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Observation of Anisotropy in the Temperature Dependence of the Positron-Annihilation Spectrum from a Single Crystal of Cadmium

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Measurements have been made on the Doppler broadening of the 511-keV photons resulting from positron annihilation in a single cadmium crystal over the temperature range 4–590 K. They show that the temperature dependence in the prevacancy region (150–350 K) is markedly different in the cases of emission in the [0001] and [10$\bar{1}$0] directions.

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Positrons provide a sensitive probe of electronic conditions within a metal. Prior to annihilation they rapidly thermalize and a fraction of them may become trapped in defects such as vacancies, dislocations, etc. Measurements of the Doppler-broadening parameters of the annihilation 511-keV radiation can be used in conjunction with the trapping model[1,2] to assess the thermal creation of vacancies and to estimate their concentrations, formation energies, and entropies, etc. Unfortunately, an unresolved problem casts doubt on the precision of these estimates: the marked temperature dependence of the parameters observed in the temperature region below the threshold of vacancy creation. In this so-called prevacancy region the physics is not understood and hence it is uncertain how the effect should be extrapolated into the vacancy region.

The most striking case is cadmium. Lichtenberger, Schulte, and MacKenzie[3] found a steep increase in the Doppler line-height parameter between 180 and 350 K. Similar prevacancy rises in annealed samples have been seen in angular correlation measurements[4] and in lifetime experiments.[5] Our own group has reported Doppler-broadening measurements on both polycrystalline[6] and single crystal[7] specimens of cadmium, and it was differences between the results of the two cases that prompted the present study.

The most generally accepted explanation for the prevacancy rise has been recently enunciated by Stott and West.[8] Taking into account volume thermal expansion and lattice vibrations, they propose that the reduction with increasing temperature in the overlap between positron and core electron wave functions might account for the observations. An alternative view by Seeger[9] based on the possibility of positrons being self-trapped in metastable states has not been confirmed experimentally—but neither has it been entirely ruled out.[7,10]

In this Letter we report the first measurements on the directional dependence of the prevacancy characteristics. A number of specimens were cut from a 99.999%-pure single crystal of cadmium, and the crystallographic axes were determined. The measurements reported here refer to one sample comprised of two elements sandwiching 80 μCi of ^{22}NaCl. Each element had been spark cut, spark planed, and chemically polished; had a final diameter of 18 mm and thickness of 2 mm; and had been annealed at $< 10^{-6}$ Torr for 6 h at 530 K, 20 h at 510 K, followed by a slow (6 h) cooling down to 300 K. The spectrometer and the experimental method were described in Ref. 6. The sample-detector distance was approximately 15 cm, for both the cryostat and the furnace. The 200-mm^2 germanium detector thus subtended an angle of less than 0.01 sr. In both the cryostat and the furnace applications the total count rate was constant at 5000 counts/sec and the total number of counts accumulated for each temperature was about 900 000.

The definition of the Doppler-broadened photon line-height parameter F was also described in Ref. 6, but the present data have been subjected to an improved background subtraction procedure.[11] This has been accurate enough to eliminate the need for any normalization of the results arising from the different geometries of the cryostat and furnace employed in the different temperature regions. In addition, a parameter W has been calculated to describe the intensity of symmetrically placed wing portions of the normalized peak area. The particular definitions of F and W were chosen to be optimum according to the sensitivity criteria of Campbell.[12]

Figures 1 and 2 show the F and W parameters, plotted over the full temperature range, corresponding to radiation emitted in [case (A)] the [0001], and [case (B)] the [10$\bar{1}$0] directions, respectively. The results shown were for a sample cut with the [0001] axis perpendicular to, and the [10$\bar{1}$0] axis in, the plane of the sandwich; other results not presented here, from another specimen cut in exactly the opposite sense, i.e., the [10$\bar{1}$0] axis perpendicular to the plane of the sandwich, verify that the conclusions are not significantly affected by the sample-apparatus configuration.

The curve fitting appropriate for the two-state trapping model has been performed on the sets of data by using[13-15]

$$F = \frac{F_f(1+\beta T) + F_v(1+\alpha T)A\exp(-H_v/kT)}{1+A\exp(-H_v/kT)}$$

in which it is assumed that the parameter F varies linearly with temperature in both the prevacancy region (150–350 K) and at the highest temperatures. The slopes β and α have the form $\Delta F/F_0\Delta T$. With $\alpha = 0$ the calculated vacancy formation enthalpies (H_v) were found to be 0.51 ± 0.01 eV for case (A) and 0.53 ± 0.01 eV for case (B). Employing the values given in Ref. 16 of 190 ps for the free positron lifetime and 2.5×10^{14} s^{-1} for the specific trapping rate of positrons at va-

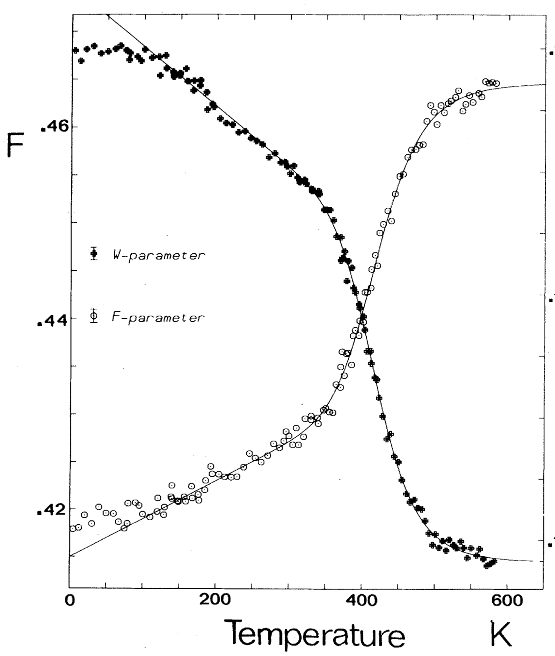

FIG. 1. Temperature dependence of the line-height parameter F and the wing parameter W for photons emerging in the [0001] direction. Typical error bars are shown.

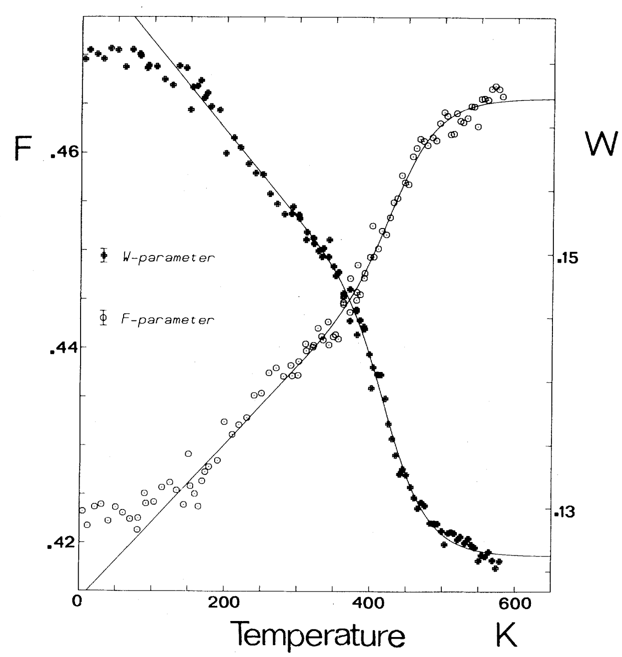

FIG. 2. Temperature dependence of the line-height parameter F and the wing parameter W for photons emerging in the [10$\bar{1}$0] direction. Typical error bars are shown.

cancies in cadmium, the vacancy formation entropies are high[16,17] ($S_v = 3.00k$ and $2.88k$, respectively). The estimated vacancy concentrations at the melting point are $C_v = 1.03\times 10^{-3}$ and 0.56×10^{-3}. Significantly higher values of H_v, S_v, and C_v are obtained if the parameter F_v is allowed a temperature dependence (i.e., $\alpha > 0$). Feder and Nowick[18] obtained 0.40 ± 0.2 eV for a single cadmium crystal from dilatometric expansion measurements above 293 K. These values cannot easily be reconciled, and the validity of the conventional linear subtraction procedure must be seriously questioned.

The extraordinary aspect of the results is that the prevacancy rise depends significantly on the direction of emission of the 511-keV radiation with respect to the crystal lattice. The fitted linear slopes (β) for the F parameter are (A) 0.97×10^{-4} K^{-1} and (B) 1.94×10^{-4} K^{-1}. (N.B. these are not absolute numbers because F is definition dependent.) At the lowest temperatures (< 100 K) the curves are flatter and they have remained unchanged in spite of several extra annealings—unlike gold[19] and lead[20] where it was found that the intermediate slopes continued downwards.

Cadmium is a hexagonal close packed crystal with a c/a ratio of 1.886, and it exhibits many anisotropic characteristics. It is important to note that the coefficients of thermal expansion at 293 K (0.54×10^{-4} K^{-1} and 0.20×10^{-4} K^{-1})[21] along the c [0001] and a axes, respectively, bear approximately the opposite relationship to the values of the prevacancy slopes (β) given above.

In our opinion the origin of the prevacancy rise with temperature in the parameter F remains an open question. The observed anisotropies must arise from the changing character of the asymmetrical environment in which the positrons annihilate. The present evidence cannot indicate whether these spaces are those of a simple lattice or possibly the sites of self-trapping. Alternatively, the results would be consistent with trapping in remnant oriented defects—e.g., dislocation lines lying the the [0001] slip planes—that can survive annealing, with a temperature-dependent effective trapping rate.

The significance of these results lies in the sensitivity of the positron wave function to anisotropies of the medium: Only the development of a directionally dependent theoretical model for the prevacancy behavior of positrons in metals as a function of temperature will reveal the true implications for the deduction of vacancy formation enthalpies.

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