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VACANCIES IN THERMAL EQUILIBRIUM IN Nb

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We have measured the diffusion of positrons in Nb(110) in the temperature range from 300K to 2450K utilizing a variable energy positron beam. The purpose was to study the vacancy formation. However, no significant sign of vacancy trapping was observed. This could be due to a high detrapping rate caused by a low positron binding energy or due to a high vacancy formation enthalpy H_{fv} . The last possibility is consistent with recent studies of the vacancy migration and with calculation of the positron binding energy. In this case we find the $H_{fv} > 3$ eV.

The positron annihilation technique has been a very successful tool in determining the basic kinetic properties of monovacancies in metals.¹⁻² The vacancy migration enthalpy H_{mv} can be extracted from non-equilibrium experiments³⁻⁴ and the vacancy formation enthalpy H_{fv} from thermal equilibrium experiments.⁵ These measurements are based on the difference in positron annihilation characteristics between positrons trapped in defects and free positrons.

The development of variable energy positron beams has given an alternative possibility. The measurements presented here are based on detecting the reduction in positron diffusion length caused by trapping. This method has many advantages and is in several respects complementary to the conventional positron annihilation techniques. The method has been successfully applied to Al.⁶⁻⁷ It should be noted that the beam still enables conventional-type measurements with the advantage of avoiding the "source" and other problems.

We present here the first high temperature measurements on a refractory metal Nb using this method. Measurements of the lineshape parameter as a function of temperature in Nb has shown a weak shape change, interpreted as the onset of vacancy formation. The absence of a stronger change was attributed to detrapping.

In extracting the diffusion lengths positrons are first implanted at an average depth \bar{z} related to the incident positron energy E through a power law,

$$\bar{z} = AE^{-2} \quad (1)$$

where A is a material constant and n has experimentally and theoretically been found to be ≈ 1.6 .⁸⁻⁹ The fraction of positrons F that after implantation diffuses back to the surface is measured. F depends on the positron implantation profile $P(z)$ and the positron diffusion length L_+

$$F = \int_0^{\infty} dz(P(z) \cdot \exp(-\frac{z}{L_+})). \quad (2)$$

The diffusion length is given by the diffusion constant D_+ and effective lifetime τ_{eff} of the positron

$$L_+ = \sqrt{D_+ \tau_{eff}}. \quad (3)$$

In the case of an exponential profile the solution is very simple:

$$F = 1/(1+(E/E_0)^2) \quad (4)$$

where E_0 is the energy at which half of the positrons return to the surface.

Recent experimental and theoretical work⁹⁻¹⁰ has shown that a Makhov-type profile gives a better description and results in an approximately 40% higher value of the derived value of D_+ . It has been shown, however, that relative changes are the same using either profile. Due to the much simpler fitting using Eq. (4) and to the fact that one of the shape parameters in the Makhov profile is still under debate, we have chosen to fit all data to Eq. 4.

Measurements of the fraction F is based on the fact that positrons inside a metal predominantly decay by $2-\gamma$ emission whereas positrons that reach the surface have a

chance of escaping and forming positronium in vacuum, where ~75% will decay by β - γ emission. It is therefore a simple matter of calibration to derive F if the ratio between 2γ and $\beta\gamma$ events are measured. This ratio can be extracted from the annihilation gamma spectrum, which is measured with an intrinsic Ge detector.

In the perfect lattice τ_{eff} is the positron bulk lifetime τ_b ($=1/\lambda_b$). Vacancies will reduce τ_{eff} due to trapping:

$$\tau_{eff}^{-1} = \lambda_b + \frac{\lambda_v + \kappa_{bv}}{\lambda_v + \kappa_{vb}} \quad (5)$$

where λ_v is the annihilation rate in vacancies, κ_{bv} is the trapping rate into vacancies:

$$\kappa_{bv} = \sigma_{IV} \exp(S_{IV}^F/k_B) \exp(-E_{IV}^F/k_B T) \quad (6)$$

and κ_{vb} is the detrapping rate from vacancies:

$$\kappa_{vb} = \nu_0 \exp(-E_{pv}/k_B T) \quad (7)$$

where σ_{IV} is the specific vacancy trapping rate, S_{IV}^F is the formation entropy, ν_0 is a frequency factor and E_{pv} is the positron binding energy to the vacancy.

In determining κ_{bv} we use the value⁵ $\sigma_{IV} \cdot \tau_b \cdot \exp(S_{IV}^F/k) = 10^6$.

A Nb(110) single crystal was studied. The crystal was heated with an electron beam inside a high temperature furnace mounted inside the UHV chamber. The pressure, which was in the 10^{-10} range at room temperature, would initially rise above 10^{-7} during heatings above 2300K. During this period strong hysteresis was found. Hysteresis was observed until it was possible to keep the sample for hours at temperatures above 2300K at a pressure not exceeding 10^{-8} torr, after which the data presented here were recorded. The purpose of the furnace is to minimize the energy required to achieve the high temperatures and to give a uniform sample temperature. The furnace has a hole for the positron beam and an aperture for temperature readings with a pyrometer. The temperature was also recorded with a W3% Re, W25% Re thermocouple.

In Fig. 1 the values of the parameter E_0 are shown as a function of temperature. We have chosen to display E_0 rather than the more direct physically related diffusion length L_+ since E_0 is actually

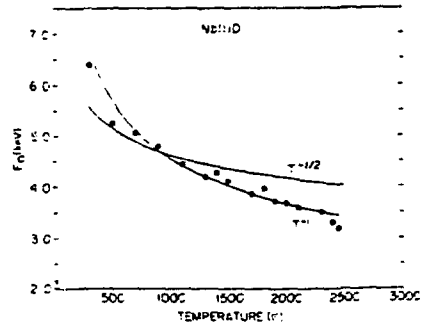


Fig. 1. Experimentally determined values of the diffusion related parameter E_0 for various temperatures. The two curves show E_0 as a function of temperature when we assume $D_+ = T^{-1}$ respectively, $D_+ = T^{-1/2}$.

the parameter directly determined in the measurement and it is related to L_+ through the simple relation $L_+ = AE_0^{-2}$. As seen in the figure there is very little if any sign of vacancy trapping observed. The figure also demonstrates the strong temperature dependence of the diffusion coefficient, which is well represented by T^{-1} . This is indeed surprising since it has been a generally accepted model that the diffusion is mainly limited by acoustical phonons leading to a $T^{-1/2}$ dependence.¹¹ The temperature-dependence of D_+ turns out to be much stronger than $T^{-1/2}$ for all metals studied as first reported by Schultz et al.¹² It has been suggested¹³ that at high temperatures there is a transition to a regime with much lower diffusivity where the positron moves via a self-trapped state. The positron diffusion coefficient will in this regime increase with temperature. Neither this, the transition, nor the corresponding low diffusivity is observed here.

As mentioned, in a previous study of Nb the lineshape parameter as a function of temperature showed a weak slope change at 1760K⁵ interpreted as the onset of vacancy formation incorporating detrapping. The data fit yielded a vacancy formation energy of 2 eV. In Fig. 2 we show curves for which we assume (a) no trapping, (b) $E_{IV}^F = 2.6$ eV and detrapping energy $E_{pv} = 1.6$ eV (frequency factor $10^{14} s^{-1}$), (c) $E_{IV}^F = 2.6$ eV and no detrapping. As seen, none of the curves compare well to the data. In order to describe the data we have to assume a positron binding energy less than 1.4 eV. This is in strong contradiction to calculated binding energies of 4.6 eV¹⁴ and 3.2 eV¹⁵ respectively.

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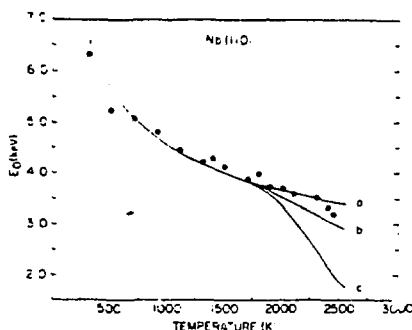


Fig. 2. The curves show E_0 versus temperature assuming $D_v \propto T^{-1}$ and a: no trapping, c: $H_{IV}^F = 2.6$ eV and b: $H_{IV}^F = 2.6$ eV with detrapping ($E_{pv} = 1.6$ eV).

A very likely explanation for the unobserved trapping is that the vacancy formation energy is higher. This is in agreement with recent positron annihilation studies¹⁵ and quenching experiments¹⁶ showing that the migration energy is very low, .6 eV. Using the self-diffusion energy reported 3.9 eV¹⁷ and 3.6 eV¹⁸ which will then give a value of H_{IV}^F of 3-3.3eV. It should also be mentioned that a strongly reduced vacancy trapping rate could explain the results.¹⁹

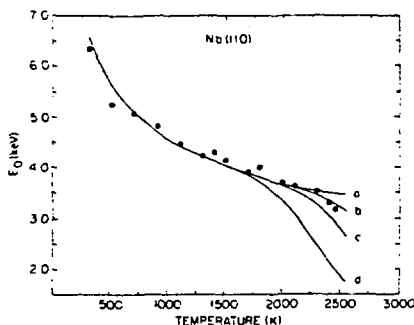


Fig. 3. The curves show E_0 versus temperature assuming $D_v \propto T^{-1}$ and a: no trapping, b: $H_{IV}^F = 3.3$ eV, c: $H_{IV}^F = 3.0$ eV and d: $H_{IV}^F = 2.6$ eV.

In Fig. 3 we show curves for E_0 versus temperature assuming no detrapping and formation energies 3.3, 3.0, and 2.6 eV

for curves b, c, and d, respectively. We can certainly conclude that in this case we have a formation energy larger than 3 eV in agreement with vacancy migration results.

In conclusion our measurements in Nb at temperatures up to 2450K shows no significant sign of trapping. Interpretation in terms of detrapping requires a very low positron binding energy in contradiction to theoretical estimated values. Assuming no detrapping results in a vacancy formation energy higher than 3 eV.

1. Hautojärvi, P., ed., Positrons in Solids, Topics in Current Physics 12, Berlin, Heidelberg, New York, Springer-Verlag, 1979.
2. Siegel, R.W., Proc. 6th Int. Conf. Positron Annihilation, ed. by P.G. Coleman, S.C. Sharma, L.M. Diana (North-Holland, Amsterdam) 1982.
3. Petersen, K., Positron Solid State Physics, ed. by W. Brandt and A. Dupasquier (North Holland, Amsterdam, New York-Oxford) 1983.
4. Vehanen, A., Hautojärvi, P., Johansson, J., Yli-kuusipila, J., and Moser, P., Phys. Rev. B 25, 762 (1982).
5. Maier, K., Peo, M., Saile, B., Schaefer, H.E., and Seger, A., Phil. Mag. A40, 701 (1979).
6. Lynn, K.G. and Schultz, P.J., Appl. Phys. A 37, 2995 (1985).
7. Lynn, K.G. in Ref. 3.
8. Mills, Jr., A.P., and Wilson, R.J., Phys. Rev. A 26, 490 (1982).
9. Valkealahti, S. and Nieminen, R., Appl. Phys. A 32, 95 (1983).
10. Nielsen, B., Lynn, K.G., Vehanen, A., and Schultz, P.J., Phys. Rev. B (accepted for publication Aug. 1985).
11. Bergersen, B., Pajanne, E., Kubica, P., Scott, M.J., and Hodges, C.B., Sol. St. Comm. 15, 1377 (1974).
12. Schultz, P.J., Lynn, K.G., and Nielsen, B. Phys. Rev. B 31 (1985).
13. Seeger, A., Appl. Phys. 7, 257 (1975).
14. Gupta, R.P. and Siegel, R.W., J. Phys. F 10, L7 (1980).
15. Hautojärvi, P., Huomo, H., Puska, M., and Vehanen, A., to be published.
16. Schwirlich, I.A. and Schultz, B., Phil. Mag. A 42, 440 (1978).
17. Einzinger, R.E., Mundy, T.N., and Holtz, H.A., Phys. Rev. B 17, 440 (1978).
18. Ablitzer, D., Phil. Mag. 35, 1237 (1977).
19. L. C. Smedskjaer, G. D. Loper, H. K. Chason, S. B. Gerber, and R. W. Siegel, this Conference.