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POSITRON ANNIHILATION IN SOLID AND LIQUID NI*

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New techniques have been developed for the study of metals via positron annihilation which provide for the in-situ melting of the samples and subsequent measurements via Doppler broadening of positron annihilation radiation. Here we report these methods currently in use at our laboratory; ion implantation of ^{58}Co and the use of Al_2O_3 crucibles for in-situ melting followed by the decomposition of the Doppler-broadened spectrum into a parabolic and a Gaussian component. Our earliest results obtained for pure Ni in the polycrystalline solid and in the liquid state are compared. An interesting similarity is reported for the distributions of the high-momentum (Gaussian) component for positrons annihilating in vacancies at high temperatures and those annihilating in liquid Ni.

1. INTRODUCTION

It is well known that Doppler broadening (DB) measurements can be utilized to study some details of the observed electron momentum density when suitable deconvolutions are performed. By virtue of limited resolution one cannot compete with detailed angular correlation experiments, but certain information, particularly the gross features of the high momentum parts of the observed spectra can be deconvoluted from the experimental observations provided that an adequate measure of the resolution function is at hand. In the present experiments DB measurements of positron annihilation are reported for solid Ni from 300-1726 K and liquid Ni from 1575-1832 K. These experiments have required the development of several new techniques. The goal has been to maintain sample purity and to perform all experiments under conditions of ultra high vacuum.

2. EXPERIMENTAL METHOD

The availability of ^{58}Co provides a natural solution to the problem of producing an internal positron source suitable for the study of Ni even in the liquid state. The ion implantation technique, originally developed for use with ^{22}Na [1], was applied in the case of ^{58}Co [2]. The ^{58}Co was implanted into several disks of Ni (nominal purity 99.995 wt.%) that were then mounted in an Al_2O_3 crucible, which in turn was surrounded by a resistively heated furnace. This assembly is shown in Fig. 1. All measurements were performed in a UHV system with a base pressure of 10^{-9} Torr. The sample temperature was measured with a Pt/Pt-10% Rh thermocouple inserted into the cavity of the crucible. The thermocouple was calibrated at room temperature and at the melting point of Ni ($T_m = 1726$ K).

The resolution of the gamma-ray detector [Ge(Li)] was 1.7 keV FWHM at the 497 keV line of

^{103}Ru . Continuous post acquisition stabilization and monitoring of the resolution function was accomplished by the simultaneous recording of both the 497 keV ^{103}Ru line and the annihilation line at 511 keV.

Fig. 1. Sample subassembly.

The sample (A) was contained in an Al_2O_3 crucible (B) mounted on a Pt/Pt-10% Rh thermocouple (C). This assembly was surrounded by a resistively heated furnace which was constructed from Ta wire (D) and a Ta heat shield (E).

3. SHAPE PARAMETER VERSUS TEMPERATURE

The shape parameter, F , defined as a normalized integral under the peak region of the DB spectrum is shown in Fig. 2. Using the "S" curve one can perform a two-state trapping-model analysis resulting in the determination of the vacancy formation enthalpy, which we have reported elsewhere [3]. The line $F_m(T)$ in Fig. 2, representing positrons annihilating in liquid Ni, is observed to be similar in its temperature dependence to the deduced temperature dependence of $F_v(T)$, characteristic of the vacancy-trapped state. Undercooling of the liquid below T_m was possible, and thus we observed positron annihilation in the liquid from 1575-1832 K. Isothermal comparisons of positron annihilation in the liquid with annihilation in high

Fig. 2. Shape Parameter vs. T. The perfect lattice, vacancy and liquid states are indicated as F_b , F_v , and F_m , respectively.

temperature equilibrium vacancy defects are thus possible. An isothermal comparison at T_m reveals that the narrowing of the momentum distribution indicated by increasing F , is such that the change from the extrapolated bulk or perfect-lattice state $F_b(T_m)$ to $F_v(T_m)$ is ~ 2.5 times as great as the change from $F_v(T_m)$ to $F_m(T_m)$.

4. DECOMPOSITION

We have found by experiment that the DB spectra could, at all temperatures, be described by a convolution of the actual asymmetric resolution function with a weighted sum of an inverted parabola (relative intensity I_p , cut off energy E_B) and a Gaussian (relative intensity $(1-I_p)$, standard deviation σ). Theoretical results of Singru and Mijnaerends [4] for Ni support the notion that, at least to a first approximation, this is acceptable with regard to the perfect lattice. Thus, for the perfect lattice it can tentatively be suggested that the parabola is due to annihilations with the nearly free electrons (I_p being the probability of positron annihilation with these electrons, and E_B being related to the energy of the top of the nearly spherical energy surface of the s -like bands). The Gaussian would then correspond to the broad momentum distribution of the more localized electrons with σ being proportional to the root mean square of their momentum distribution.

With regards to extending this model to the liquid state, present theory indicates that the electronic structure retains some of the overall features found in the perfect lattice, thereby providing some justification for using the same description for the liquid metal positron state as for the perfect lattice [5]. For the electron states in a vacancy in Ni virtually nothing is known, but it is one of the purposes of this work to make a contribution towards understanding this problem, and we have thus applied the same model to the vacancy state as well.

Three temperature regions were analyzed, 300-974 K, 1597-1717 K and 1676-1832 K,

corresponding to the perfect lattice, $\sim 100\%$ trapping in vacancies, and the liquid regions respectively. All the spectra within a temperature region were fit simultaneously to the model, allowing for temperature dependences of I_p , E_B and σ . This method reduces the possibility for "mixing" of the parabolic and Gaussian components. The χ^2 sums for the three regions were 1.10, 1.12, and 1.11, based on 2805, 1403, and 1401 degrees of freedom, respectively. The agreement between the individual spectra and the fits were excellent with no systematic errors being observed.

No temperature dependence could be measured for E_B in the perfect lattice, but this does not mean that E_B is temperature independent, only that such a temperature dependence was not measurable to within statistics. For I_p and σ a first order temperature dependence could be deduced for the perfect-lattice state. At high temperatures (vacancy and liquid regions), the temperature regions were too narrow to determine any temperature dependences for E_B , I_p and σ , and only average values are reported. The inability to measure a temperature dependence for E_B in the perfect lattice arises both from the small I_p and the finite resolution. For σ this is not the case, since the Gaussian is much broader than the resolution function.

A summary of the results for the three regions is given:

Perfect Lattice

$$E_B = 1.59 \pm 0.02 \text{ keV}, \quad I_p = I_{p0}[1 + \gamma(T-581)],$$

$$I_p(300) = 0.15, \quad I_p(T_m) = 0.194, \text{ and}$$

$$\sigma = \sigma_0[1 - \delta(T-581)],$$

$$\text{where: } I_{p0} = 0.162 \pm 0.003, \quad \gamma = (1.9 \pm 0.3) \cdot 10^{-4} \text{ K}^{-1},$$

$$\sigma_0 = 1.655 \pm 0.004 \text{ keV}, \quad \delta = (15.0 \pm 3.5) \cdot 10^{-6} \text{ K}^{-1},$$

and T is given in K.

Vacancy

$$E_B = 1.63 \pm 0.02 \text{ keV},$$

$$I_p = 0.275 \pm 0.005$$

$$I_p(T_m) = 0.275$$

$$\sigma_v = 1.59 \pm 0.01 \text{ keV}$$

Liquid

$$E_B = 1.61 \pm 0.02 \text{ keV},$$

$$I_p = 0.317 \pm 0.006$$

$$I_p(T_m) = 0.317$$

$$\sigma_L = 1.58 \pm 0.01 \text{ keV}$$

The E_B values are all the same, within statistics, and can be related to corresponding features in the theory [4]. For the liquid and vacancy we are not aware of any calculations of E_B and I_p . In addition, E_B has not been corrected for positron localization. The extrapolated value of I_p at 0 K for the perfect lattice is 0.144, which is in reasonable agreement with the theoretical work of Anderson [6] which yielded 0.13 for the fraction of electrons in the s -like bands. Another interesting point is the change in $I_p(T_m)$ for the three states. In the context of the decomposition, the major part of the differences in $F_b(T_m)$, $F_v(T_m)$, and

$F_m(T_m)$ arise from the changes in the intensity of the parabolic component. One must note at this point that changes are also occurring in the σ term for the Gaussian component and that the decomposition analysis permits us to expose this additional information, specific to a subset of the electrons, which could not be extracted from a parameter such as $F(T)$.

5. THE GAUSSIAN COMPONENT

Figure 3 summarizes both the temperature and state dependences of σ , but is cast in the more appropriate form of $\Delta a/a_0$, the relative change in the lattice constant. For the perfect lattice state we note the similarity between the values of δ and the linear expansion coefficient α for Ni [$\alpha = 13.4 \times 10^{-6} \text{ K}^{-1}$ (293 K)]. We have estimated the volume expansion effect on σ , assuming that the variations in the positron wavefunction can be neglected in the region of overlap with localized electrons. The theoretical estimate is discussed by us elsewhere in more detail [7]. The result obtained was $\partial(\ln\sigma/\partial T) = -1.35\alpha$ and the corresponding experimental result is $-(1.0 \pm 0.2)\alpha$; the difference may well be attributable to neglected variations in the positron wavefunction. Note that the value for σ_L lies on the extrapolation (extrapolation error is indicated in Fig. 3 by the dashed lines) of the temperature dependence of σ in the perfect lattice suggesting that σ_L can be accounted for by density alone. A generalization of the theoretical estimates used above [7] predicts that σ_L is $\sim 4\%$ less than σ for the perfect lattice state at room temperature, consistent with the present observations (Fig. 3).

The quantity σ_V should have been plotted at a $\Delta a/a_0$ appropriate for the first shell around the vacancy. However, short of knowing this distance, we have plotted σ_V at the $\Delta a/a_0$ value characteristic of the defect-free host lattice surrounding the vacancy. From Fig. 3 it is then seen that the value of σ_V cannot be described in terms of the lattice parameter of the defect-free host lattice alone. This brings us to an interesting observation for σ_V . Despite a

Fig. 3. Sigma vs. relative change $\Delta a/a_0$ in lattice constant.

significant I_p difference between the vacancy and liquid states, σ_V and σ_L are almost equal. The observation that the σ_L measured for the liquid and the essentially defect free lattice are consistent, in that they correlate with the mean distance between atoms, suggests that this relationship could also be true when the positron is trapped in a vacancy. One might speculate, as have Tam and Siegel [8], that positron localization can "push out" surrounding atoms, conceivably leading to an effective sampled density similar to the liquid, and that such a mechanism might be operative in the liquid as well. One might also consider that the electron orbitals within the first shell of the vacancy might rearrange so as to accommodate a coordination number of ~ 11 , which is also the coordination number of the liquid [5].

6. CONCLUSION

The new techniques developed in the present investigation will be useful in further studies of transition metals and their alloys in both the solid and liquid states. It has been shown that the major part of changes in σ can be explained on the basis of density alone. The observed similarity between σ_V and σ_L requires further investigation and raises fundamental concerns about our understanding of the positron-defect state, or possibly the defect itself. An important future experiment would be to determine if vacancy defects at low temperatures are perceived by the positron in the same way.

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