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Deformation-induced microvoids in bismuth and possible positronium formation

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Abstract. Positron annihilation spectroscopy is used to study the annealing stages in cold worked single and polycrystalline bismuth. A large drop (onset ~240 K) is observed in the doppler-broadening lineshape measurement, in agreement with previous work. Results of positron lifetime experiments, conducted around the main annealing stage, suggest the formation of positronium at microvoids in cold worked Bi.

1. Introduction

Several authors have reported positron trapping behaviour at lattice defects in bismuth [1, 2, 3, 4, 5]. Interest has largely been triggered by bismuth's semimetallic nature, the position of the Fermi level in the presence of defects (or impurities) and the consequences of these for positron trapping and annihilation characteristics. General observation has been that, unlike metals, positron trapping does not occur in thermally generated vacancies at high temperature, even near the melting point T_m [1, 2] (where mono-vacancy concentration $C_v \sim 10^{-4}$ atom^{-1}). This lack of trapping has been attributed to the charge state of the thermal vacancies [3, 6]. However, positron trapping is observed at defects in deformed [3] and electron and neutron irradiated [4, 5] samples. These and other [7] annealing studies reveal a number of recovery stages which are assigned to defects such as vacancies, vacancy clusters and dislocations. The annealing stage, observed in cold worked (at 77 K) Bi [3], between ~ 220–290 K manifests as an unusually large change in the positron annihilation characteristics, prompting the hypothesis that the defects responsible are three-dimensional microvoids and that part of the large change results from the formation and annihilation of positronium in these defects. Here, we present and discuss results of experiments to test this conjecture.

When a thermalized positron annihilates in condensed matter, the predominant mode of annihilation results in the emission of two roughly anti-parallel γ-photons. The momentum component of the electron–positron pair in the mean direction of photon emission causes a Doppler broadening in the annihilation photon energy. This broadening can be monitored using the so-called line shape parameter S [8], which is extensively used in the studies of lattice defects and their annealing behaviour in a variety of materials. The net effect of positron trapping in, and annihilation from, open volume defects is to increase S with defect concentration and size (for vacancy concentrations $< 10^{-4}$ atom^{-1} and radii < 50 Å [9]). Additional information about the positron environment can be gleaned from positron

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lifetime measurements. Lifetime values typically lie in the range ~ 100–250 ps and ~ 200–450 ps for defect free solids and open volume defects respectively. The existence of a long lifetime component in the range 400–500 ps has long been associated with annihilation at microvoids. Since the earliest demonstration of positron trapping in voids produced by irradiation, there have been strenuous efforts to deduce the nature of the trapped state (see e.g. [10] and references therein).

One school of thought suggests the formation of a positron surface state. Most of the literature has focussed on Al. Recent non-local density functional calculations for positrons trapped at external Al surfaces [11] produce values of 599 ps which agree well with experiment (580 ps [12]). Similar calculations for internal (void) surfaces [13] result in positron lifetimes ranging from 250 ps for monovacancies to a saturation value of 565 ps for voids bigger than 10 Å diameter. This compares with experimental lifetimes close to 500 ps for large voids in Al.

If, as is conventionally assumed, the positron in a surface state is strongly localized normal to the surface but is essentially delocalized in the plane of the surface, one would expect strong anisotropy in its momentum density. However, in relatively large faceted voids in single-crystal Al (where major void surfaces were [111]) no such anisotropy was observed [14]. It was conjectured that the observed long 'void' lifetime of ~ 470 ps could well arise from annihilation of positronium which is created within the void.

The formation of the positron–electron bound state known as positronium (Ps) [15] may be facilitated by the presence of sufficiently large open volume defects (e.g. microvoids). Experimentation with low energy positrons show that Ps can be formed at external surfaces and may be emitted into vacuum. Such a phenomenon can also occur at the internal surface of a void. Ps formation at any surface is governed by the balance between the electron and positron work functions and the Ps binding energy and thus may be influenced by contamination of the void surface by impurity atoms. Ps forms either a spin 0 singlet state (para positronium: pPs) or spin 1 triplet state (ortho positronium: oPs). In vacuum the singlet and triplet states annihilate with lifetimes of 125 ps and 140 ns and emit 2 and 3 γ-photons respectively. In a void the Ps may interact with void walls (quenching [15]) leading to an observed lifetime close to the spin averaged value (~ 500 ps) for Ps. A high quenching rate will also preclude significant 3γ emission arising from oPs annihilations. However, substantial 3γ annihilations in voids of radii of a few tens of Å is observed in insulating materials. In metallic systems, there has been conclusive evidence for pPs formation in voids. Hasegawa *et al* [16] have observed narrow peaks at low momenta in angular correlation spectra which provides a clear indication of the existence of thermalized pPs within the voids. In recent more comprehensive lifetime measurements, Hasegawa *et al* [17] have also found long lifetime components between ~ 1 ns and 5 ns as a function of temperature in voids with oxygen contaminated internal surfaces.

In light of the varying evidence in the literature briefly outlined above, it would appear that in small voids the positron may exist in either state. In view of the fact that the measured and predicted lifetimes for a positron trapped at a surface seem to lie, at least for some metals, within ~ 20% of the spin averaged Ps lifetime, it is difficult to unambiguously identify the positron state in the void in the absence of additional evidence, e.g. a narrow pPs peak or 3γ annihilations. However, the existence of a positron lifetime well in excess of the spin averaged Ps lifetime must, in our view, signify oPs formation and quenching with the void walls.

2. Experimental Details

Samples of single-crystal Bi (7N purity) and polycrystalline Bi (5N purity) were mechanically and chemically polished and then deformed in a hydraulic press under liquid nitrogen. Final thickness reductions amounted to 30% and 40% for the single and polycrystalline specimens respectively. Doppler line shape data was obtained using a gain stabilized solid state (Ge) detector. Spectra were accumulated at 30 minute intervals during a heating and cooling cycle which took the single and polycrystalline deformed samples from 100 K to 450 K and back at $10\,\mathrm{K\,h^{-1}}$. Each energy spectrum contained $\sim 2.25 \times 10^6$ counts, from which the line shape parameter S was calculated and $S(T)$ determined.

A pair of polycrystalline samples were cold worked (thickness reduction 40%) and transferred to the sample chamber where they reached an ambient temperature of 110 K. Lifetime spectra were collected at four annealing temperatures of 110 K, 150 K, 190 K and 230 K and a final measurement was taken at 150 K following a 2 h anneal at 400 K. A further measurement was taken on a well annealed single-crystal Bi. Lifetime data was accumulated on a 'fast–fast' coincidence spectrometer [18] with timing resolution of 180 ps FWHM. Each measurement lasted $\sim$ 10 h and resulted in a lifetime spectrum containing $> 2 \times 10^6$ counts. Control experiments were performed to assess spectrometer resolution and some aspects of data analysis.

Positron lifetime spectra, have the form

$$S(f) = f * \int I_i \exp(-\lambda_i t)\mathrm{d}t \qquad (1)$$

where f is the timing resolution of the spectrometer. Here λ_i are the positron annihilation rates from states i (positron lifetime $\tau_i = \lambda_i^{-1}$) and I_i are the corresponding relative intensities. Spectra were analysed using two different computer programmes. The first, PFPOSFIT [19], utilizes least square fitting techniques and returns discrete values of τ_i and I_i. The second, CONTIN-PALS [20], based on Laplace transform, returns a number of solutions based on continuous ranges of τ_i and I_i. Among the input parameters required by PFPOSFIT are guesses for i and τ_i for a particular spectrum, implying *a-priori* knowledge of the possible positron states. Under some circumstances initial guess values for τ_i may influence the fitted values returned by PFPOSFIT. Consequently, the problem of fitting convoluted exponentials is ill-posed and often fraught with ambiguity. CONTIN-PALS, unlike PFPOSFIT requires no assumptions about i or τ_i. Provided with the spectrum to be analysed and a known reference as the input, it returns solutions for the so-called 'regularization parameter' α. Solutions are biased by α to parsimony, such that low values of α result in artifacts and high values smooth out details. The only user intervention required is the choice of a value for α large enough to exclude artifacts. A solution with high probability is always provided by the program. However, in our analysis, the values of I_i were found to be sensitive to α and PFPOSFIT was considered more stable in this respect. In light of the above, the strengths of both approaches were utilized to try and minimize the ambiguities of the resulting lifetime parameters, i.e. mean values of τ_i obtained from CONTIN-PALS were used as input parameters for PFPOSFIT.

3. Results and discussion

The temperature dependencies of the line shape parameter S for cold worked samples of poly and single crystal Bi are shown in figures 1(*a*) and 1(*b*) respectively. Both samples exhibit an annealing stage the onset of which occurs at $\sim$ 240 K. In the polycrystalline sample the recovery, which amounts to a ~ 6% change in S, appears to be complete at 300 K and the stage (between 300–400 K) previously attributed to dislocations [4] cannot be discerned. Annealing of the cold worked single crystal (figure 1(*b*)) takes place over a broader temperature range. Here, recovery is complete at 375 K and involves a 4.9% change in S, consistent with the smaller degree of deformation. These results are in broad agreement with those previously reported for plastically deformed [3] Bi.

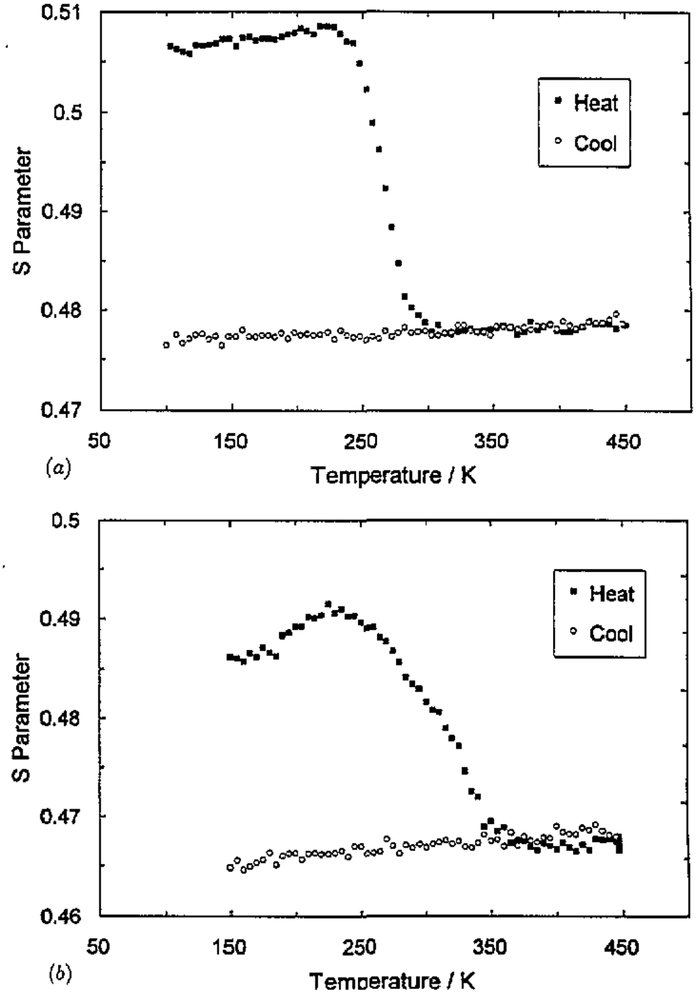

Figure 1. Positron lineshape parameter S for (*a*) 40% deformed polycrystalline and (*b*) 30% deformed monocrystalline Bi as a function of temperature.

Discrete (PFPOSFIT) and continuous (CONTIN-PALS) analysis of positron lifetime spectra on the well annealed sample, reveal a single bulk lifetime component τ_b of 225 ± 2 ps, somewhat lower than the 235 ps [4] or 238 ps [5] quoted elsewhere. However, using the same positron source and analysis technique we obtained a single component τ_b for a well annealed Ni single crystal that is equal to the well established value.

The same positron source was also used to measure lifetime spectra for 40% cold worked polycrystalline Bi. Measurements were taken at selected annealing temperatures, designed

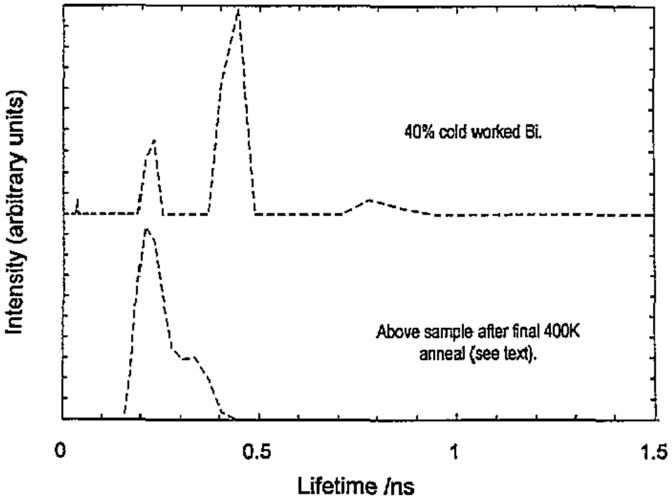

Figure 2. Laplace transform analysis of positron lifetimes in as-deformed and 400 K annealed Bi.

to identify the presence or otherwise of Ps, rather than reproduce the annealing behaviour of figures 1(*a*) and 1(*b*). In the as-deformed specimen measured at 110 K, three lifetime components were found; two long lifetimes: $\tau_3 \sim 1$ ns with an intensity $I_3 = 4 \pm 0.3\%$ and $\tau_2 = 400 \pm 5$ ps with an intensity $I_2 = 80 \pm 2\%$, as well as a low intensity bulk component $\tau_1 = 180 \pm 10$ ps. Following the anneals of 10 h each at 150, 190 and 230 K we observed a drop in I_2 (to $\sim 70\%$) and corresponding increase in I_1, whilst I_3 fell but still remained a significant component at 1%. τ_3 remained at ~ 1 ns—but there was a slight increase in τ_2 to ~ 420 ps. After annealing for 2 h at 400 K (lifetime measured after cooling to 150 K), as many lifetimes were measured as before but with significant differences. I_3 fell to $\sim 0.3\%$, and τ_2 dropped to 300 ± 10 ps, with an intensity of $50 \pm 10\%$. Evidently, the specimen was not completely annealed after the short heat treatment at 400 K and this state is not comparable to the state of the specimens at 400 K in figure 1. The CONTIN-PALS results (figure 2) clearly illustrate the effects of the 400 K anneal compared with the as-deformed specimen. The as-deformed state contains lifetime values in the middle range (centred about 425 ps) and a small but distinct peak at ~ 0.8 ns. Following the annealing sequence above, we note an absence of the peak at 0.8 ns and a shifting of the mid-range values to far below 400 ps.

The magnitude of τ_2 below 230 K returned by both lifetime analysis techniques ($\sim$420 ps) is longer than the value of 325 ps suggested for monovacancies in Te and Sn doped Bi [5] and therefore we attribute this lifetime to annihilation at microvoids in accordance with others. The fact that both τ_2 and $S(T)$ for the deformed polycrystalline specimen show slight increases below 230 K indicates that such microvoids may grow during the initial stages of annealing. The much longer lifetime of ~ 1 ns has significant intensity at all annealing temperatures below the major stage at 260 K but diminishes above. That combined with the complete absence of a 1 ns lifetime component in well annealed Bi leads us to suggest that Ps forms and annihilates in microvoids in as-deformed Bi and this signal cannot have arisen from positron source or external surface contributions.

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References

[1] Segers D, Dorikens M and Dorikens-Vanpraet L 1978 *Phys. Status Solidi* a **48** 133
[2] Szymanski Cz, Chabik St, Pajak J and Rozenfeld B, 1980 *Phys. Status Solidi* a **60** 375
[3] Lemahieu I 1985 *Positron Annihilation* (Singapore: World Scientific) p 561
[4] Lemahieu I, Dorikens-Vanpraet L, Segers D, Dorikens M, Moser P, Corbel C and Bois P 1987 *Phys. Status Solidi* a **102** 659
[5] Corbel C, Bois P, Moser P and Lemahieu P 1987 *Mat. Sci. Forum* **15** 721
[6] Seeger A 1973 *J. Phys. F: Met. Phys.* **3** 248
[7] Bittar A and Lesueur D 1978 *Phys. Status Solidi* a **48** K123
[8] MacKenzie I K 1984 *Positron Solid-State Physics* (Amsterdam: North-Holland) p 196
[9] Nieminen R M and Manninen M J 1979 *Positrons in Solids* (Berlin: Springer) ed P Hautojarvi
[10] Kogel G 1992 *Mat. Sci. Forum* **105–110** 431
[11] Jenson K O and Walker A B 1988 *J. Phys. F: Met. Phys.* **18** L277–85
[12] Lynn K G and Schultz P J 1988 *Rev. Mod. Phys.* **60** 701
[13] Dunn G M, Jenson K O and Walker A B 1991 *J. Phys.: Condens. Matter* **3** 2049
[14] Alam A, Walters P A, West R N and McGervey J D 1984 *J. Phys. F: Met. Phys.* **14** 761
[15] Jean Y C and Schrader D M 1988 *Positron and Positronium Chemistry 57*, (Amsterdam: Elsevier)
[16] Hasegawa M, Kuramoto E, Kitajima, Hirabayashi M, Ito Y, Takeyama T, Takahashi H and Ohnuki S 1982 *Positron Annihilation* eds P G Coleman, S C Sharma and L M Diana (Amsterdam: North Holland) p 425
[17] Hasegawa M, Berko S and Kuramoto E 1988 *Positron Annihilation* eds L Dorikens-Vanpraet, M Dorikens and D Segers (Singapore: World Scientific) p 73
[18] Paulus T J 1978 Proc. Chinese Nuclear Society Seminar, Beijing, China
[19] Puff W 1983 *Comp. Phys. Commun.* **30** 359
[20] Gregory R B and Zhu Y 1990 *Nucl. Instrum. Methods* A **290** 172