THEORY OF THE TEMPERATURE DEPENDENCE OF POSITRON
BULK LIFETIMES-IMPLICATIONS FOR VACANCY FORMATION
ENTHALPY MEASUREMENTS VIA POSITRON EXPERIMENTS

S. W. Tam, S. K. Sinha, and R. W. Siegel

CONF-761027-26

RECEIVED

Prepared for

International Conference on the
Properties of Atomic Defects in Metals
Argonne National Laboratory
Argonne, IL
October 18-22, 1976

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

U of C-AUA-USERDA

28
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

operated under contract W-31-109-Eng-38 for the
U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Energy Research and Development Administration, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	Kansas State University	The Ohio State University
Carnegie-Mellon University	The University of Kansas	Ohio University
Case Western Reserve University	Loyola University	The Pennsylvania State University
The University of Chicago	Marquette University	Purdue University
University of Cincinnati	Michigan State University	Saint Louis University
Illinois Institute of Technology	The University of Michigan	Southern Illinois University
University of Illinois	University of Minnesota	The University of Texas at Austin
Indiana University	University of Missouri	Washington University
Iowa State University	Northwestern University	Wayne State University
The University of Iowa	University of Notre Dame	The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Energy Research and Development Administration.

THEORY OF THE TEMPERATURE DEPENDENCE OF POSITRON
BULK LIFETIMES-IMPLICATIONS FOR VACANCY FORMATION
ENTHALPY MEASUREMENTS VIA POSITRON EXPERIMENTS*

S. W. Tam,[†] S. K. Sinha,⁺⁺ and R. W. Siegel
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

By acceptance of this article, the
publisher or recipient acknowledges
the U.S. Government's right to
retain a nonexclusive, royalty-free
license in and to any copyright
covering the article.

FEBRUARY 1977

Presented at the *International Conference on the Properties of Atomic
Defects in Metals*, held at Argonne National Laboratory, Argonne, Illinois,
October 18-22, 1976.

- * Work supported by the U. S. Energy Research and Development Administration.
- † Present Address: EES Division, Argonne National Laboratory, Argonne, IL 60439
- ++ SSS Division, Argonne National Laboratory, Argonne, IL 60439

THEORY OF THE TEMPERATURE-DEPENDENCE OF POSITRON
BULK LIFETIMES-IMPLICATIONS FOR VACANCY FORMATION
ENTHALPY MEASUREMENTS VIA POSITRON EXPERIMENTS*

S. W. Tam,[†] S. K. Sinha,^{††} and R. W. Siegel

Materials Science Division
Argonne National Laboratory
Argonne, Illinois 60439

Positron annihilation experiments are being widely used for the determination of vacancy formation enthalpies in metals. Recently, however, interesting temperature dependent effects, which may have a bearing on such determinations, have been observed in positron annihilation in certain metals [1-4]. These effects have been observed to occur both at temperatures below those at which positron annihilation is most sensitive to equilibrium vacancies (e.g., in Cd [1,2]) and at temperatures well within the vacancy-sensitive region (e.g., in Al [3] and Pb [4]). In an attempt to understand these phenomena we have investigated the effect of thermal lattice displacements on positron lifetimes in metals.

A thermalized positron in a metal interacts with the electrons via a Coulomb interaction. However, both the electrons and the positron are also coupled to the phonons in the metal. Due to the opposite signs of the electron-ion and positron-ion interactions, a phonon-induced relative separation of the positron and electron charge clouds may arise leading to an increase of the positron bulk-lifetime, τ_b , in a metal. In order to investigate how this phonon-induced change in τ_b behaves as a function of temperature, one must consider the contributions to this change from both valence and core electrons.

* Work supported by the U.S. Energy Research and Development Administration.

† Present Address: EES Division, Argonne National Laboratory, Argonne, Ill. 60439

†† SSS Division, Argonne National Laboratory, Argonne, Ill. 60439

The positron bulk-annihilation rate, $\lambda_b = \tau_b^{-1}$, may be written as [5]

$$\lambda_b = \tau_b^{-1} = \sum_{\vec{k}} S^+_{\vec{k}} S^-_{\vec{k}} \equiv \frac{\pi r_0^2 c}{(2\pi)^3} \sum_{\vec{k}} \langle n^+(\vec{k}) n^-(-\vec{k}) \rangle, \quad (1)$$

where r_0 is the classical electron radius, c is the velocity of light and $n^+(\vec{k})$ and $n^-(\vec{k})$ represent the $\vec{k}^{\text{th}}$ Fourier-expansion density-fluctuation operators for the positron and electrons, respectively. The term $n^-(\vec{k})$ can be broken up into valence and core contributions, $n^-_v(\vec{k})$ and $n^-_c(\vec{k})$. The expectation value in Eq. (1) must be evaluated over the states of the interacting system of electrons, positron and phonons. The Hamiltonian for this system may be written as

$$H = H_{el} + H_{el-el} + H_{pos} + H_{el-pos} + H_{el-lat} + H_{pos-lat} + H_{lat}, \quad (2)$$

where the various terms represent the one-electron term, the electron-electron interaction, the positron term, the electron-positron interaction, the electron-phonon interaction, the positron-phonon interaction and the phonon term, respectively.

In considering the contribution to λ_b from the valence electrons, $S^+_{\vec{k}} S^-_{\vec{k}}$, a canonical transformation given by

$$\tilde{c}_{\vec{k}} = [\exp(A)] c_{\vec{k}} \quad ; \quad \tilde{c}_{\vec{k}}^\dagger = [\exp(-A)] c_{\vec{k}}^\dagger \quad (3)$$

was made, where $c_{\vec{k}}$ and $c_{\vec{k}}^\dagger$ are the annihilation and creation operators for the electron state $\vec{k}$ (with spin index suppressed). An identical transformation was made for the positron annihilation and creation operators $a_{\vec{k}}$ and $a_{\vec{k}}^\dagger$. The operator A is given by $A^{(1)} + A^{(2)} + \dots$, where $A^{(1)}$ is first-order in the phonon operators, $A^{(2)}$ is second-order, etc. $A^{(1)}$ was chosen to be of the form

$$A^{(1)} = \sum_{\vec{q}j} \sum_{\vec{k}} \left[R_{\vec{k}+\vec{q},\vec{k}}^{-}(\vec{q}j) c_{\vec{k}+\vec{q}}^{\dagger} c_{\vec{k}} \left(b_{\vec{q}j} + b_{-\vec{q}j}^{\dagger} \right) \right. \\ \left. + R_{\vec{k}+\vec{q},\vec{k}}^{+}(\vec{q},j) a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}} \left(b_{\vec{q}j} + b_{\vec{q}j}^{\dagger} \right) \right] \quad (4)$$

where $b_{\vec{q}j}$ and $b_{\vec{q}j}^{\dagger}$ are the phonon annihilation and creation operators for phonon mode $(\vec{q}j)$, respectively, and the $R_{\vec{k}+\vec{q},\vec{k}}^{-}(\vec{q}j)$ and $R_{\vec{k}+\vec{q},\vec{k}}^{+}(\vec{q},j)$ are chosen such that the electron-phonon and positron-phonon interactions are eliminated to first order in the phonon operators in the transformed Hamiltonian. An explicit form for $A^{(2)}$ is not required, as discussed below. We may now express the valence electron contribution to $S^{+-}(\vec{k})$ as an average over uncoupled states of the electron-positron and phonon systems of the transformed operator product $\langle \exp(-A) n^{+}(\vec{k}) n_{\vec{v}}^{-}(-\vec{k}) \exp(A) \rangle$. Expanding this to second-order in the phonon displacements, we obtain

$$S_{\vec{v}}^{+-}(\vec{k}) = \langle 0 | n^{+}(\vec{k}) n_{\vec{v}}^{-}(-\vec{k}) | 0 \rangle + \frac{1}{2} \langle 0 | [A^{(1)}, [A^{(1)}, n^{+}(\vec{k}) n_{\vec{v}}^{-}(-\vec{k})]] | 0 \rangle \\ + \langle 0 | [n^{+}(\vec{k}) n_{\vec{v}}^{-}(-\vec{k}), A^{(2)}] | 0 \rangle \quad (5)$$

Terms which are first-order in the lattice displacements do not contribute to averages over unperturbed phonon states within the harmonic approximation. When anharmonicity is included, such terms will give rise to the effects from thermal expansion on τ_b , which must therefore be taken into account in addition to the effects discussed here.

The first term in Eq. (5) represents the rigid lattice contribution $S_{\vec{v}}^{+-}(\vec{k})$. The other two terms may be evaluated in terms of a sum over phonon modes. The third term, which is intrinsically second-order, was assumed to

be $\vec{q}$ -independent. By conditions of translational invariance it may be shown [6] that this term subtracts off the $\vec{q} = 0$ contribution from the second term. The resulting expression for $S_V^{+-}(\vec{k})$ is too lengthy to be explicitly reproduced here, however by the use of certain averaging procedures over the valence electron states an approximate expression for $S_V^{+-}(\vec{k})$ was obtained in the form

$$S_V^{+-}(\vec{k}) = [1 + f_V(\vec{k})] S_{0V}^{+-}(\vec{k}) \quad , \quad (6)$$

where $f_V(\vec{k})$ measures the change due to the distortion of the valence electron wave-functions and the positron wave-function caused by the lattice motion.

The core electron contribution $S_C^{+-}(\vec{k})$ was evaluated using the assumption that the core electrons move rigidly with the nuclei during lattice motion. The net result can be expressed in the approximate form

$$S_C^{+-}(\vec{k}) = [1 + f_C(\vec{k})] S_{0C}^{+-}(\vec{k}) \quad , \quad (7)$$

where $S_{0C}^{+-}(\vec{k})$ is the core contribution to $S^{+-}(\vec{k})$ in the rigid lattice. The term $f_C(\vec{k})$ is a measure of the change in the overlap among the core electrons and the positron due to the lattice motion. A good indicator of the relative strength of this effect is the amount of core-electron contribution to the positron annihilation process as revealed through angular correlation experiments. It should be expected that the larger the core contribution, the greater the sampling of the ionic potential will be, leading to greater sensitivity to ion core motion. The dominant term in $[1 + f_C(\vec{k})]$ is a Debye-Waller like term, which varies as $\exp(-\gamma K^2)$, where γ is a temperature dependent coefficient. The valence and core contributions may be added to give

$$S^{+-}(\vec{k}) = S_0^{+-}(\vec{k}) + f_V(\vec{k}) S_{0V}^{+-}(\vec{k}) + f_C(\vec{k}) S_{0C}^{+-}(\vec{k}) \quad . \quad (8)$$

Using this formalism the magnitude of the effect of electron-phonon-positron coupling upon $\tau_b(T)$ can be calculated.

Since the distortions of the positron and valence electron wave-functions caused by lattice motion occurs primarily in the interstitial regions where the positron wave-function varies more slowly than in the core regions, one can expect the change in the electron-positron overlap as measured by $f_v(\vec{k})$ to be relatively small. The contribution due to this term in Eq. (8) has been estimated within the Debye model using free electron and positron band structures. For Cd at 500 K the estimated change in τ_b , the positron bulk-lifetime, due to the phonon induced distortion of the valence electrons amounted to < 1 ps, while for Al the change was < 0.5 ps, even at 400 K. These are much smaller than the effects on $\tau_b(T)$ from thermal expansion alone. However, this estimate should be regarded as preliminary in nature, since Umklapp processes were not included. A more detailed calculation of the valence electron contribution is in progress. Therefore, in the following we concentrate on the core electron contribution only.

In order to calculate the core contribution, $S_{0c}^{+-}(\vec{k})$ was parameterized as a Gaussian [$a \exp(-bK^2)$], and the parameters a and b were determined by comparing with positron lifetime and angular correlation data [7,8] from low temperatures at which thermal expansion and phonon-coupling effects are expected to be small. This Gaussian was combined in Eq. (7) with the Debye-Waller like factor $[1 + f_c(\vec{k})] = \exp(-\gamma K^2)$ to give $S_c^{+-}(\vec{k})$. Here,

$$\gamma = (3\hbar^2/Mk_B\Theta_D) \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x}{e^x - 1} dx \right], \text{ where } M \text{ is the mass of the ion}$$

core and the other symbols have their usual meanings [8]. The core contribution to $\tau_b(T)$ was then obtained using Eq. (1), and is given approximately by

$$\tau_b(T)/\tau_b(0) \simeq \left[A_v + A_c(1 + \gamma/b)^{-3/2} \right]^{-1}, \quad (9)$$

where $\tau_b(0) = \tau_b(T = 0 \text{ K})$, and A_v and A_c are the fractions of positron annihilations with valence and core electrons, respectively.

The results for Al and Cd using Eq. (9) are shown in Fig. 1. Also shown for comparison is the approximate variation of τ_b with temperature due only to lattice expansion. This latter has been estimated from $\left[\tau_b(T)/\tau_b(0) \right] = 1 + 3\alpha T$, where α = coefficient of linear expansion at 300 K (taken = $(2\alpha_{||} + \alpha_{\perp})/3$ for Cd). It can be seen that the core contribution to $\tau_b(T)$ from phonon-coupling effects is somewhat smaller than the contribution from thermal expansion in both Al and Cd. For Al it is $\sim 18\%$ and for Cd it is $\sim 43\%$ of the fractional volume expansion at $\sim 300 \text{ K}$. It can also be seen in Fig. 1 that $\tau_b(T)$, from both lattice expansion and phonon-coupling effects, varies essentially linearly with T in Al over most of the temperature range. On the other hand, for Cd the variation of τ_b with T due to phonon-coupling effects is not linear, but is similar in form to the experimentally observed variation of the positron mean lifetime with T [1,2]. When the effects of phonon-coupling and lattice expansion are appropriately combined, they yield a change of τ_b with T in reasonable agreement with experiment [3] for Al below 600 K. However, for Cd the calculated combined effect is, although of a similar functional form, smaller by a factor of ~ 3 than that experimentally observed [1,2]. It would therefore seem that, while the anomalous temperature dependence of the positron annihilation parameters in Cd can be qualitatively explained by phonon-coupling effects, further work (in progress) is necessary to yield quantitative agreement with the available experimental data.

It should be noted that the effect of phonon coupling is larger in Cd than in Al. This is mainly a result of the larger core contribution, A_c , in Cd and to a lesser extent to its lower Θ_D . Therefore, it is expected that the largest contributions to $\tau_b(T)$ from phonon coupling may be found in metals with large core-electron contributions to positron annihilation, such as the transition metals.

In conclusion, from an operational point of view it would appear that the effects treated in the present work can be adequately taken into account empirically in Al by extrapolating $\tau_b(T)$ from low temperature data when extracting values of the vacancy formation enthalpy, E_v^F , from positron annihilation data, as is normally done. However, for Cd and other metals exhibiting similar anomalous behavior of $\tau_b(T)$ further work is required to accurately estimate the magnitude of the effect of the temperature dependence from phonon-coupling effects upon the determination of E_v^F .

REFERENCES

- [1] L. C. Smedskjaer, M. J. Fluss, M. K. Chason, D. G. Legnini, and R. W. Siegel, J. Phys. F: Metal Phys. 7 (1977) --.
- [2] D. Herlach, H. Stoll, W. Trost, H. Metz, T. E. Jackman, K. Maier, H. E. Schaefer, and A. Seeger, Appl. Phys. 12 (1977) 59.
- [3] M. J. Fluss, L. C. Smedskjaer, M. K. Chason, D. G. Legnini, and R. W. Siegel, this Conference.
- [4] S. C. Sharma, S. Berko, and W. K. Warburton, Phys. Lett. 58A (1976) 405.
- [5] P. Bhattacharyya and K. S. Singwi, Phys. Rev. Lett. 29 (1972) 22.
- [6] S. K. Sinha and R. P. Gupta, to be published.

7. D. C. Connors, V. H. C. Crisp, and R. N. West, J. Phys. F: Metal Phys. 1 (1971) 355.
8. S. M. Kim and W. J. L. Buyers, J. Phys. F: Metal Phys. 6 (1976) L67.
9. D. Pines, Elementary Excitations in Solids (W. A. Benjamin, New York, 1964) p. 43.

FIGURE CAPTION

Fig. 1. The percentage change in τ_b with temperature due to phonon-coupling effects is compared with that from lattice expansion in Cd and Al.
Neg. No. MSD-64-127.

Fig. 1. The percentage change in τ_b with temperature due to phonon-coupling effects is compared with that from lattice expansion in Cd and Al.