vacuum sluice to prevent oxidation.

Figure 1 shows Mössbauer spectra obtained for ^{57}Fe implanted into Li, Na, and K. The accessible temperature range for our experiments was limited by the effective Debye-Waller factor. All spectra are composed of two or sometimes three single lines, barely resolved in Li, more so in Na, and clearly separated in K. These multiplets of resonance lines immediately reveal that implantation of ^{57}Fe leads to different lattice positions distinguished by the isomer shift. The main parameters of the lines are given in Table I. At higher measuring temperatures only one line remains; it will be termed single line 1 (SL1). The component at higher electron densities (positive velocities) will be termed SL2, the component at lower electron densities SL3 (in Na and K). SL3 is present only below 50 K. SL2 also shows a rapid intensity loss but is visible within an appreciable part of the total measuring regime. The center position of each line follows the second order Doppler shift within the accuracy of our measurements. Figure 2 shows the spectral intensities of SL1–SL3 as a function of temperature.

In all three metals we interpret SL1 as due to Fe atoms on substitutional lattice sites and SL2 as due to Fe on interstitial sites. The third component, visible only for $T < 50$ K, is interpreted as an implantation induced defect site which does not form at higher temperatures. Such a component was also observed for Fe implants in α-Zr [10]. In the following we focus on the main spectral intensities comprised in SL1 and SL2. The lattice site assignment is based on the evaluation of two parameters: (i) the isomer shift, reflecting considerably higher electron density at SL2 and (ii) the dependence of the resonance intensities on temperature.

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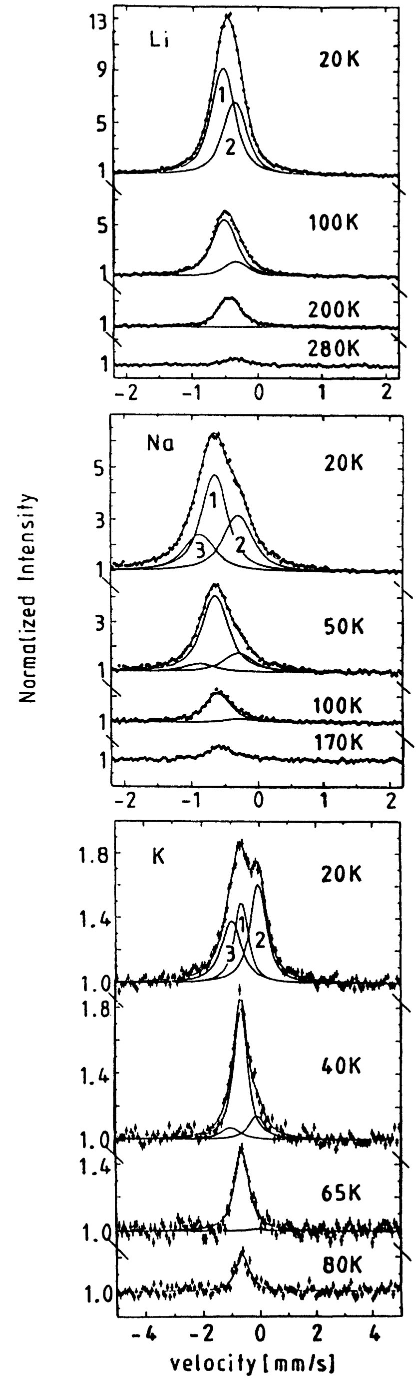

FIG. 1. Mössbauer spectra of ^{57}Fe in Li, Na, and K as a function of temperature. Velocity scale relative to stainless steel absorber.

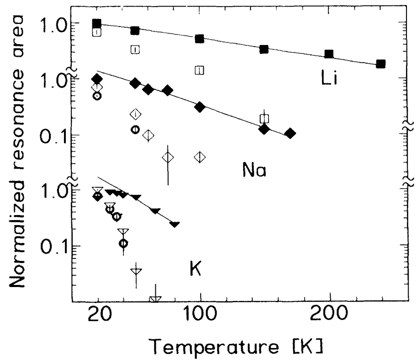

FIG. 2. Normalized resonance area as a function of temperature for SL1 (full symbols), SL2 (open symbols), and SL3 (half-filled circles for Na and K) of ^{57}Fe in Li, Na, and K.

Since the isomer shifts measured for Fe in the alkalis cannot easily be interpreted in an isolated way, we present them in a systematic context of Fe impurity shifts with particular emphasis on host metals in which Fe solubility is strongly restricted. In Fig. 3 the isomer shift δ is plotted as a function of the outer electron number of the host metals as suggested in earlier publications [12]. Outer electrons are those occupying the last *s*, *p*, and *d* shell. Full symbols are from IBMS data; crosses are literature data for Fe in 3*d* and 4*d* metals in which Fe is well soluble and therefore reliable data from conventional Mössbauer experiments exist [12]. The results from the present experiments (Li, Na, K) are included under the assumption of substitutional (SL1) and interstitial (SL2) site assignment [13].

Quite obviously there is an overall systematics: Substitutional iron shows an increase in electron density from s^1 (alkali metals) to a maximum at five outer electrons (V, Nb), followed by a fairly linear decrease with filling of the *d* shell which continues to Al, where *p* electrons begin to contribute (thirteen outer electrons). The linear trend within the *d* elements is well known and has been described before in terms of electronegativity; for a review and most recent interpretation see [12]. Reliable experimental data in the region to the left of V, Nb were scarce heretofore due to the lack of Fe solubility in these metals. Figure 3 now clearly establishes a systematic decrease of the electron density towards the strongly electropositive metals which obviously is contrary to any explanation in terms of electronegativity. *Ab initio* calculations using the Korringa-Kohn-Rostocker Green's function method for Fe in the alkali metals confirm that the electron density is indeed strongly reduced with respect to Fe in iron [14].

It is striking to see that δ for the interstitial position follows the trend shown for the substitutional position only separated by a strongly increased electron density $\Delta\delta$ of 0.4 mm/s to 0.8 mm/s (for the lightest element Li only 0.2 mm/s). This very systematic behavior suggests that the primary effect influencing δ is a volume compression of the outer *s* electrons when Fe is squeezed into the much smaller position of an interstice. For a simple quantitative estimate of this effect we use the volume dependence of δ deduced from high pressure experiments which can be expressed as $\Delta\delta = c\Delta V/V$ [15]. Experimen-

TABLE I. Fit parameters of single lines SL1, SL2, and SL3 of the Mössbauer spectra of ^{57}Fe in Li, Na, and K at 20 K. The isomer shift δ is given relative to an α-Fe source at RT. Γ is the linewidth (FWHM) fitted as a Lorentzian not including a separate Gaussian distribution which accounts for the special shape of the stainless steel absorber. Host Debye temperatures were taken as 400, 150, and 100 K for Li, Na, and K, respectively.

	SL1				SL2			SL3		
	Relative intensity %	Debye temp. Θ_D' (K)	Isomer shift δ (mm/s)	Linewidth Γ (mm/s)	Relative intensity %	Isomer shift δ (mm/s)	Linewidth Γ (mm/s)	Relative intensity %	Isomer shift δ (mm/s)	Linewidth Γ (mm/s)
Li	59(2)	126(8)	0.45(2)	0.31(2)	41(2)	0.27(3)	0.32(2)	...	...	...
Na	45(1)	85(1)	0.57(1)	0.34(1)	32(2)	0.22(1)	0.44(1)	23(1)	0.77(1)	0.46(1)
K	28(1)	63(1)	0.54(2)	0.48(1)	41(1)	−0.05(1)	0.58(1)	31(3)	0.88(1)	0.74(5)

tal data for ^{57}Fe in various metals specify the constant c between 0.5 and 1.8 mm/s [15]. Taking a crude mean value of $c \approx 1.2$ mm/s one obtains from our isomer shift data a volume compression $\Delta V/V$ of the interstitial site between 30% and 70% with respect to the substitutional site.

The second clue to the identification of the interstitial sites comes from the resonance intensities. Common to all three alkali metals is the fast "decay" of intensity SL2 compared to SL1 as a function of temperature. If one uses a Debye model to express the temperature dependence, inspection of Fig. 2 shows that SL1 can be well fitted with an effective Debye temperature Θ_D' given in Table I.

Deviations in the low temperature region for Na and K are due to the above-mentioned third spectral component which possesses part of the total intensity for $T \leq 50$ K. In a simple model Θ_D' is related to Θ_D, the host Debye temperature (see Table I), by $\Theta_D' = \Theta_D\sqrt{m/m'(\gamma'/\gamma)}$, where m,m' are the mass of host atom and iron impurity, respectively, and γ,γ' are force constants describing the coupling of the atoms m,m' to the lattice [16]. The values γ'/γ of about 0.8 (Li, Na) correspond well to other metals with ^{57}Fe as a substitutional impurity [16,17]; $\gamma'/\gamma = 0.6$ for K indicates a somewhat weaker coupling to the lattice. The very fast intensity decay of SL2, on the other hand, cannot reasonably be described within a Debye model. We interpret this behavior along the lines outlined for Fe in Al [9] and Zr [10]: The Fe atom performs large local vibrations or local diffusional jumps which in effect leads to a drastically smaller Debye-Waller factor. In this way the interstitial component is physically present but finally becomes invisible to the Mössbauer effect.

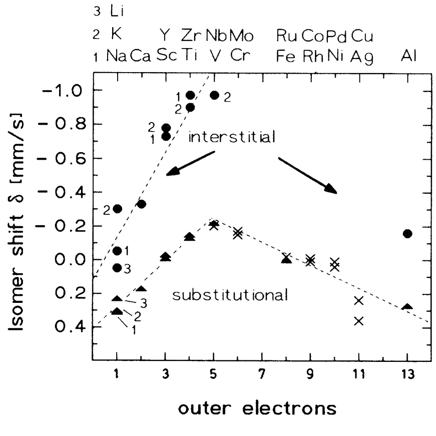

FIG. 3. Isomer shift of ^{57}Fe at RT (relative to an α-Fe source at RT) in various metals as a function of the outer electron number. Negative δ implies higher electron density. Full symbols: IBMS data (▲, substitutional sites; ●, interstitial sites extrapolated to RT); ×: data for substitutional Fe taken from [12]. All values are volume corrected; see Ref. [13]. Dashed lines are to guide the eye.

The disappearance of the third spectral component in Na and K for $T > 50$ K, however, seems to be of different origin: The loss of SL3 goes along with an increase of the substitutional intensity as can be clearly seen in K and also in Na. A thermally activated annealing process of an implantation induced defect associated with the probe atom, e.g., the annealing of a vacancy, might explain such behavior. A detailed discussion is given in [18].

The linewidths observed (Table I) are in accordance with this interpretation: For Li and Na narrow lines are measured close to our experimental resolution. For K the lines show some broadening which may reflect some distant damage. The interstitial line may additionally contain some unresolved quadrupole splitting due to noncubic symmetry. No line broadening is associated with the fast intensity decrease (SL2) in keeping with models of local dynamical behavior [10], thereby excluding a long range diffusion process between interstitial sites which is always accompanied by line broadening [11].

Table I shows the Mössbauer spectral intensity of the various components corresponding to different lattice sites. Neglecting effects due to different recoil-free fractions these intensities directly reflect the Fe site population. The large interstitial fraction in all three alkali metals confirms our recent findings that solid solubility and site population are closely related [9–11]. From our data base obtained by IBMS [11] including the present results we can formulate the rule that extensive solubility of Fe implies substitutional implantation and restricted solubility always implies a sizable fraction implanted interstitially.

It is of considerable interest to compare our results with the data on local moment formation which were obtained with the PAD technique performed on ^{54}Fe. Since the implantation technique and the characteristic lifetime of the probe ($T_{1/2}=360$ ns) matches the conditions of IBMS almost perfectly, results should be directly comparable. A single substitutional lattice site for the Fe atoms as deduced from PAD [3-5] is certainly not in agreement with our results. To resolve this discrepancy one could speculate that a two-component fit with different Larmor frequencies might better describe some of the spectra on display in [3], implying that a second lattice site with different magnetic properties might have escaped detection. Indeed, in a recently reported PAD experiment for Fe in Ce [19], a two-site analysis was performed showing one fraction carrying a local moment and a second one being nonmagnetic. The magnetic fraction was interpreted as substitutional iron whereas the nonmagnetic part was assigned to an interstitial position [19]. From this example and subsequent results for Fe in several other hosts [20], it became obvious that the interstitial position forms a new class of local moments. This finding stimulated theoretical work and first calculations using the jellium model [21] indicated that local magnetism for *d* impurities in the alkali metals might exist not only on substitutional but also on interstitial sites. Another theoretical approach employing a real-space linear muffin-tin orbital approximation can predict the magnetic and electronic structure of Fe in Zr [22]: In this case substitutional Fe forms a local moment whereas Fe is nonmagnetic on interstitial sites which agrees with experiment [20]. Also, a strongly enhanced *s*-electron density on interstitial sites is calculated [22], which again agrees with experiment [10] and with the systematics formulated in the present Letter. It is thus obvious that the magnetic and electronic structure of a *d* impurity depends on its lattice site and therefore a lattice site sensitive analysis of the experiment is a prerequisite for a meaningful comparison with theory. Besides Fe in the alkalis this is also important for Fe in Ca [23] which according to our recent IBMS results [18] has the majority of iron on interstitial sites, making a reanalysis of the data necessary.

In conclusion, in-beam Mössbauer spectroscopy has revealed that Fe atoms upon implantation in alkali metals occupy substitutional as well as interstitial sites. The interstitial fraction is characterized by a strongly increased *s*-electron density. Using all data from our recent IBMS experiments, a systematics is presented for the isomer shift of Fe on interstitial sites, showing that the increased *s*-electron density is a general feature which can be explained by the resulting lattice pressure. We conclude that recently reported PAD results on local magnetic moments contain contributions or are even dominated by interstitial Fe with important consequences for the theory of local moment formation.

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