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Self-Trapping of Positively Charged Particles in Metals

A. Seeger
Max-Planck-Institut für Metallforschung, Institut für Physik,
and Institut für theoretische und angewandte Physik,
University of Stuttgart, D-7000 Stuttgart, Fed. Rep. Germany

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Abstract. It is shown that the existence of a metastable state in which positrons in metals are "self-trapped" by strong interaction with the lattice gives rise to an anomalous temperature dependence in positron annihilation properties. The "intermediate" temperature variation of the shape of the annihilation photon line discovered by MacKenzie *et al.* is well accounted for by this mechanism; alternative interpretations in terms of thermal expansion effects may be refuted. This result calls for considerable revision of some of the published monovacancy formation energies obtained from positron annihilation measurements. Approximate criteria for the existence and the metastability of a self-trapped state of positively charged particles in metals are given. It is found that metastable self-trapping may occur for positrons; hydrogen isotopes and positive muons should be self-trapped in configurations that are always stable relative to the Bloch-wave states of these particles.

Index Headings: Self-trapping in metals – Positrons – Monovacancy formation energies

Following the application of the so-called trapping model [1, 2] to the pioneering experiments of MacKenzie *et al.* [3], the measurement of the temperature dependence of positron annihilation in metals has become an important tool for the determination of the formation enthalpy of monovacancies, H_{1V}^F. (For reviews see [4–8].) Recently Lichtenberger *et al.* [9] have called attention to an anomaly in the temperature dependence of positron annihilation in metals which in a number of cases may interfere with the determination of H_{1V}^F from positron annihilation data.

Using the specific case of the S-parameter characterizing the lineshape of the photon annihilation line in cadmium, Lichtenberger *et al.* [9] show that there is very little temperature dependence between 100 and 230 K, an approximately linear increase of the S-parameter with temperature between 230 and 360 K, followed by the stronger temperature dependence, with saturation near the melting point, characteristic for the trapping of positrons by point defects in thermal equilibrium. The entire temperature dependence is reversible. Since there is strong evidence that the temperature dependence above 360 K is indeed due to positron trapping by the point defects with the highest equilibrium concentration, viz., the monovacancies, the "intermediate" temperature dependence between 230 and 360 K cannot be due to defects in thermal equilibrium. As Lichtenberger *et al.* [9] emphasized it cannot be due to thermal expansion either, since in such a case one could not understand the break in the temperature variation of S at about 230 K. Rather, from the small temperature dependence of S and of other parameters characterizing positron annihilation at low temperatures we may conclude that the effect of thermal expansion on the annihilation of "free" or "untrapped" positrons is small.

Similar results were obtained on other metals, among them Cu and Pb [10], so that the existence of the intermediate temperature dependence appears to be

a fairly general phenomenon in metals. It is not confined to the shape of the annihilation line, i.e., to Doppler broadening, either. The temperature variation of the angular correlation of the noble metals [11, 12] shows such an "intermediate" temperature dependence below the trapping-by-monovacancies regime, too, extending down to about room temperature. Triftshäuser and McGervey [12] are of the opinion that this temperature dependence is a thermal expansion effect.

Angular correlation and Doppler broadening are very similar; they both probe the momentum or velocity distribution of the electrons in the metal. Therefore, the reasoning given above indicates strongly that the intermediate temperature variation in the angular correlation experiments should not be attributed to thermal expansion. A further argument leading to the same conclusion, though not as clear-cut as the preceding one, is the following: From a theoretical viewpoint it is not at all clear that the annihilation of free positrons in metals should show a temperature dependence as strong as the bulk thermal expansion coefficient of metals [13], let alone a stronger one as has to be assumed in the interpretation of Triftshäuser and McGervey [12].

From the preceding discussion it follows that the intermediate temperature dependence is neither associated with lattice defects in thermal equilibrium nor with thermal expansion. Its explanation is likely to lie in the interaction of thermalized positrons with the crystal lattice, possibly taking the form of a self-trapping effect. An explanation along this line of reasoning has been proposed by Lichtenberger *et al.* [9]. However, any such explanation has to overcome the difficulty that the intermediate temperature dependence sets in very suddenly, whereas at low temperatures the "self-trapping" is not seen at all. This is incompatible with the idea that a self-trapped positron has a lower free energy than a free ("Bloch-wave type") positron. We shall show that the answer to this problem lies presumably in a self-trapped positron configuration with a *negative* binding energy, i.e., one which is *metastable* with respect to a free positron state.

Self-trapping of charged particles has first been treated theoretically in ionic crystals, and important insights into the present problem may be obtained from this work. We shall therefore begin the qualitative discussion of Section 2 with a review of the relevant results on ionic crystals. The semi-quantitative treatment of Section 3 will indeed start from a recent paper of self-trapping in ionic crystals [14]. It is important to realize that experimentally the self-trapping of positively charged particles in metals has been with us for a long time: Most of the experiments on hydrogen in metals are interpreted in terms of protons localized on interstitial lattice sites and moving by a thermally activated trapping process. We should therefore view the problem of self-trapping of an elementary positive charge in a metal as a fairly general problem, in which the mass of the particle plays an important rôle. Positrons form just one end of a sequence, with protons, deuterons etc. on the other end, and positive muons (with 207 times the positron mass or 1/9 of the proton mass) in between. For simplicity, in our theoretical treatment we shall refer to the particle carrying the elementary positive charge as "positron" and consider its mass as one of the variables of the problem.

1. Qualitative Discussion of Self-Trapping

In an attempt to account for the phenomena in ionic crystals now known to be associated with F-centres, Landau [15] introduced the concept of a self-trapped electron. The electric field exerted by the electron on the neighbouring ions may displace the ions in such a way that an attractive potential, behaving at large distances r as $-e^2(\varepsilon_\infty^{-1}-\varepsilon_0^{-1})/r$, is set up ($\varepsilon_\infty$ = high-frequency dielectric constant, ε_0 = static dielectric constant, e = elementary electric charge). In this potential well a series of bound states for an electron is formed; an electron in such a bound state surrounded by a polarized medium may form a stable configuration. Mott and Gurney [16], who discussed this "Landau trapping" in some detail, called such an electron "trapped by digging its own hole". They pointed out that analogous arguments predict the self-trapping of *positive holes* in ionic crystals. The electron spin resonance work of Castner and Känzig [17] has demonstrated that in a number of alkali halides positive holes may indeed be self-trapped, though more by the formation of halogen molecule-ions than by developing strong polarisation fields around the holes.

The theory of the interaction of electrons or positive holes with the lattice polarization of ionic crystals was developed under the name "polaron" theory in considerable detail by Pekar [18], Fröhlich [19], Feynman [20] and others (for reviews see Fröhlich [19], Appel [21], and Jones and March [22]). The strength

of this interaction is determined by the magnitude of the coupling constant

$$\alpha = \frac{e}{h}\left(\frac{m^*}{2h\omega_l}\right)^{1/2}, \tag{1}$$

where ω_l denotes the circular frequency of longitudinal optical phonons, m^* the band-mass of the electrons or holes, and h Planck's constant.

An important result of the above-mentioned work on "polaron theory" is that the transition, with increasing α, from "free" electrons and holes to self-trapped quasi-particles does not involve any discontinuities. In 1961, however, Toyozawa [23] showed that if the interaction with acoustical phonons is included, the polaron properties may change *discontinuously* as a function of the coupling strength between the electrical charge and the acoustical phonons. This difference is associated with the fact that the interaction of an electron or hole with the optical phonons is of long range, whereas that with the acoustical phonons is of short range [23, 24]. The significance of the range of the interactions for the self-trapping problem had already been stressed by Mott and Gurney [16]. Sumi and Toyozawa [24] showed that the existence or non-existence of a discontinuity as a function of the coupling parameters does not depend on whether a continuum or a discrete description for the crystal is used, provided in the former description a Debye-type cut-off is introduced.

Because of the screening of electric fields by a redistribution of the conduction electrons, the interaction between an additional electric charge and the ions in a *metal* is of short range, hence the arguments of Toyozawa [23] and Sumi and Toyozawa [24] should be applicable. In metals we may thus expect a discontinuity as a function of the strength of the interaction. If the coupling between the electric charge and the phonons is sufficiently strong, two different configurations associated with the extra charge are possible: One in which the interaction is weak, i.e., in which the charged particle remains in what is essentially a Bloch state, and another one which corresponds to the self-trapping picture outlined above, i.e., a strongly localized wave-function.

If the coupling strength is such that both configurations are "mechanically stable", one of them will in general be metastable with respect to the other. As will be borne out by the quantitative treatment of Section 3, it is the *negative* binding energy of the self-trapped state which is needed to account for the "intermediate" temperature variation of positron annihilation, as recently observed by Lichtenberger *et al.* [9, 10] on a number of metals.

2. Quantitative Treatment of Self-Trapping in Metals

An elementary positive charge inserted into a metal is "screened" within a distance comparable with the interatomic distance [25, 26]. In a simplified picture this screening effect may be thought of as consisting of two contributions: (i) Near the inserted charge the conduction electrons, attracted by the positive charge, redistribute themselves in such a way that a self-consistent screening is achieved. (ii) The positively charged ion cores near to the inserted positive charge are pushed away. This results in a local reduction of the total positive charge to be screened by the conduction electrons.

Mechanisms (i) and (ii) are clearly coupled. Unfortunately a convincing solution of the coupled problem has not yet been found inspite of a large amount of good work on the individual problems. Fortunately, for answering the main question of the present paper a simple treatment of the coupled problem suffices. Following Toyozawa and Sumi [14] we describe the interaction between the positron wavefunction $\Psi_+(\boldsymbol{r})$ and the crystal in the simplest possible way, namely through a coupling of the elastic dilation $\Theta(\boldsymbol{r})$ with the positron charge density $|\Psi_+(\boldsymbol{r})|^2$, and use the following "Ansatz" for the energy functional

$$\begin{aligned} E[\Psi_+, \Theta] &= \frac{K}{2}\int [\Theta(\boldsymbol{r})]^2\, d^3\boldsymbol{r} \\ &+ \varepsilon_d \int [\Psi_+(\boldsymbol{r})]^2 \cdot \Theta(\boldsymbol{r})\, d^3\boldsymbol{r} + \frac{\hbar^2}{2m_+}\int [\nabla\Psi_+(\boldsymbol{r})]^2\, d^3\boldsymbol{r}\,. \end{aligned} \tag{2}$$

In (2) the first term represents the elastic energy associated with the dilation (K denotes a combination of elastic constants containing the modulus of compression but also shear moduli, since a more complete treatment should take into account also the long-range shear field associated with a centre of elastic dilation), the second term the coupling between the positive charge and the elastic strain (ε_d denotes the positron deformation potential parameter introduced earlier [28]), and the third is the kinetic energy associated with the positron wavefunction $\Psi_+(\boldsymbol{r})$. Here $\hbar$ denotes Planck's constant divided by 2π, and m_+ the positron band mass. All integrations in (2) extend over the entire crystal.

By minimizing (1) with respect to the positron wave-function $\Psi_+(r)$ we obtain the adiabatic potential $E[\Theta(r)]$ for the lowest positron state as a functional of $\Theta(r)$. The extrema of this potential can alternatively be found by extremizing (2) first with respect to Ψ_+ and subsequently with respect to Θ. The first step gives us

$$\Theta(r) = -\frac{\varepsilon_d}{K}|\Psi_+(r)|^2 \tag{3}$$

and, after inserting (3) into (2),

$$E[\Psi_+] = \frac{\hbar^2}{2m_+}\int[\nabla\Psi_+]^2\,d^3r - \frac{\varepsilon_d^2}{2K}\int[\Psi_+(r)]^4\,d^3r\,. \tag{4}$$

Since a spherically symmetric solution of the differential equation resulting from the extremalization of (4) cannot be found is closed form, we follow Toyozawa and Sumi [14] further in using the trial function

$$\Psi_+(r) = (2\kappa^2)^{3/4}\exp(-\pi\kappa^2 r^2)\,, \tag{5}$$

where κ is an adjustable parameter with the dimension of a wavenumber. Insertion of (5) into (4) gives us for the energy of the system

$$E(\kappa) = \frac{3\pi\hbar^2}{2m_+}\kappa^2 - \frac{1}{2}\frac{\varepsilon_d^2}{K}\kappa^3\,. \tag{6}$$

As a function of κ, (6) has a minimum at $\kappa = 0$. This minimum, corresponding to the positron energy $\varepsilon = 0$, represents a non-localized positron, i.e., a Bloch-wave type of solution if the periodic lattice potential had been allowed for.

A second minimum of (6) may arise because of the physical meaning of κ as a wave-number, which introduces an upper cut-off κ_0 approximately equal to a reciprocal interatomic distance. Whether such a second minimum, with energy

$$\varepsilon(\kappa_0) = \frac{3\pi\hbar^2\kappa_0^2}{2m_+} - \frac{1}{2}\frac{\varepsilon_d^2\kappa_0^3}{K}\,, \tag{7}$$

exists, depends on whether the maximum of (6) occurs at a value

$$\kappa_{\max} = 2\pi\frac{K}{\varepsilon_d^2}\frac{\hbar^2}{m_+} \tag{8}$$

that is smaller than κ_0.

The minimum at κ_0 corresponds to a very concentrated positron wave-function, i.e., to a *localized* positron. The centre of the positron wave-function is surrounded by a localized dilation field according to (3) and (5)[1]. This means that we are dealing with an analogue to the "polaron", namely a positron self-trapped by strong interaction with *acoustic* phonons. The properties (lifetime, mobility, etc.) of these self-trapped positrons are different from those of the "free" (Bloch-wave type) positrons; we shall distinguish the two states by subscripts *st* and *f*, respectively.

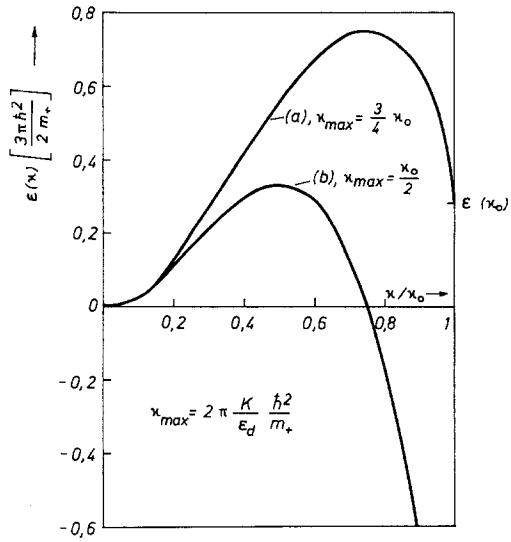

Fig. 1. Energy of positively charged particles in metals (in units of $3\pi\hbar\kappa_0^2/2m_+$) as a function of κ/κ_0 according to (6). (a): Energy minimum at $\kappa = \kappa_0$ metastable with respect to that at $\kappa = 0$. (b): Energy minimum at $\kappa = \kappa_0$ stable with respect to that at $\kappa = 0$

If the condition

$$\kappa_{\max} < \kappa_0 \tag{9}$$

is satisfied, two basically different situations may arise (Fig. 1): (i) $\varepsilon(\kappa_0) > 0$ (Fig. 1, curve a). Then the self-trapped state is metastable relative to low-lying free positron states. At very low temperatures all positrons will be in Bloch states, but with increasing temperature an increasing fraction of them will become self-trapped. As will be discussed in more detail below, this results in an additional temperature dependence of the experimentally observed positron properties.

(ii) $\varepsilon(\kappa_0) < 0$ (Fig. 1, curve b). In this case the self-trapped state is stable, whereas the free positron states are metastable. However, this case is less likely to be

[1] This localized dilation field may be considered as a centre of dilatation. It is surrounded by shear strains decaying at large distance r as r^{-3}. Since in metals the interaction of extra charges with shear strains is weaker than that with dilations, we have neglected the long-range strain field.

realized than case (i), since the condition $\varepsilon(\kappa_0)<0$ is considerably stronger than (9). This may be seen by rewriting (7) as

$$\varepsilon(\kappa_0)=\frac{3\pi\hbar^2}{2m_+}\kappa_0^2\left(1-\frac{2}{3}\frac{\kappa_0}{\kappa_{\max}}\right). \tag{10}$$

When working out, for the case $\varepsilon(\kappa_0)>0$, the temperature dependence of the fractions f_f of free and f_{st} of self-trapped positrons, one has to take into account the fact that the state $\kappa=0$ is the lowest state of a quasi-continuum of Bloch states, with three-dimensional wave-vectors k as good quantum numbers. Application of quantum statistics gives us

$$f_f(T)=\frac{1}{1+AT^{-3/2}\exp[-\varepsilon(\kappa_0)/k_BT]} \tag{11a}$$

$$f_{st}(T)=\frac{1}{1+A^{-1}T^{3/2}\exp[\varepsilon(\kappa_0)/k_BT]}=1-f_f(T). \tag{11b}$$

In (11) k_B denotes Boltzmann's constant, T the absolute temperature and

$$A\equiv\prod_j\left(\frac{\nu_j}{\nu_j'}\right)(2\pi\hbar^2/m_+k_B)^{3/2}/\Omega_0, \tag{11c}$$

where Ω_0 = atomic volume and ν_j, ν_j' = vibrational frequencies of the crystal with free or self-trapped positrons. The product $\prod_j$ extends over all vibrational modes of the crystal; it is expected to be smaller than but not very different from unity.

The dimensionless quantity $AT^{-3/2}$ is always very much larger than unity. For $\varepsilon(\kappa_0)>0$, i.e., case (i) above, the interesting possibility arises that at a temperature T^* which is well below $\varepsilon(\kappa_0)/k_B$ a change-over takes place from $f_{st}/f_f\ll 1$ to $f_{st}/f_f\gg 1$. The condition for the temperature T^* at which $f_{st}=f_f=1/2$ reads

$$\varepsilon(\kappa_0)=k_BT^*\ln(A/T^{*3/2}). \tag{12}$$

In the temperature range of this transition one observes a weighted average of a positron property F according to

$$F(T)=F_ff_f(T)+F_{st}f_{st}(T). \tag{13}$$

3. Discussion

We propose that the "intermediate" temperature dependence in positron properties pointed out by Lichtenberger *et al.* [9, 10] and also shown in other experimental work [11, 12] is caused by the additional temperature variation introduced by a meta-

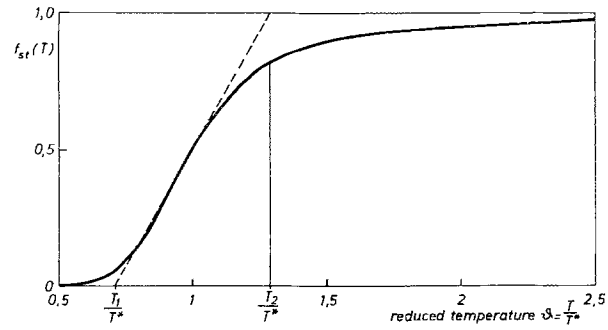

Fig. 2. Fraction f_{st} of self-trapped positrons ($\varepsilon(\kappa_0)>0$) as a function of the reduced temperature $\vartheta=T/T^*$. For the definitions of T_1, T_2, and T^* see text

stable self-trapped state according to (13). In Fig. 2 we have plotted $f_{st}(T)$ as a function of the reduced temperature

$$\vartheta=T/T^* \tag{14}$$

under the assumptions $\varepsilon(\kappa_0)>0$, $T^*=400$ K, $\Omega_0=12.10^{-30}$ m^3, $\prod_j(\nu_j/\nu_j')=1$ and $m_+=m_0$ = free electron mass. These assumptions give $A/T^{*3/2}=4.31\cdot 10^3$ and $\varepsilon(\kappa_0)=0.288$ eV. We see that the fraction of self-trapped positrons is negligible for $\vartheta<0.6$, and that for $\vartheta\gtrsim 2.5$ practically all positrons are self-trapped. The additional temperature dependence of a positron property $F(T)$ according to (13) is highly non-linear. This explains why the self-trapping effect is not seen at low temperatures. The approximate linearity of the temperature dependence in an intermediate temperature regime [9, 11, 12] is seen to result from the fact that over a limited temperature range near $\vartheta=0.9$ Eq. (13) may be approximated by a linear T-dependence.

In the simplest case that F_f and F_{st} may be considered as temperature independent the application of the present theory to the analysis of experiments involves the adjusting of four parameters, namely F_f, F_{st}, A, and $\varepsilon(\kappa_0)$. F_f may be easily found from measurements of F at sufficiently low temperatures. In metals in which positrons are trapped by vacancies in thermal equilibrium, F_{st} must be found by a curve-fitting procedure based on the trapping model and (13). Such a fitting procedure will also give A and ε_0. An estimate of ε_0 can be obtained in the following way: An empirical straight-line approximation to $F(T)$ in the intermediate temperature regime will have approximately the slope

$$F_f(df_f/dT)_{T=T^*}+F_{st}(df_{st}/dT)_{T=T^*}=(F_f-F_{st})\frac{1}{4T^*}\left(\frac{3}{2}-\ln\frac{A}{T^{*3/2}}\right). \tag{15}$$

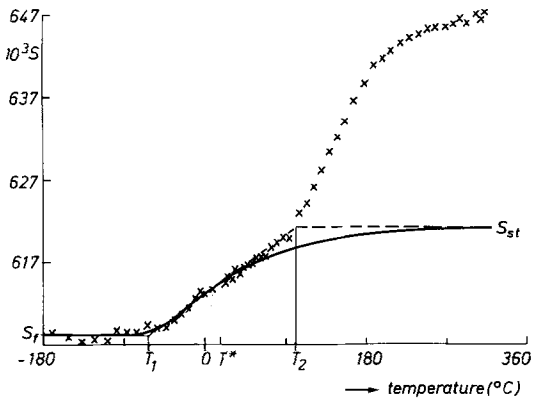

Fig. 3. Temperature dependence of S-parameter characterizing the photon line-shape of positron annihilation of Cd. The full curve gives the fit according to (13), as described in the text

This straight-line approximation intersects the straight-line approximation to the low-temperature regime at a temperature

$$T_1 = T^* \left[1 - \frac{2}{\ln\left(\frac{A}{T^{*3/2}}\right) - \frac{3}{2}} \right]. \tag{16}$$

With the help of estimates of the parameters entering into A one may obtain T^* from the experimental value T_1 and thus, with the help of (12), the energy $\varepsilon(\kappa_0)$. In the example of Fig. 2 we have $T_1 = 0.71\ T^*$. An estimate of F_{st} may be obtained from the rule of thumb that in an $F-T$ plot the straight line $F = F_{st}$ is intersected by the straight-line approximation to the intermediate regime at a temperature

$$T_2 = T^* \left[1 + \frac{2}{\ln\left(\frac{A}{T^{*3/2}}\right) - \frac{3}{2}} \right]. \tag{17}$$

Figure 3 shows the application of the theory to the measurements of the parameter S characterizing the lineshape of the annihilation photons in Cd [9]. We have chosen (somewhat arbitrarily) A as in Fig. 2 and find that an excellent fit may be obtained with $T^* = 292$ K ($T_1 = 210$ K, $T_2 = 374$ K, $\varepsilon(\kappa_0) = 0.21$ eV). The deviations of the measurements from this fit become detectable from about 340 K upwards. In Cd this corresponds to a vacancy concentration in thermal equilibrium of about 10^{-6} [6].

In the case of copper Lichtenberger's measurements indicate $T_1 \approx 335$ K. We choose A equal to between a third and a quarter of the above value and find $T^* \approx 540$ K, corresponding to $\varepsilon(\kappa_0) \approx 0.3$ eV. These values are somewhat uncertain. Nevertheless we see that, provided in the case of angular-correlation peak-height counts F_{st} may be taken as temperature independent, an almost temperature independent background should be subtracted in the temperature range between 950 and 1200 K, where Triftshäuser and McGervey [12] determined H_{1V}^F. Instead Triftshäuser and McGervey [12] subtracted a correction proportional to bulk thermal expansion, which in this temperature range is considerably larger than in the "intermediate" temperature range. The authors [12] do not give details of their correction procedure; we estimate that their procedure gave them a slope in the Arrhenius plot for the determination of H_{1V}^F which is too large by about 20%. Applying a negative 20%-correction to their Cu-value $H_{1V}^F = (1.29 \pm 0.02)$ eV gives us $H_{1V}^F \approx 1.03$ eV.

The preceding discussion is supported by a consideration of the entropy of monovacancy formation, S_{1V}^F. The concentration of monovacancies in thermal equilibrium reads

$$C_{1V}^{eq} = \exp(S_{1V}^F/k_B) \exp(-H_{1V}^F/k_B T). \tag{18}$$

Disregarding, for simplicity, a possible divacancy concentration and inserting the melting-point concentration $C_{1V}^{eq}(T_m) = 2.10^{-4}$ [29] together with $H_{1V}^F = 1.29$ eV gives us $S_{1V}^F = 2.5\, k_B$. This value is much larger than the values found for comparable metals [6] and rather difficult to understand theoretically. A plausible value is $S_{1V}^F = 0.6\, k_B$ [6]; this leads to $H_{1V}^F = 1.06$ eV, which is within the uncertainty range of the above revised analysis of Triftshäuser's and McGervey's [12] measurements.

A similar discussion may be carried out for the Ag and Au measurements of Triftshäuser and McGervey [12]. The correction to be applied is smallest in Au, for which Triftshäuser and McGervey [12] give $H_{1V}^F = (0.97 \pm 0.01)$ eV. Correction of this value according to the present interpretation brings it into the range of $H_{1V}^F = (0.92 \pm 0.02)$ eV, which has been established by quenching experiments beyond any reasonable doubt [30, 31]. The latter value leads to a formation entropy $S_{1V}^F = 0.6\, k_B$, too [6, 31].

The preceding discussions have shown that the present interpretation in terms of a metastable positron self-trapping appears to lead to good accord with the observations and that it brings positron annihilation data on vacancy formation enthalpies and entropies that where unreasonably large back into the established range of values. Nevertheless, a quantita-

tive least-square analysis of the temperature dependence of a large number of metals is desirable. Such an analysis may remove remaining discrepancies, e.g., the unreasonably large value for H_{1V}^{F} deduced from positron annihilation measurements on In [32, 4].

In Section 3 we have given criteria for the existence and the observability of the self-trapping effect. The essential feature is that a *metastable* self-trapped positron configuration exist. [If $\varepsilon(\kappa_0) < 0$, self-trapping is virtually complete at all temperatures, and can therefore not be detected by a sudden break in the temperature dependence of annihilation properties.] Due to the crude nature of the electron theory aspects of this paper, these criteria have only qualitative significance. Fortunately this does not impair the quantitative application of the statistical theory, since in this theory the metastable self-trapped state is completely characterized by three parameters, namely $\varepsilon(\kappa_0) > 0$, $\ln(A T^{*-3/2}) > 0$, and F_{st}[2].

The energies $\varepsilon(\kappa_0)$ resulting from the comparison of positron annihilation data with the statistical theory came out small compared with the Fermi energy, which is of the order of magnitude $h^2 \kappa_0^2/m^*$. This means that there is substantial cancellation between the two terms in (7)[3]. A moderate increase in m_+ would make $\varepsilon(\kappa_0)$ negative, i.e., give us a self-trapping state which is stable with respect to the Bloch-wave-type positron state. There is indeed overwhelming evidence that, as expected from this consideration, protons and deuterons in metals are "self-trapped", i.e., localized on interstitial sites surrounded by lattice distortions. Our considerations show that this should also be the case for positive muons. The measurements of Gurevich *et al.* [33] indicate indeed that positive muons in copper are localized and move by a thermally activated hopping process.

The preceding results show that positive muons, protons, deuterons, and tritons in metals may be treated in terms of a uniform model over the entire temperature range. They are localized on interstitial sites from the lowest temperatures upwards; their movement from site to site may be treated in terms of thermally activated rate processes (or—at very low temperatures—in terms of tunneling through the barriers between adjacent sites). The situation is quite different for positrons in those metals in which *metastable* self-trapped positron states are formed. At low temperatures the majority of the positrons are in Bloch states; their mobility may be treated in terms of scattering processes, e.g., by phonons [28]. Above the temperature T^* the majority of the positrons is localized in self-trapped states (this is to be distinguished clearly from the localization in wave-packets formed from Bloch states discussed elsewhere [34]). In these states the positrons have clearly a much higher effective mass than in the Bloch states; as a consequence, their mobility will be much smaller. The mobility or the diffusion coefficient of positrons cannot be measured directly (in contrast to positive muons and hydrogen isotopes). Experimental information on the positron diffusion coefficient has to come from trapping rates, which, however, depend also on the probability, characterized by a rate coefficient k_j, with which a trap captures a neighbouring positron [8, 35]. Whereas for Bloch-state positrons k_j may be very small and hence the trapping rate may well be controlling the rate of capture, this is unlikely to be so for self-trapped positrons. A self-trapped positron adjacent to a trap, e.g., a monovacancy, should have no difficulty in giving up energy to the lattice and falling into the bound state of the trap. Thus we expect that in metals showing self-trapping of positrons, high-temperature trapping measurements do indeed give information on the positron diffusion coefficient. By comparison with theoretical expressions [28] the effective positron mass m_+ may deduced. In this way we may obtain information on the displacement of the ions surrounding the positron, since this gives the main contribution to the effective positron mass in the self-trapped state.

From the preceding discussion it is obvious that extreme care must be exercised in attempts to deduce the temperature dependence of the positron diffusion coefficient from measurements of trapping rates at widely different temperatures [6, 13, 34, 36–39]. We have seen that in the case of metastable self-trapping quite different physical quantities may control the trapping rate at low and at high temperatures (positron diffusion coefficient D at high temperatures, capture rate k_j at low temperatures). This may explain why so far all attempts have failed to relate measurements of trapping rates over a wide temperature range to theories of the temperature dependence of positron mobility.

[2] There is, however, the possibility that in addition an "excited" self-trapped state with a higher energy exists, and that this has to be taken into account at high temperatures.

[3] This may be used to obtain, from (7), an estimate of the positron deformation potential parameter ε_d in terms of $K/\kappa_0 m_+$. Since a detailed discussion of the "effective" elastic constant K is beyond the scope of this paper, we postpone numerical estimates to a later paper.

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