Dynamics of an Indium Impurity in the Relaxed Divacancy in Iridium

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Perturbed γ-γ angular correlation experiments reveal an unexpected dynamical behavior of ^{111}In atoms in a trivacancy complex in iridium. The measured quadrupole interaction is static at 12 K but becomes strongly time dependent around 100 K resulting in a typical damping of the interaction pattern. At 293 K again a static interaction of different magnitude is observed. This behavior can be described by a jump motion of the indium atom between a stable position in the center of the ⟨111⟩ three-vacancy triangle at low temperatures and the surrounding vacant sites at high temperatures.

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Since the first applications of nuclear methods to the study of defects in metals, the dynamic behavior of defect-probe-atom complexes has been a main point of interest. The reason is that it is directly related to the mechanism of the elementary diffusion jump in the various host matrices. And in contrast to the classical diffusion studies employing tracer atoms, whose macroscopic distribution is determined, e.g., through sectioning techniques, the nuclear methods are able to give direct information about the movement of the probe atom on a microscopic scale and thus improve our understanding of the diffusion process.

Generally, the nuclear methods exploit the hyperfine interaction between the nuclear moments of a probe nucleus and the electromagnetic fields generated by a defect in the vicinity of the probe. In the case of a trapped defect, this causes a static hyperfine interaction, which gives information about the nature of the defect and the geometrical configuration of the probe-defect complex. Distortions of the complex during the time of observation lead to time-dependent hyperfine interactions which can be directly related to the dynamical behavior of the probe atom or its surrounding. In recent review, Petry and Vogl[1] discuss the application and specific advantages of the various nuclear methods for diffusion studies.

The γ-γ perturbed-angular-correlation (PAC) technique has been particularly successful in the investigation of vacancies in metals.[2-4] It observes the perturbation of the directional correlation of two γ rays emitted consecutively in the decay of an unstable parent nucleus. The hyperfine interaction between the quadrupole moment of the nuclear state intermediate to the γ-γ cascade and electric-field gradients caused by disturbances of the cubic charge symmetry surrounding the probe atom causes a characteristic perturbation pattern. It can be described by a perturbation function of the form

$$G_{22}(t)=\sum_{n=0}^{n_{\max}} s_{2n}(\eta)\cos[c_n(\eta)\nu_Q t]\,.$$

Here $\nu_Q=eQV_{zz}/h$ is the quadrupole interaction (QI) frequency with Q the quadrupole moment of the intermediate nuclear state and V_{zz} the largest component of the electric-field-gradient (EFG) tensor.[5] $\eta=(V_{xx}-V_{yy})/V_{zz}$ varies between 0 and 1 and describes the asymmetry of the EFG. The Fourier coefficients s_{2n} and the frequency factors c_n are well known functions of η.[5] $n_{\max}$ is determined by the spins and multipolarities of the levels and transitions involved. The influence of EFG's changing their strength or direction, e.g., caused by diffusive motions of the probe atom during the lifetime of the intermediate state, on $G_{22}(t)$ has been treated theoretically by Blume.[6] However, generally dynamical effects require a prohibitive computational effort to calculate the expected perturbation function. This problem has recently been solved by Baudry and Boyer,[7] who showed that for large domains of jump frequencies w the perturbation can be described by a single exponential damping term $e^{-\lambda t}$ multiplied to the static perturbation function given above.

As a result of theoretical calculations, Hashimoto *et al.*[8] predicted the existence of local-vibration modes in impurity vacancy complexes with strongly enhanced displacements towards the vacancy. This prompted several studies of the temperature dependence of vacancy-induced QI frequencies. However, in all investigations involving trapped monovacancies the observed effects were negligible within the margins of error.[9]

In this Letter we report for the first time on a PAC measurement showing directly that this model is inadequate since we observe the transition from a probe atom occupying a fixed position in a vacancy complex to a situation where it jumps rapidly between the various available vacancy sites leading to a "motional narrowing" of the interaction frequency.

The first substantial variation of a vacancy-induced QI frequency with the lattice temperature was found by Collins and Schuhmann[10] for a defect configuration characterized by $\nu_Q=212(1)$ MHz and $\eta=0$. Similar variations of vacancy-agglomeration-induced EFG's were observed in Cu and several hexagonal metals.[11,12] Since for such configurations Hashimoto *et al.*[8] had obtained in theoretical calculations very large impurity dis-

placements, the variations of the EFG's were assumed to be due to changing vibration amplitudes of the probe atoms, which thus sample lattice regions with different EFG's. Because of the vibration frequencies of the local modes[8] ($>10^{12}$ s^{-1}) which are high compared to the time window fixed by the lifetime of the intermediate nuclear state ($t_{1/2}\sim 10^{-7}$ s) this would lead to the observation of a unique QI because of an averaged EFG.

Recently, Hoffmann, Willmeroth, and Vianden[13] observed the trapping of a defect configuration at ^{111}In in Ir, characterized by a strongly temperature-dependent QI with $\nu_Q^D = 228$ MHz at 293 K. As a microscopic model which best described the known properties of this complex, it was suggested that it is formed by the trapping of two vacancies at the indium probe, which subsequently relaxes from its substitutional position to the center of an equilateral triangle consisting of three nearest-neighbor vacancies in the ⟨111⟩ plane of the fcc Ir lattice. Since this complex is stable up to 700 K, it seems especially well suited for a detailed study of the temperature behavior of such a configuration over a large temperature range.

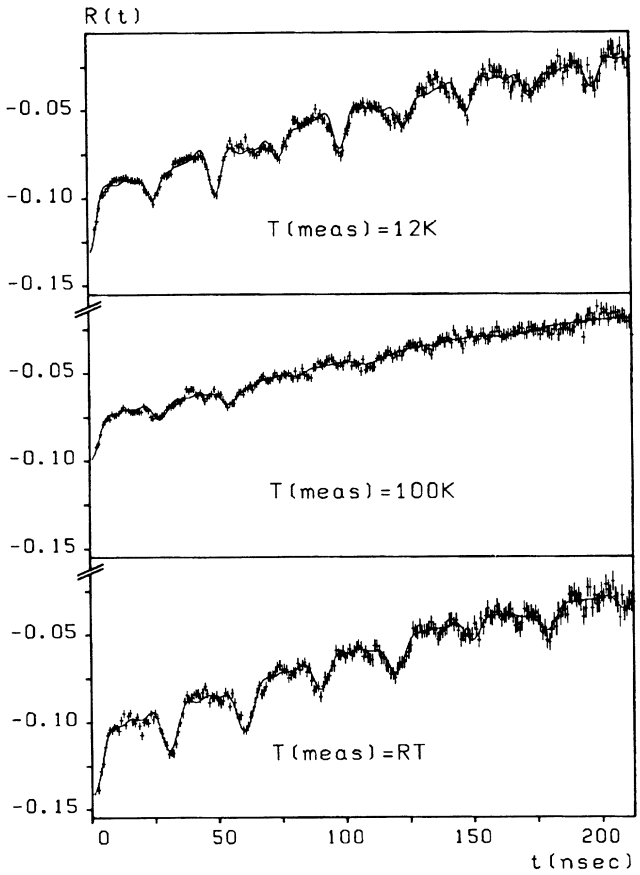

FIG. 1. Time-differential PAC spectra taken for ^{111}In in Ir after annealing at 573 K at the sample temperatures indicated. The solid line show the results of least-squares fits to the data.

For the present study, the PAC probe ^{111}In was implanted with 160 keV in well annealed iridium foils of 99.9% purity. Subsequently the foils were deformed by rolling at room temperature and annealed in a vacuum of $p < 10^{-7}$ kPa for 10 min at 573 K. By repeating this procedure the fraction of probe atoms in the desired configuration could be increased to $f\sim 15\%$. A fraction of 5% remained with an associated monovacancy contributing a QI frequency of $\nu_Q^M = 118$ MHz to the PAC spectrum. Measurements were carried out at various temperatures between 12 and 700 K.

The most remarkable feature of the PAC spectra (Fig. 1) is the nearly complete disappearance of the interaction pattern around 100 K and its reappearance at 12-K sample temperature. Apart from this also ν_Q^D changes strongly [Fig. 2(a)]. These variations were found to be completely reversible. ν_Q^M shows no measurable temperature dependence or damping[13] and accounts mainly for the remaining modulation on the spectrum taken at 100

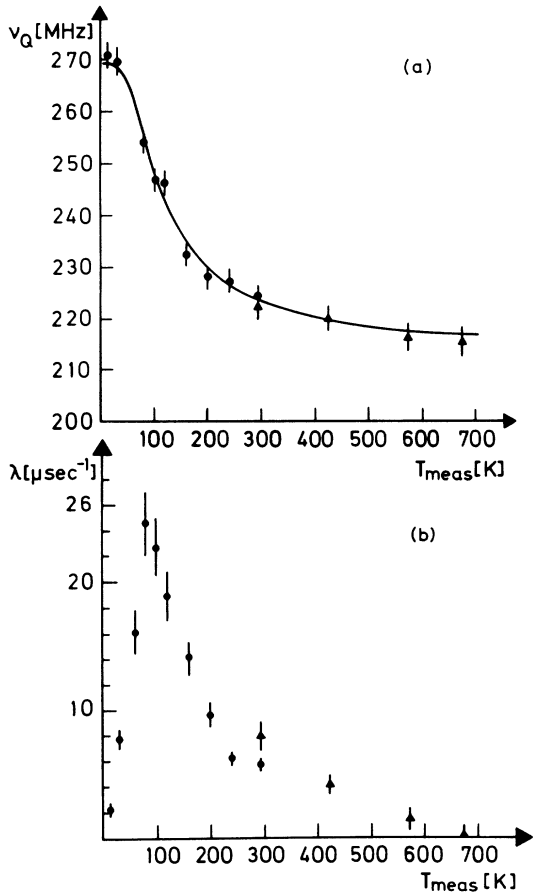

FIG. 2. Variation of (a) the quadrupole interaction frequency ν_Q and (b) the damping parameter λ for ^{111}In in Ir associated with a relaxed divacancy with sample temperature. The solid line in (a) shows the result of a least-squares fit to the data as explained in the text. The different symbols refer to results obtained in samples with different implanted ^{111}In doses.

K (Fig. 1).

In the local-vibration-mode model described above, such a behavior is completely unexpected and unexplainable. Because of the high vibration frequency of the probe atom, the quadrupole moment always interacts with an averaged EFG, leading to a unique and undamped QI pattern. Further, since vacancies are immobile in Ir at and below 293 K and no other defects are present, the fraction of In atoms with associated defects cannot change with temperature.

A natural explanation of the observed behavior can be given if one leaves the picture of a local vibration about an equilibrium position and assumes instead, that the probe atom jumps with a temperature-dependent jump frequency between different lattice sites. At sufficiently low temperatures, the QI is static with the In probe situated in the center of the vacancy triangle. This explains the unique interaction frequency, the asymmetry parameter $\eta=0$, and the $\langle 111\rangle$ orientation of the largest EFG component.[14] When the temperature is raised the probe starts to jump from the center to the surrounding vacant lattice positions. There it experiences a different EFG which should be axially asymmetric.[2] With a further increase in temperature, a situation of maximum damping is reached around 100 K and the pattern practically vanishes. At even higher temperatures the jump rate becomes so high that the probe nucleus feels an EFG averaged between the central position and the three possible vacancy sites, which leads again to an undamped QI frequency and axial symmetry, i.e., $\eta=0$.

An attempt to describe the situation theoretically over the whole temperature range would require the knowledge of the EFG tensor in the different sites, the average residence time, and the jump paths between the sites. Then a diagonalization of the full time-development operator is necessary. In view of the uncertain assumptions entering in this complicated calculation, a simplified description of the spectra was adopted. Following Baudry and Boyer[7] the influence of the increasing jump rate w is approximately described by an exponential damping $e^{-\lambda t}$ of the static perturbation function for $w<\nu_Q^D$ or $w>20\nu_Q^D$. As mentioned above, the EFG in the low- and high-temperature limit is axially symmetric, whereas in the intermediate region an axial asymmetry should occur. However, because of the strong relaxation of the perturbation pattern in this temperature range the determination of a possible asymmetry parameter η is unfeasible. Therefore, a perturbation function for an axially symmetric EFG is employed and the change in the averaged EFG is taken into account by allowing the QI frequency ν_Q^D to vary with temperature. Such a function led to good least-square fits of the data (solid lines in Fig. 1) even in the intermediate region $\nu_Q^D<w<20\nu_Q^D$. In Fig. 2(b) the variation obtained for λ is plotted versus temperature. The larger value of λ observed at 293 K in the sample used for the measurements above room temperature is due to a slightly higher dose of implanted ^{111}In, i.e., the damage level, which is not removed by the 523-K annealing. As one would expect, the values of ν_Q are not influenced by the implantation conditions [Fig. 2(a)].

The following conclusion can be drawn from the present data: The weak damping at low and high sample temperatures and the maximum of λ observed around 100 K proves that the In probe performs a jumping motion between sites of different EFG's. From the temperature where the maximum of λ occurs, the jump rate can be estimated to be of the order of $w=8\times10^8\ \mathrm{s}^{-1}$.[7] These results indicate that although a local-vibration mode may exist, the vibration amplitude u of the probe atom in this vacancy complex does not change significantly with temperature. Estimates in the point-charge model[2] show that variations in u of the order of 5% would cause measurable changes in the EFG. This apparent absence of large vibration amplitudes also explains the fact that in the case of monovacancy complexes no temperature dependence of the corresponding QI was observed. Similarly in the bcc metal W, where upon trapping of two vacancies no relaxation takes place, the EFG is independent of temperature.[15] However, Masuda[16] predicts also for this configuration the existence of a local mode, which should lead to considerable changes in the EFG. Therefore, a new theoretical *Ansatz* seems to be necessary to describe the dynamical behavior of atoms adjacent to vacancy complexes.

The variation of ν_Q^D itself with the sample temperature can be described in the same jump model. Around 12 K the probe atom experiences a static EFG V_{zz}^c caused by the surrounding three vacancies. In the high-temperature limit the probe samples rapidly the EFG on the central site and on each of the three vacancies, i.e., substitutional sites. If we assume that the residence time on each site is the same, the average EFG in the substitutional site with two associated vacancies can be derived from the following formula:

$$V_{zz}(T)=[V_{zz}^c+3V_{zz}^{3V}P(T)]/[1+3P(T)],$$

with the Boltzman distribution factor $P(T)=e^{-\Delta E/kT}$ describing the occupation probability of the central and the three substitutional states. A least-squares fit of this function to the data is shown in Fig. 2(a). It yields the following values: $V_{zz}^c=13.4(1)\times10^{17}$ V/cm^2, $V_{zz}^{3V}=9.6(1)\times10^{17}$ V/cm^2, and $\Delta E=17.9(3)$ meV. The ratio of the EFG's in the high- and low-temperature limit $V_{zz}^{3V}/V_{zz}^c=0.72(1)$ could now be compared with a calculation in the above-mentioned point-charge model. Under the assumptions that the conduction-electron contribution is the same in both situations and equal population of the four sites accessible at high temperature, one obtains $V_{zz}^{3V(\mathrm{th})}/V_{zz}^{c(\mathrm{th})}=0.42$. This discrepancy could be the result of a lattice relaxation, i.e., the off-center potential minimum is not at the substitutional site but

closer to the central site. Agreement of the above ratio with the experimental value can be obtained if one assumes that the probe jumps between the corners of a smaller equilateral triangle, with the "substitutional" positions displaced ~ 0.6 Å towards the central site.

The assumption that the movement of the In probe is thermally activated can be further checked by an analysis of the high-temperature data ($T > 250$ K). In this temperature range the jump rate w is inversely proportional to λ,[7] and $\ln\lambda$ should exhibit a linear behavior in a $1/T$ plot. Indeed, the values of $\ln\lambda$ for 293 K and above are in rough agreement with an Arrhenius behavior and an activation energy of $\sim 75(25)$ meV can be estimated.

Currently, studies in other metals like Pt and Al, where similar defect-probe-atom configurations exist, are in progress. They could supply a broader data base for these calculations and reveal more details about the dynamical behavior of impurities in vacancy complexes.

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[1]W. Petry and G. Vogel, Mater. Sci. Forum **15–18**, 323 (1987).

[2]E. Recknagel, G. Schatz, and Th. Wichert, in *Hyperfine Interactions of Radioactive Nuclei,* edited by J. Christiansen, Topics in Current Physics Vol. 31 (Springer-Verlag, Berlin, 1983), p. 133.

[3]R. Sielemann, Mater. Sci. Forum **15–18**, 25 (1987).

[4]R. Vianden, in *Proceedings of the NATO Advanced Science Institute on Nuclear Physics Applications on Materials Science, Viana do Castelo, Portugal, 1987,* NATO ASI Series E (Kluwer, Dordrecht, 1988), p. 239.

[5]R. M. Steffen and K. Alder, in *Electromagnetic Interaction in Nuclear Spectroscopy,* edited by W. D. Hamilton (North-Holland, Amsterdam, 1975).

[6]M. Blume, Phys. Rev. **174**, 351 (1968).

[7]A. Baudry and P. Boyer, Hyperfine Interact. **35**, 803 (1987).

[8]M. Hashimoto, Y. Ishida, R. Yamamoto, and M. Doyama, J. Phys. F **11**, L119 (1981).

[9]M. Deicher and Th. Wichert, University of Konstanz Annual Report, 1980 (unpublished), p. 8.

[10]G. Collins and R. B. Schuhmann, Hyperfine Interact. **15/16**, 395 (1983).

[11]W. Witthuhn, H. Föttinger, D. Forkel, M. Iwatschenko-Borho, F. Meyer, and H. Wolf, Phys. Lett. A **119**, 304 (1986).

[12]H. Koch, U. Feuser, and R. Vianden, Verhandl. Dtsch. Phys. Ges. (VI) 22, M1.8 (1987).

[13]A. Hoffmann, A. Willmeroth, and R. Vianden, Z. Phys. B **62**, 335 (1986).

[14]A. Hoffmann, dissertation, University of Bonn, 1985 (unpublished), and unpublished results.

[15]H. Koch, U. Feuser, and R. Vianden, Verhandl. Dtsch. Phys. Ges. (VI) 21, M98 (1986).

[16]K. Masuda, in *Point Defects and Defect Interactions in Metals,* edited by J. I. Takamara, M. Doyama, and M. Kiritani (Univ. of Tokyo Press, Tokyo, 1982), p. 130.