Positron-lifetime studies in YNi_2B_2C

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Positron-lifetime measurements have been carried out in the temperature range of 300 to 5 K in the borocarbide superconductor, YNi_2B_2C. The positron lifetime 189 ps at 300 K is observed to decrease to 179 ps at 5 K. No change in lifetime is seen across the superconducting transition at $\sim$ 16 K. The observed magnitude of lifetime and its temperature variation are discussed with support from theoretical computations of positron density distribution and annihilation charactertistics for a perfect crystal of tetragonal YNi_2B_2C and for various plausible defect configurations. On the basis of these calculations, it is inferred that the lifetime and its temperature dependence are governed by positron annihilation from carbon vacancies.

With the discovery of superconductivity in the Y-Ni-B-C system,[1,2] a class of quaternary borocarbide superconductors have emerged. Superconductivity has been observed in several rare earth (Lu, Tm, Er, and Ho) nickel borocarbides,[3] and with transition metals Pd, (Refs. 4 and 5) and Pt.[5] Amongst these, the Y-Ni-B-C system, having a transition temperature of 15.5 K has been investigated in greater detail. The superconducting phase having the composition of YNi_2B_2C crystallizes in a tetragonal structure with alternating layers of Y-C and Ni_2B_2 layers.[6] While several experimental methods such as magnetization, resistivity, tunnelling, NMR, muon spin resonance etc. have been used,[7] a complete characterization of the superconducting and normal state has not been obtained, and a clear consensus on the mechanism of superconductivity is yet to emerge.

Positron annihilation spectroscopy,[8,9] which is a powerful technique for the investigation of electronic structure and defect properties of solids, has been widely applied[10] to the study of copper oxide superconductors. These include (i) studies on the temperature dependence[10,11] of positron annihilation characteristics across T_c, (ii) investigation of oxygen defects,[12,13] and (iii) elucidation of the nature of the Fermi surface.[14] In the light of these earlier studies on cuprates, we expect positron annihilation spectroscopy to contribute to the understanding of some aspects of structure and superconductivity in the borocarbide superconductors. Of particular interest is the temperature variation of lifetime across T_c to see if they behave similar to the cuprate superconductors. With this motivation, the present experiments on the temperature variation of positron lifetime in the temperature range of 300 to 5 K have been carried out.

YNi_2B_2C samples were prepared by arc melting Y(99.9 %), Ni (99.9 %), B(99.8 %), and C (99.7 %) several times in a protective flowing atmosphere of argon gas. The samples were then homogenized at 1050 °C for 12 h after which they were slow cooled to room temperature in $\sim$ 5 h. X-ray diffraction pattern, obtained using Cu K_α radiation, is shown in Fig. 1. This could be indexed to a tetragonal cell with lattice parameters $a = 3.528$ Å and $c = 10.559$ Å, consistent with the reported[6,15] structure of YNi_2B_2C. A small, $\leqslant$ 5 % amount of impurity phase could also be detected that could be indexed to orthorhombic $Y_2Ni_3B_6$ phase[16] with lattice parameters $a = 7.710$ Å, $b = 8.679$ Å, and $c = 3.487$ Å. ac susceptibility measurements on the sample showed superconducting transition with onset temperature of $\sim$ 16 K and the magnitude of the diamagnetic signal was comparable to that in Nb. Positron lifetime measurements were carried out using a fast-fast coincidence spectrometer having a resolution of 250 ps. The positron source, ^{22}NaCl deposited on a 1.25 μm Ni foil, was sandwiched between powdered YNi_2B_2C sample in a copper sample cell and this was mounted inside a JANIS continuous flow cryostat, using which the temperature variation between 300 to 5 K was achieved.

The measured lifetime spectra at various temperatures, were best analyzed ($\chi^2 \leqslant 1.1$) in terms of two lifetime components, after taking into account annihilations in the source foil.[17] The first component of lifetime, τ_1, was seen to be $\sim$ 189 ps and the second component, τ_2 was $\sim$ 800 ps, with an intensity $I_2 \sim 1\%$. The occurrence of this long lifetime second component with a small intensity could arise due to[8] annihilations in the interstices (pores) of the powder sample

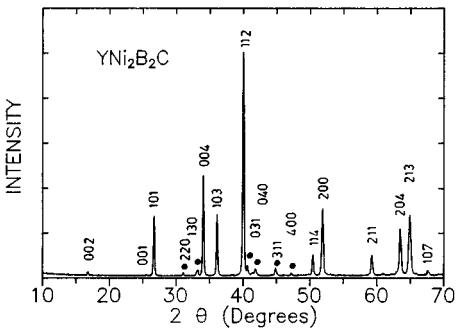

FIG. 1. X-ray diffraction pattern of Y-Ni-B-C sample, using Cu-K_α radiation. The diffraction pattern can be indexed to tetragonal YNi_2B_2C with lattice parameters a=3.548 Å and c=10.559 Å. The weak diffraction peaks, marked with dots, can be indexed to orthorhombic $Y_2Ni_3B_6$.

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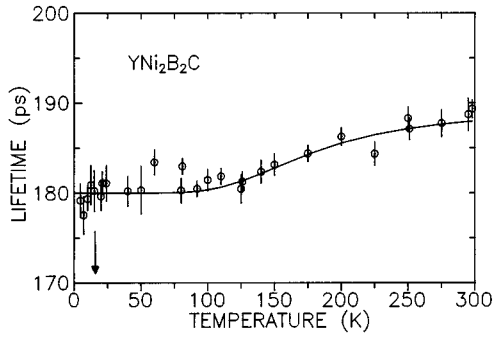

FIG. 2. Positron lifetime versus temperature in YNi_2B_2C. The continuous line is a fit based on a model incorporating detrapping of positrons from isolated carbon vacancies (see text). The arrow corresponds to T_c.

and is not intrinsic to the system. Further analysis was carried out with the second component fixed at 800 ps and the temperature variation of lifetime, which is due to annihilations inside the sample, is shown in Fig. 2. A monotonic decrease in lifetime with temperature is observed over the entire range of 300 K to 5 K. Such a decrease of lifetime on lowering the temperature could arise due to thermal contraction of the lattice resulting in an increase in the overlap of the positron density with the surrounding electrons. However, using the data of lattice parameter variation with temperature,[15] it is seen that only 0.1 ps change is expected, whereas the decrease in lifetime is $\sim$ 10 ps in the temperature range of 300 to 5 K. In the following the observed magnitude of lifetime and its temperature variation are discussed with support from theoretical computations.

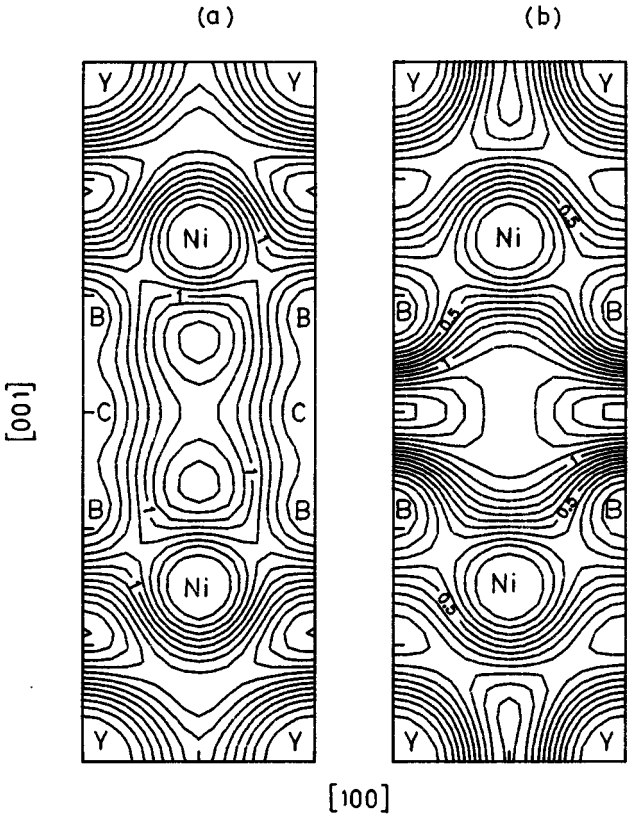

FIG. 3. (a) Contour plot of the positron density distribution in the (010) plane of YNi_2B_2C. The maxima of the positron density distribution is in the interstitial region between the Ni atoms and between the Y and B atoms can be seen. (b) Contour plot of the positron distribution in the carbon vacancy ordered structure of YNi_2B_2. The maxima of the positron density is at the site of carbon vacancies.

TABLE I. Calculated positron lifetimes and binding energy at vacancies in YNi_2B_2C. The positron binding energy is taken as the difference in the eigenvalue in a vacancy and that in the Bloch state.

System	Lifetime (ps)	Binding energy (eV)
YNi_2B_2C	144	
Isolated C_V	162	0.1
Ordered C_V	185	1.0
Y_V	245	4.1

Theoretical calculations of positron distribution and lifetime in YNi_2B_2C have been carried out following the method of Puska and Nieminen[18] as described in detail in Ref. 19. The calculational scheme consists of three major steps: (i) construction of the positron potential, (ii) numerical solution of the Schrödinger equation under appropriate boundary conditions, and (iii) calculation of the lifetime by evaluating the overlap of the positron and electron densities. The calculated positron density distribution in the (010) plane of YNi_2B_2C is shown in Fig. 3(a). From this contour plot, it is seen that the positron density spans the entire unit cell with maxima at all the interstitial regions. In the projection shown, the maxima of the positron density distribution between the Ni atoms and between the Y and B atoms can be clearly seen. It may be remarked that this uniform sampling of the entire unit cell in the case of YNi_2B_2C is different from the behavior seen[11] in some of the cuprates, such as $YBa_2Cu_3O_{7-x}$, wherein the Cu-O chains are preferentially sampled by the positron.

The positron lifetime was obtained by evaluating[18,19] the overlap of the calculated positron density with the core and valence electron densities, obtained from a superposition of atomic densities.[20] In these calculations, the $4d^1$, $5s^2$ electrons of Y; $3d^9$, $4s^1$ electrons of Ni; $2p^1$ of B and $2p^2$ electrons of C were treated as valence electrons and the remaining electrons as core electrons. The resultant lifetime was seen to be 144 ps, much smaller than the experimental lifetime of 189 ps. Calculations repeated by neglecting the Y contribution to the total valence electron density, as suggested by band structure calculations,[21] yielded a lifetime value of 155 ps, still much smaller than the observed lifetime.

It is possible that the larger value of lifetime[22] in YNi_2B_2C, compared to the theoretical expectation, could be due to positron annihilation from vacancy type defects which are potent traps for positrons.[8,9] Initial calculations were carried out for vacancy at carbon site. This was primarily motivated by two reasons: (1) structural refinements[15] of YNi_2B_2C indicate large thermal factors corresponding to carbon, and (2) recent ^{11}B NMR experiments[23] indicate a signal corresponding to a disordered environment of B, including one associated with carbon vacancies. The positron density distribution in the presence of a vacancy at carbon

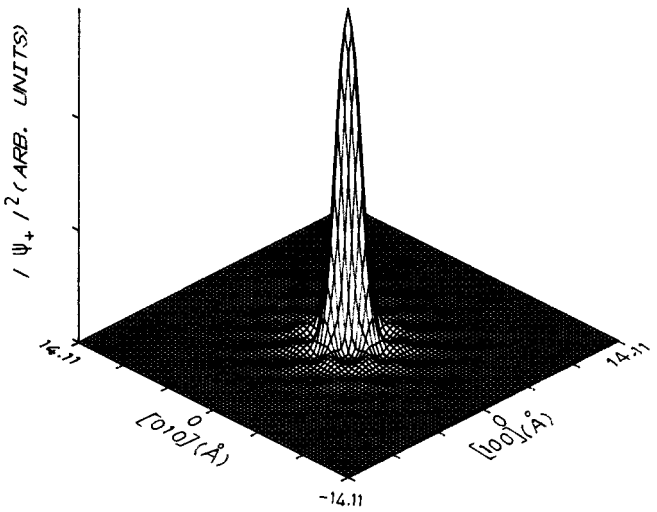

FIG. 4. Perspective plot of the positron density distribution in the (001) plane showing the localization of positron at an isolated carbon vacancy.

site was obtained by numerical solution of the Schrödinger equation under the boundary condition that the positron wave function vanishes at the boundaries of a large cube having vacancy at the center and having dimensions of $8a \times 8a \times 8a$, where the lattice parameter, $a = 3.528$ Å. The perspective plot of the localized positron distribution is shown in Fig. 4. The lifetime corresponding to this localized state was calculated, according to the method discussed earlier[13] to be 162 ps—still smaller than the experimental value of 189 ps.[24]

In the presence of significant carbon deficiency, it is possible that there exist regions of the sample with aggregates of carbon vacancies which act as traps for positrons. Calculations of positron density and lifetimes can be carried out for carbon vacancy clusters of various sizes, taking into account their correct geometry.[18] However in this work, in order to estimate the positron lifetime at a carbon vacancy cluster, a limiting case wherein all the carbon atoms at (0.5, 0.5, 0) sites of the YNi_2B_2C structure are removed, was considered. The positron density distribution corresponding to this ordered carbon vacancy structure is shown in Fig. 3(b). In comparison with Fig. 3(a), it is seen that the positron density is peaked at sites of carbon vacancies. The positron lifetime in this ordered carbon vacancy structure is calculated to be 185 ps. This is in excellent agreement with the experimental results, suggesting that the positron lifetime at room temperature is determined by the trapping and annihilation at aggregates of carbon vacancies.

With regard to the temperature variation of lifetime, we have already noted that this cannot be accounted for in terms of thermal contraction. It is well known[8,9,13] that in a system with a variety of positron trapping sites, in particular in the presence of shallow positron traps, the fraction of positrons trapped at various sites is dependent on temperature, leading to a temperature dependence of the average lifetime. Such a model has been used to explain the temperature dependence of lifetime in oxygen deficient $Nd_{1.85}Ce_{0.15}CuO_{3.98}$ (Ref. 13) and $YBa_2Cu_3O_{7-x}$,[25] wherein the vacancies at oxygen sites act as shallow traps[19] for positrons. In the current context of YNi_2B_2C, the two competing traps envisaged are the isolated carbon vacancies and aggregates of carbon vacancies which act as shallow and deep traps, respectively, for the positron (see Table I). The temperature dependence of lifetime can be understood as follows. At room temperature, where the shallow traps at isolated carbon vacancies are ineffective, the positron annihilates from the deep traps at aggregates of carbon vacancies characterized by a lifetime of 185 ps. As the temperature is lowered, the preponderant shallow traps at isolated carbon vacancies become effective resulting in lowering of lifetime. Following this physical picture, an equation for the average lifetime can be written down within the framework of positron trapping model, taking into account the detrapping of positrons from shallow traps.[8] Under the condition that the concentration of carbon vacancies is large, the annihilations from the delocalized Bloch state can be neglected, the average positron lifetime is then dictated by annihilations from isolated carbon vacancies and at carbon vacancy clusters, and is given by[26]

$$\tau_{\mathrm{av}} = (1 + \kappa_2 . \tau_2)/(\kappa_2 + 1/\tau_1),$$

where τ_1 and τ_2 are the lifetimes at isolated carbon vacancy and at carbon vacancy clusters, respectively. $\kappa_2 = \kappa_0 \exp^{-E_b/kT}$ is the thermally activated detrapping rate from the shallow trap at isolated carbon vacancy leading to the positron trapping at carbon vacancy clusters. The above equation gave a good fit to the experimental variation of lifetime (cf. Fig. 2) for the lifetime values of $\tau_1 = 177$ ps and $\tau_2 = 190$ ps, and a positron binding energy $E_b = 0.06$ eV, for the shallow traps. These parameters corresponding to the good fit are seen to be in reasonable agreement with the theoretically calculated values shown in Table I, giving credence to the above mentioned model for the observed temperature dependence of positron lifetime in YNi_2B_2C.

In the results shown in Fig. 2, it is seen that there is neither a change in slope or magnitude of lifetime across the superconducting transition at $\sim$ 16 K. This feature is similar to the results seen[10] in the conventional BCS superconductors, where no change in lifetime is seen or expected[27] across T_c. This however is at variance with the results in several of the cuprate superconductors wherein changes in positron lifetime correlated with T_c has been observed and these have attracted considerable attention.[10] The absence of lifetime variation across T_c in the present experiments on YNi_2B_2C can be taken in support of the phononic mechanism of superconductivity, however, it is also possible that this behavior is related to the positrons being localized at carbon vacancies rather than in the Bloch state. This calls for further experiments on the other rare earth borocarbides, which possibly are free from carbon defects and have a lifetime characteristic of annihilation of the positron from the Bloch state.

To summarize, the present positron lifetime experiments in YNi_2B_2C, coupled with theoretical calculations, indicate that the lifetime at room temperature is determined by trapping of positrons at clusters of carbon vacancies. The decrease in lifetime on lowering the temperature arises due to an increase in the fraction of positrons annihilating from the shallow traps at isolated carbon vacancies, which are characterized by a smaller lifetime. The definitive evidence for the existence of carbon vacancies and their clusters in

YNi_2B_2C, which is presented by these positron annihilation studies, may have significant implications on the detailed understanding of superconducting properties in borocarbides. Further, the present experiments indicate no change in lifetime across T_c - a feature that is similar to that seen in conventional superconductors and different from some cuprate superconductors.

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