Effect of Ordering on Monovacancy and Divacancy Formation in β-Brass Observed by Positron Annihilation

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Measurements of the trapping of positrons in β-brass have shown that the vacancy formation energy dramatically increases with the ordering of the alloy below the order-disorder transition temperature. Based on predictions from our trapping-model analysis of the monovacancy behavior, we have searched for, and found above 430 °C, direct evidence for the cusp-shaped rise in the trapping of positrons by divacancies that is characteristic of the rapid growth in the thermal divacancy population as the order parameter goes to zero.

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The ordering of atoms in alloys causes important changes in mechanical and physical properties. Thus it is of considerable interest to know how the point-defect properties, such as formation and migration of vacancies, are affected by the ordering of atoms. We have chosen the bcc order-disorder alloy β-brass for a detailed study by the positron-annihilation–peak coincidence technique. Because positrons can be trapped at a very low concentration of vacancies, the technique is a sensitive probe of monovacancy formation energies in metals,[1] and has been used to determine the change in the vacancy concentration across magnetic and structural phase transitions.[2]

The applicability of the technique to the observation of divacancies has not yet been clearly demonstrated. Doppler line-shape measurements in β-brass[3] showed that positron trapping at monovacancies saturates at about 350 °C, which is well below the ordering temperature (T_c = 462 °C) or the melting temperature (T_m = 870 °C). Thus by extending positron measurements to higher temperatures, divacancies are likely to be detected. Although high-temperature equilibrium measurements of vacancy concentration in pure metals have often been interpreted by assuming the presence of divacancies,[1,4] there has been no sharp feature in the data itself that could be attributed to divacancies. Other positron measurements on β-brass near T_c have been made, but these were of a survey nature, and some have subsequently been found to be nonreproducible.[5,6]

In this Letter we report the first observation by positron trapping of a vacancy formation energy that grows rapidly with the growth of long-range order in an alloy. We also report what we believe to be the most clearcut example of trapping at divacancies. The β-brass specimen (Cu, 48 wt.% Zn) was from the same ingot used by Schultz *et al.*[3] and was prepared from 99.999% Cu and Zn. Quantitative energy-dispersive x-ray spectroscopy confirmed the Cu/Zn ratio of the β' phase. The specimen was examined for possible α-phase peaks by means of neutron diffraction and x-ray diffraction. None was found and all peaks could be indexed as β' phase. To minimize dezincification, the measurements were made in a 27-kPa argon atmosphere for $T \leq 560$ °C. A disk-shaped specimen (1 cm × 0.64 cm) was attached to an Ohmically heated iron strip described previously.[2] With Chromel-Alumel thermocouples on the sample, the temperature was controlled to ± 1 °C for measurements between 100 and 320 °C and ± 2 °C for other temperatures. The specimen surface facing the external ^{64}Cu positron source was positioned to within 0.05 mm at all temperatures. About $(4-5)\times10^5$ peak counts were accumulated at each temperature in five to seven scans with a resolution of 1 mrad × 93 mrad. Precise angular correlation measurements at 8 °C before and after these scans showed no evidence of dezincification.

The results (Fig. 1) show an S-shaped rise and complete saturation of positron trapping at monovacancies between 8 and 430 °C. In the Doppler measurements of Schulz *et al.*,[3] however, the wing parameter (the wing normally varies inversely to the peak rate) first increases and then decreases as the temperature is raised above 100 °C. This anomaly does not appear in our peak rate, except for the preliminary scans between 5 and 240 °C. These scans showed a similar anomaly that annealed out on subsequent temperature cycles. We believe, therefore, that the behavior observed by Schultz *et al.* was not an equilibrium property of β-brass. As the temperature is

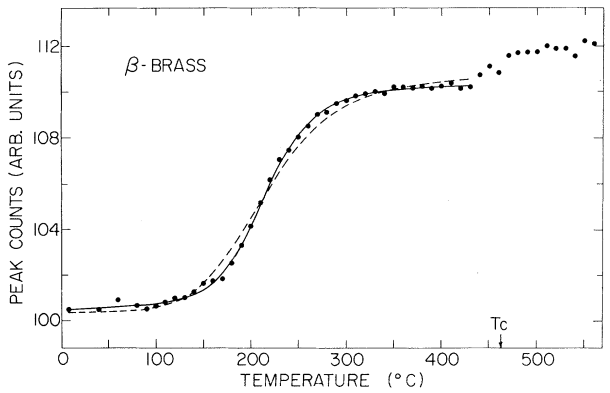

FIG. 1. The peak coincidence counts (solid circles) in β-brass between 8 and 560 °C. The broken curve is the normal–trapping-model fit with $A_v = 3\times10^5$, and the full curve takes into account the effect of ordering on vacancy formation. These fits were made for peak rates below 430 °C.

raised further the peak rate shows a rapid rise just below T_c, the order-disorder transition temperature, and then rises slowly up to 560 °C. We attribute this rise to positron trapping at equilibrium divacancies. The rise cannot be due to monovacancies from a minority phase of α-brass because (1) the monovacancy rise in α-brass is much too slow near 450 °C,[7] and (2) a rise of the magnitude observed would require at least 20% of α-brass whereas neutron diffraction has set an upper limit of 1% on any α-brass contamination.

The peak-rate data between 8 and 430 °C were first analyzed according to the trapping model, which has been widely used in previous positron studies and in which the monovacancy concentration is assumed to be controlled by a constant formation energy E_v^f. In this model the temperature dependence of the peak rate is given by[1]

$$F(T)=\frac{F_f(1+\alpha T)+F_v(1+\beta T)A_v\exp(-E_v^f/kT)}{1+A_v\exp(-E_v^f/kT)}, \quad (1)$$

where F_f and F_v are the free and trapped peak rate, α and β are thermal expansion parameters, and $A_v=\mu_v\tau_f\exp(S_v/k)$, where μ_v is the trapping rate, τ_f the free-positron lifetime, and S_v the nonconfigurational entropy of vacancy formation. A least-squares analysis of the data ($\chi=0.82$) with use of Eq. (1) gave $E_v^f=0.80\pm0.04$ eV but with an unacceptably high trapping parameter, $A_v=1.9\times10^8$. This value is two to three orders of magnitude larger than almost all the previous measurements of A_v.[1,2] On the other hand, when the parameter A_v was constrained to lie within a reasonable range, 0.5×10^5 to 1.5×10^6,[1,2,8] a good fit could not be obtained. As an example we show in Fig. 1 by a broken curve the poor fit obtained with $A_v=3\times10^5$ and $\alpha=\beta=0$ (because the model is poor, both α and β become negative if allowed to vary). This fit gave $E_v^f=0.53$ eV with $\chi=1.92$. Clearly the peak rate in β-brass cannot be described with a constant E_v^f and reasonable values for the trapping parameter A_v. When allowance is made, however, for an increase in vacancy formation energy as the alloy orders, a good fit is obtained with a reasonable value for A_v. Physically this is to be expected because the mean vacancy-formation energy, E_v^f, exceeds that in disordered β-brass when atoms of one type begin to be surrounded by atoms of the other type, since the strength of a Cu-Zn atomic bond is stronger than the average strength of a Cu-Cu bond and Zn-Zn bond. Indeed it is this same difference, $v=v_{\mathrm{Cu-Zn}}-\frac{1}{2}(v_{\mathrm{Cu-Cu}}+v_{\mathrm{Zn-Zn}})$, that drives the order-disorder phase transition.

Girifalco[9] calculated the dependence on order parameter of the vacancy formation energy within a localized bonding model based on the Bragg-Williams (mean field) approximation and obtained for β-brass $E_v^f(T)=E_v^f(0)+2vR^2(T)$, where $E_v^f(0)$ is the vacancy formation energy in the disordered phase and $R(T)$ is the order parameter. With use of this equation and with the x-ray[10] or neutron data[11] on $R(T)$, a good fit to our peak rate could not be obtained for any value of v, but a good fit can be obtained if we assume, for $T\geq300$ K, that

$$E_v^f(T)=E_v^f(0)+U(1-T/T_c)^{1/2}, \quad (2)$$

where U is a constant ($U=0$ for $T>T_c$). Since ordering is complete below 300 K,[10,11] we set $E_v^f(T<300\ \mathrm{K})=E_v^f(300\ \mathrm{K})$. It is known that for a pure metal, which has a constant configurational entropy per vacancy, if E_v^f varies with temperature S_v also varies with temperature, but the effect is small.[4,12] In an ordered alloy, however, the configurational entropy varies with temperature (or order parameter) via the random probabilities of occurrence of local configurations, and this we expect to give rise to the dominant variation of E_v^f with temperature. In the presence of this large entropy variation, the variation of nonconfigurational or phonon entropy is relatively small, as in a pure metal, and is assumed here to be temperature independent.

We have fitted our peak-rate data using Eqs. (1)

and (2) for various values of U, the order-induced part of E_v^f, assuming that A_v lies within a reasonable range. Good fits to the data ($\chi = 0.80$–0.81) were obtained with U in the range of 0.36–0.61 eV, which gave a range for $E_v^f(0)$ of 0.10–0.38 eV with 0.71 eV $\leq E_v^f(0) + U \leq 0.75$ eV. In Fig. 1 we show with a full curve the fit ($\chi = 0.80$) obtained with U fixed at 0.4 eV. Other parameters are $E_v^f(0) = 0.35 \pm 0.04$ eV, $A_v = (9.4 \pm 8.6) \times 10^5$, $\alpha = (2.8 \pm 1.2) \times 10^{-5}/°C$, and $\beta = (1.5 \pm 1.0) \times 10^{-5}/°C$. Both α and β are much smaller than the volume-thermal-expansion coefficients in β-brass of $8.7 \times 10^{-5}/°C$. The low value of $E_v^f(0)$ can be attributed partly to the dependence of E_v^f on the electron-per-atom ratio[3] and partly to the crystallographic structure (bcc) of β-brass, since it has been found from work on Fe and stainless steels that E_v^f is appreciably lower in low-coordination bcc phases than in fcc phases.[2,8]

Kuper *et al.*[13] measured the activation energy, Q, for diffusion of Zn in β-brass and found that Q increases from 0.81 eV in the disordered phase to ~1.5 eV in the nearly ordered phase. We have analyzed their data assuming that Q depends on temperature as $Q(T) = Q(0) + W(1 - T/T_c)^{1/2}$, similar to Eq. (2), where $Q(0)$ is the activation energy in the disordered phase and W is a constant ($W = 0$ for $T > T_c$). We obtained a good fit with $Q(0) = 0.81$ eV and $W = 0.49 \pm 0.06$ eV. This suggests that ~65% or more of the order-induced change in $Q(T)$ in β-brass is due to the order-induced change in $E_v^f(T)$ since $Q(T) = E_v^f(T) + E_v^m(T)$, where $E_v^m(T)$ is the vacancy migration energy.

These results point up inadequacies in the existing theories for the phase transition and vacancy formation in order-disorder alloys. For example, the models of Girifalco[9,14] predict that T_c is within 16% of the mean-field result, $kT_c = \frac{1}{2}zv$, where z is the coordination number, and that $0.77U \sim zv/4$. From the observed transition temperature of 735 K, he then deduces $U \sim 0.04$ eV, an order of magnitude smaller than that determined from the present positron studies. Our results show that current theories of alloys need to be extended so as to be consistent with both alloy ordering temperatures and measured vacancy-formation energies.

The strong temperature dependence of the monovacancy formation energy necessarily entails that the divacancy formation energy, E_{2v}^f, also decreases strongly with temperature since $E_{2v}^f = 2E_v^f - E_{2v}^B$, where E_{2v}^B is the divacancy binding energy. Indeed, we find that the steep rise of peak rate just below T_c, shown in Fig. 1, can be understood from the trapping model if and only if E_{2v}^f decreases rapidly as the temperature is raised to T_c. We now show that the same description already developed for the monovacancy formation energy does in fact predict a sharp rise due to divacancies in agreement with our observations. When positron trapping at divacancies is included in the trapping model, it is easy to show that[1]

$$F(T) = \frac{F_f(1+\alpha T) + F_v(1+\beta T)A_v \exp(-E_v^f/kT) + F_{2v}(1+\gamma T)A_{2v} \exp[-(2E_v^f - E_{2v}^B)/kT]}{1 + A_v \exp(-E_v^f/kT) + A_{2v} \exp[-(2E_v^f - E_{2v}^B)/kT]}, \quad (3)$$

where F_{2v} and γ are the peak rate and its temperature dependence for positrons trapped at divacancies, and $A_{2v} = \frac{1}{2}z\mu_{2v}\tau_f \exp[(2S_v + \Delta S_{2v})/k]$, where ΔS_{2v} and μ_{2v} are the association entropy and trapping rate for divancies. Since calculations[15] show that $\mu_v < \mu_{2v} < 3\mu_v$, the parameter A_{2v} can be estimated to be in the range $(15\text{–}200)A_v$ if we take $S_v \simeq (0.4\text{–}0.8)k$ and $\Delta S_{2v} \simeq (1\text{–}2)k$, the values suggested by Seeger and Mehrer[4] for Al, Cu, and Au. With these parameters the rise in peak rate due to positron trapping at divacancies would be very gradual if E_v^f is constant. Our knowledge of how E_v^f falls with temperature, however, predicts a consequent exponential enhancement of the divacancy contribution that is quite sufficient to explain the cusp-shaped rise in peak rate between 430 °C and T_c.

To assess the consistency of our monovacancy and divacancy descriptions, the entire peak-rate data shown in Fig. 1 were fitted with Eqs. (2) and (3) for various values of U and A_{2v} under the assumption that $E_{2v}^B > 0$, $5 \times 10^4 \leq A_v \leq 1.5 \times 10^6$, and $\beta = \gamma \geq 0$. Good fits ($\chi = 1.03$–1.05) could only be obtained with U in the range 0.36–0.44 eV, which gave $E_v^f(0)$ in the range 0.30–0.39 eV. In Fig. 2, we show with a full curve the fit obtained with $U = 0.4$ eV. The other parameters are $E_v^f(0) = 0.34 \pm 0.03$ eV, $E_{2v}^B = 0.07 \pm 0.08$ eV, $A_v = (7.7 \pm 6.1) \times 10^5$, $A_{2v} = 2.2 \times 10^7$, $\beta = \gamma = 0$, and $F_{2v}/F_v = 1.045 \pm 0.012$. The fact that the entire peak-rate data can be described well with values of important parameters $[E_v^f(0), U, A_v]$ very close to those that describe the monovacancy trapping region only, confirms our hypothesis that the rise below T_c is caused by thermally activated divacancies.

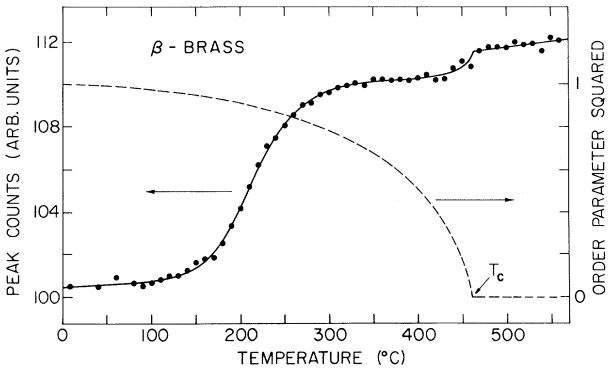

FIG. 2. The peak coincidence counts (solid circles) in β-brass between 8 and 560 °C. The full curve is a trapping-model fit which takes into account the effect of ordering on monovacancy and divacancy formation. The broken curve is the square of the order parameter of Ref. 10.

We conclude that the vacancy formation energy in β-brass increases strongly with the degree of order. As a result, it has been possible to observe in a clearcut manner by the positron technique, the rapid formation of equilibrium divacancies below T_c driven by the falling order parameter.

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Infrared and Optical Properties of Sodium Metal

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A surface-plasmon–mediated absorption mechanism is proposed to explain the measured frequency dependences of both the optical conductivity and infrared mass of smooth sodium surfaces.

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In this Letter, it is proposed that the observed optical conductivity feature in Na which has been identified with interband transitions is instead the signature of a surface-plasmon–mediated absorption process, i.e., a Holstein-like process[1] where within an electromagnetic skin depth the electron simultaneously absorbs an incident photon and emits a surface plasmon. A phenomenological model based on this idea is shown to be consistent with the optical data and the calculated band mass.

The optical properties of the alkali metals have been measured many times over the last two decades.[2,3] Much of the early stimulus was provided by the work of Mayer and co-workers,[4] who found in bulk samples an additional absorption anomaly at frequencies smaller than the optical feature associated with interband transitions. Although recent measurements[5] seem to indicate that this extra absorption feature is activated by