Quenching Studies of Lattice Vacancies in High-Purity Aluminium

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The experimental techniques for obtaining reliable enthalpies of formation and migration of vacancies in pure metals and the importance of achieving high accuracy are critically discussed, with emphasis on studies based on the quenching-in of ‘thermal’ vacancies. From measurements of the residual electrical resistance introduced into high-purity Al foils (thickness 0.1 mm) from ultrafast quenches to deduce the migration enthalpy of monovacancies, \( H^0_{1V} \approx (0.65 \pm 0.01) \text{ eV} \), and the entropy, \( S^0_{1V} = (0.76 \pm 0.04) \text{ JK}^{-1} \text{ mol}^{-1} \) (Boltzmann’s constant), of monovacancy formation as well as the resistivity of migration, \( D_{1V} \), the enthalpy, \( H_{1V} \), is found to be \( H_{1V} = (1.9 \pm 0.1) \text{ mJ} \text{ cm}^{-2} \text{ mol}^{-1} \) per unit atomic concentration of vacancies are derived. Combining these results with the Al self-diffusion data deduced from nuclear magnetic resonance leads to the migration enthalpy of monovacancies, \( H^0_{1V} \approx (0.61 \pm 0.02) \text{ eV} \) and the pre-exponential factor \( D_{1V}^0 = 6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \) of the monovacancy diffusivity \( D_{1V} = D_{1V}^0 \exp(-H^0_{1V}/k_B T) \). The divacancy binding enthalpy is found to be \( H^0_{2V} = (0.175 \pm 0.02) \text{ eV} \). This is in full agreement with earlier determinations by Doymaza and Koehler and by Levy, Lanore and Hillairet, who employed a different technique, but in stark contrast to the recent assertion \( H^0_{1V} \approx 0 \) of Carling et al.

1. Introduction and General Background

Vacant lattice sites (for short called ‘vacancies’) are the simplest intrinsic atomic defects in crystals. In the study of lattice defects in metals they play several key roles.

(i) In recent years it has become possible to perform numerically accurate ab-initio computations of the enthalpies of formation of monovacancies, \( H^F_{1V} \), of simple metals. Examples are calculations on Li, Na, Na+, and, in particular, on Al, the subject of the present paper. Based on the density functional theory (DFT), the majority of the computations make use of the local density approximation (LDA) of Kohn and Sham, whose reliability in this context can at present not be judged by theoretical arguments alone. Comparison between experimental and computed values of \( H^F_{1V} \) provides not only a test of the reliability of LDA in calculations on defects in metals but may also shed light on various related questions, e.g. on whether the defect calculations should be based on the measured or on the LDA-computed lattice parameters of the metals, or whether the use of the generalized gradient approximation (GGA) improves or worsens the results.

(ii) With rare exceptions, the experimental investigation of defects in metals involves several different types of defects simultaneously. The standard way to separate their effects on physical properties, e.g. on the residual electrical resistance, is to study their recovery during annealing treatments. Ideally, as a result of such annealing experiments, which are analogous to the fractional distillation techniques in physical chemistry, we can assign numerical values to the enthalpies of migration, \( H^M \), of the various atomic defects. In practice, however, without additional information this is by no means straightforward. To illustrate this, we recall the enormous confusion (reflected, e.g., in the Landolt–Börnstein data collection) that has resulted from insufficient recognition of

\[ H^F_{1V} + H^M_{1V} = H^D_{1V} \] (1)

between these two quantities on the one hand and the activation enthalpy of the monovacancy contribution to the self-
diffusion, \( H_{\text{IV}}^{\text{SD}} \), on the other hand. On several fcc metals, the right-hand side of eq. (1) has been determined quite accurately by careful analysis of self-diffusivity measurements over a wide temperature range, using radioactive tracers, or, as in the case of Al, nuclear magnetic resonance (NMR) techniques. Here two circumstances were helpful: (1) Diffusivity measurements are insensitive against the interaction of the diffusion vehicles (i.e., the vacancies in the present case) with impurities.\(^{13}\) Therefore the tracer self-diffusivity, \( D_T(T) \), may be obtained accurately even at temperatures \( T \) that are so low that a substantial fraction of the thermal-equilibrium vacancies is associated with impurities.\(^{2}\) (2) In contrast to bcc metals such as Li, Na, etc., fcc metals do not undergo low-temperature phase transformations that affect the self-diffusivity by fluctuation enhancement.\(^{3,4,15}\)

Whereas in quite a few fcc metals \( H_{\text{IV}}^{eq} \) is known from experiment with an accuracy of about 1%, it is much more difficult to obtain the quantities on the left-hand side of eq. (1) accurately enough to make the various comparisons discussed above meaningful. With the exception of positron (e\(^+\)) annihilation, the experimental determinations of \( H_{\text{IV}}^{eq} \) are based on the assumption (so far not contradicted by experiments or theory) that in fcc metal crystals even at the highest temperatures the equilibrium concentration of self-interstitials is negligibly small, so that the only intrinsic defects that have to be taken into account in thermal equilibrium are vacant lattice sites (monovacancies \( V_1 \), divacancies \( V_2 \), . . . ). These may be studied either at high temperatures, i.e., in thermal equilibrium, or under non-equilibrium conditions after rapidly quenching the specimen to low enough temperatures for the quenched-in defects to be immobile. In the following, we discuss merits and problems of these two alternatives. A fuller discussion with detailed references may be found elsewhere.\(^{6}\)

**High-temperature studies:** Since in metals even at the melting point, \( T_m \), the concentration of vacant lattice sites in thermal equilibrium is quite small (in Al slightly less than \( 10^{-4} \) in atomic units), separating the vacancy contribution to the measured quantity from the ‘background’ due to the undisturbed crystal is a major problem. Two methods achieving this separation with or no further assumptions are available, viz. (a) differential measurements of thermal expansion (for short called **differential dilatometry**) and (b) positron annihilation.

(a) The difference between the change of the specimen volume relative to a vacancy-free low-temperature reference state as measured by dilatometry and as calculated from the temperature variation of the lattice parameter gives us the absolute concentration of the vacancies in high-temperature thermal equilibrium. From the point of view of deducing \( H_{\text{IV}}^{eq} \), the weakness of this method is its **limited sensitivity**. It allows only fairly large vacancy concentrations (\( \geq 1 \times 10^{-4} \)) to be determined accurately, of which, however, a substantial fraction may be present as divacancies or even larger agglomerates. Since the method measures the **total concentration** of vacant lattice sites,

\[
C_{\text{eq}}^{V}(T) = C_{\text{eq}}^{V1} + 2C_{\text{eq}}^{V2} + \cdots ,
\]

we have to estimate the divacancy concentration, \( C_{\text{eq}}^{V2}(T) \), and correct for it before the monovacancy formation enthalpy may deduced from the temperature dependence of the equilibrium concentration of monovacancies, \( C_{\text{eq}}^{V1}(T) \), according to

\[
H_{\text{IV}}^{F} = -\frac{\partial \ln(C_{\text{eq}}^{V1}(T))}{\partial (1/\kappa_B T)} \bigg|_{p=\text{const}},
\]

where \( p \) denotes the hydrostatic pressure and \( \kappa_B \) Boltzmann’s constant.

(b) The various e\(^+\) annihilation techniques are applicable to those metals in which even at high temperatures positrons are trapped by vacancies for at least their lifetime (typically \( 2 \times 10^{-10} \) s). In contrast to (a), here the experimentally determined quantity is \( C_{\text{eq}}^{V1}(T) \) plus \( \sigma_V C_{\text{eq}}^{V2} \), where \( \sigma_V \) denotes the e\(^+\) trapping rate per unit vacancy concentration. If \( \sigma_V \) is temperature-independent or only weakly temperature-dependent (theory\(^{16}\)) suggests proportionality to \( T^{-1/2} \), this feature does not seriously interfere with the determination of \( H_{\text{IV}}^{eq} \). There are, however, also instances where \( \sigma_V \) obeys an Arrhenius law with an activation enthalpy, \( H^+ \), of a few hundred meV. Then, the activation enthalpy deduced from e\(^+\) high-temperature annihilation experiments is \( H_{\text{IV}}^{eq} + H^+ > H_{\text{IV}}^{eq} \). Unfortunately, it is quite difficult to establish the temperature dependence of \( \sigma_V \) by independent measurements. The phenomenon appears to be important in copper but not in aluminium.\(^{16,17}\) In Sect. 4.7 the present results will be used to determine the high-temperature value of \( \sigma_V \) in aluminium.

Compared with differential dilatometry, in e\(^+\) studies the ‘divacancy problem’ is much less serious owing to the location of the ‘concentration window’ of e\(^+\) measurements in which the temperature dependence of the equilibrium vacancy concentration may be determined. The window is somewhat less than three powers of ten wide and extends in cases such as Al typically between \( 10^{-2} \) to \( 10^{-4} \). At these concentrations, the fraction of vacant sites in \( V_2 \) is much smaller than in the concentration regime in which differential dilatometry gives accurate results. This clearly simplifies the interpretation of the e\(^+\) data.

Both techniques, differential dilatometry and positron annihilation, have the common advantage that they allow us to verify the vacancy character of the defects studied. In (a), the sign of the measured effect would be reversed if the dominant high-temperature defects were self-interstitials. In (b), isolated self-interstitials do not trap positrons (or at most only very weakly); hence the high-temperature e\(^+\) traps must be vacancies.

The remaining high-temperature techniques for studying the equilibrium concentrations of vacancies all suffer from the ‘background problem’. We consider specific-heat or heat-capacity measurements as examples. Here, the contribution of the monovacancies to the specific heat per atom at constant pressure, \( \partial(H_{\text{IV}}^{eq} C_{\text{V}}^{eq})/\partial T |_{p=\text{const}} \), must be separated from the much larger contribution of the lattice vibrations. The usual procedure, based on extrapolation from lower temperatures, is fraught with uncertainties. As will be shown in Appendix B, with sufficient effort the effects of phonon anharmonicities, which become significant at high temperatures, may be estimated. However, there may be high-temperature excitation modes that are radically different from the phonon modes dominating at intermediate temperatures. Computer simulations of high-temperature bcc Na\(^{18,19}\) have furnished evidence for the formation of Frenkel pairs at high temperatures.
that are too short-lived to show up in the techniques (a) and (b) discussed above but might contribute significantly to the specific heat. It remains to be seen whether this process is at least partly responsible for the discrepancy between the equilibrium vacancy concentrations deduced from specific heat or heat capacity and those obtained from differential thermal expansion or \( e^+ \) annihilation.\(^{16,20}\)

Low-temperature (quenching) studies: Rapid quenching from high temperatures and subsequent investigation of the retained atomic defects, by measuring the residual electrical resistance after successive annealing treatments, is the oldest method for obtaining information on the equilibrium defects in metals.\(^{21,22}\) In the early work, the assumption that the quenched-in defects were predominantly vacancies had to be justified by theory. Its correctness was subsequently established by the positron-annihilation and differential-dilatometry measurements discussed above.

Quenching experiments encounter several problems:

1. The quenching should be as fast as possible but, nevertheless, should avoid, or at least minimize, plastic deformation of the sample during the quench. Plastic deformation creates defects (dislocations, self-interstitials, vacancies), which give additional contributions to the residual electrical resistance. Some of these defects may act as sinks for vacancies, thus reducing the concentration of the quenched-in vacancies.

2. During the quenching, reactions between the vacancies may take place, leading to the formation of divacancies or even larger vacancy clusters. Thus, even if we succeeded in quenching-in all the vacant sites present in thermal equilibrium at the quenching temperature \( T_q \), we must not a priori assume that their distribution over the various aggregates (monovacancies, divacancies, etc.) is the same as at \( T_q \).

3. For rapid quenching, an efficient cooling medium is needed. This may introduce impurities into the samples in a manner that depends not only on the medium but also on the chemical properties of the metal.

4. On the one hand, thinner specimens make it easier to achieve faster cooling rates. On the other hand, they are more susceptible to damage by plastic deformation, to vacancy losses to surface sinks, and to contamination.

An optimum has to be found.

Over the years, considerable understanding of the problems involved in quenching experiments and of their inherent potential has been achieved. Compared with the high-temperature studies mentioned above, an advantage of properly executed quenching experiments on metals is that, by using the residual electrical resistivity as indicator, rather low vacancy concentrations can be investigated quantitatively. It was therefore unjustified that the Landolt-Börnstein collection of data on atomic defects in metals\(^{23}\) tended to disregard quenching results without any justification when proposing ‘recommended values’ for vacancy formation and migration enthalpies. As has been shown by way of examples, this has lead to serious errors with far-reaching consequences.\(^{16}\)

The present paper reports on a quenching investigation of high-purity aluminium aiming at deducing reliable values of the enthalpies of formation and migration of monovacancies and at obtaining information, necessarily not quite as precise, on divacancies in this metal, too. Aluminium was chosen for five reasons. (1) Owing to the very stable oxide layer of Al, contamination problems are minimal. (2) Although there have been many previous studies of vacancies in Al by a rather wide range of techniques, a generally accepted quantitative picture has not yet emerged. (3) Extensive information is available on self-diffusion in Al in the temperature range in which it is virtually entirely determined by the monovacancy mechanism,\(^{11,12}\) hence \( H_{IV}^{SD} \) is well known. This allows critical tests as well as improvements of the conclusions to be drawn from quenching data. (4) Numerical values of the formation enthalpy of monovacancies in Al from \textit{ab-initio} calculations are available; their reliability may be tested by comparison with experimental results. (5) In certain Al alloys, vacancies play a key role in the electromigration damage occurring in the metallic leads of miniaturized electronic devices. For a fundamental understanding of the underlying atomistic process, reliable information on the behaviour of vacancies in pure Al is a necessity.

An outstanding feature of the present experiments was an extremely high quenching rate. It allowed us to minimize the vacancy losses and also vacancy agglomeration during quenching. Even so, in order to reduce to manageable proportions the complications associated with the tendency of vacancies to agglomerate during the quench, the vacancy concentrations and thus the quenching temperatures \( T_q \) must not be too high. In the present case, the quenching temperatures cover the range 530 K \(< T_q < 810 K \), corresponding to 0.57 to 0.86 of the melting temperature \( T_m = 933 K \). The rather small vacancy concentrations involved in the annealing studies following the quenching from low \( T_q \) necessitated the use of residual resistance measurements as defect indicators. These measurements do not differentiate between mono- and divacancies; hence for the analysis of the data a model will be required.

The paper is organized as follows. Section 2 describes the sample preparation and the experimental procedure. Section 3 reports the experimental results and their analysis. Finally, Section 4 compares them with the older quenching data, with other techniques, and in particular with self-diffusion data. It will be seen that our data are fully compatible with the highly accurate NMR information on self-diffusion in Al and that monovacancy formation and migration enthalpies with fairly narrow uncertainty margins as well as the binding enthalpy of divacancies can be derived. A recent theoretical study that comes to different conclusions\(^{23}\) will be discussed in some detail.

### 2. Experimental Procedures

#### 2.1 Sample preparation

The starting material of 5N nominal purity was obtained from Johnson Matthey & Co. in the form of 0.25 mm \( \times \) 100 mm \( \times \) 125 mm foils. The foils were cut into samples of 0.25 mm \( \times \) 8 mm \( \times \) 106 mm. By polishing in a solution of 25 ml of sulfuric acid, 70 ml of phosphoric acid, and 5 ml of nitric acid at 373 K, the thickness of the foils was reduced to 0.1 mm. Finally, the samples were annealed in a vacuum of \( \sim 10^{-10} \) bar for 90 minutes at 470 K and for 6 h at 870 K. After this treatment, the residual resistance ratio of the
samples was about 2700.

2.2 Quenching, resistance measurements, and annealing procedure

The desired high quenching rates were achieved by means of a technique similar to that of Lengeler.\textsuperscript{24, 25} Figure 1 shows a schematic drawing of the quenching apparatus. Sample and holding block surrounded a stainless-steel housing that prevented the cooling of the sample before it dropped into the quenching bath.

The quenching was performed in a high-purity Ar atmosphere. In a vertical tubular electrical furnace the sample was heated to the desired quenching temperature which was measured by a nicrosil–nisil thermocouple sensor placed close to the sample. Subsequently, the sample-holder frame was released. Just before it reached the bath, the retaining ring stopped the main frame and the housing, allowing only the holding block with the sample to drop into the bath.

In search of the highest achievable quenching rate, different quenching baths were tested: liquid nitrogen, methanol, petroleum, and a mixture (volume ratio 1:3) of distilled water and hydrochloric acid, all cooled to below 210 K. The quenching rates were determined with a thermocouple, spot-welded to a dummy specimen, and with a memory digital oscilloscope. The water–hydrochloric-acid mixture gave the highest quenching rate and was subsequently used in the quenching experiments reported in the present paper. As the example of Fig. 2 shows, during the cooling the sample temperature decreased approximately exponentially. By means of least-squares fits, the initial quenching rate for the water–hydrochloric-acid mixture was found to be about $2 \times 10^6 \text{K s}^{-1}$. This is at least one power of ten faster than the rates reported for any previous quenching experiments on Al.\textsuperscript{26}

The quenched samples were mounted in liquid N\textsubscript{2} on a sample holder for electrical-resistance measurements and transferred to a liquid-helium cryostat\textsuperscript{27, 28} without warming. The standard four-point direct-current method was used to measure the resistance of the sample before and after annealing. During the measurements, the current direction was reversed repeatedly and the voltage was averaged in order to compensate any offsets of thermal emf.

Isochronal anneals were performed in a gaseous helium atmosphere in two electrically heated chambers: one inside the cryostat for temperatures below 300 K, the other one sitting on top of the cryostat for temperatures above 300 K. A stepper motor was used to move the sample between the annealing chambers and the liquid helium, where the measurements were performed. The annealing temperatures were monitored by a standard platinum resistance thermometer mounted close to the sample. During annealing the temperature was controlled to better than $\pm 0.5$ K. The isochronal annealing times were 10 minutes.

3. Experimental Results

3.1 Quenching experiments

The quenched-in electrical resistivities, $\rho_q = \rho_q(T_q)$, are shown as open circles in the Boltzmann plot $\ln \rho_q$ vs. $1/T_q$ of Fig. 3. The comparison with the quenching data of other authors\textsuperscript{29–37} demonstrates that the resistivities quenched-in in the present work tend to be significantly larger than those of the earlier work. This is no surprise in view of our rather high quenching rates. The estimates of Appendix A indicate that while in the high-$T_q$ work of other authors there may have been quite noticeable losses, in the present work the loss of vacant sites by diffusion to the specimen surfaces is small even at the highest $T_q$.

According to the dilatometric measurements to be discussed in Sect. 4.1, at the highest quenching tempera-
ture, 810 K, the total equilibrium vacancy concentration is $C_{\text{eq}}^\text{eq}(T_q) = 1.1 \times 10^{-4}$. This value is small enough for $C_{\text{eq}}^\text{eq}(810 \text{ K}) \ll C_{\text{eq}}^\text{eq}(810 \text{ K})$ to hold, hence we may base the further analysis of the present quenching experiments on $C_{\text{V}}^\text{eq}(T) \approx C_{\text{V}}^\text{eq}(T_q) - \exp(S_{\text{V}}^\text{F}/k_B T_q) \exp(-H_{\text{F}}^\text{V}/k_B T_q)$. (4) where $S_{\text{V}}^\text{F}$ denotes the entropy of formation of a monovacancy. However, as will be discussed in Section 4.2, during the quenching some of the vacancies will form divacancies or larger agglomerates. This reduces the resistivity quenched-in from high $T_q$ somewhat below that expected for a “perfect” quench. It follows that even if no vacancies are lost to surface sinks and we are justified in using eq. (4), at elevated $T_q$ the ‘quenching formation enthalpy’, $H_{\text{F}}^\text{V} := -\Delta \ln \rho_q(\Delta \ln (1/k_B T_q))$, will not be $T_q$-independent. (For a more detailed discussion of its relationship to $H_{\text{F}}^\text{V}$ see Sect. 4.2.) Since, on the other hand, at low $T_q$ the error bars of the resistivity measurements increase, in the analysis of $\rho_q(T_q)$ according to

$$\rho_q = \rho_{q,0} \exp(-H_{\text{F}}^\text{V}/k_B T_q)$$

the highest weight has been given to the data at intermediate $T_q$. This leads to the full line in Fig. 3 with

$$H_{\text{F}}^\text{V} = (0.65 \pm 0.01) \text{ eV}, \quad \rho_{q,0} = (4.1 \pm 0.1) \mu \Omega m.$$  (7)

3.2 Annealing experiments

The recovery of the quenched-in resistivity in isochronal annealing experiments (annealing times 600 s at the annealing temperatures $T_a$ indicated) is shown in Fig. 4, with the quenching temperatures $T_q$ as parameter. In Fig. 4(a) the relative change of the quenched-in resistivity, $\Delta \rho/\rho_q$, is plotted as function of the annealing temperature in the conventional way. Figure 4(b) gives the remaining part of the quenched-in resistivity as function of the annealing temperature. This way of plotting the annealing data provides a better insight into the recovery processes, particularly into those at elevated temperatures, since during the recovery the defect reaction rates are proportional to the instantaneous defect concentration and not to the starting concentration.

Figure 4 demonstrates that the recovery of the electrical resistivity depends strongly on the quenching temperature and thus on the quenched-in resistivity. The shift of the recovery towards lower temperatures with increasing $T_q$ may be understood as follows. In the face-centred cubic structure nearest-neighbour vacancies may migrate, without dissociating, by one of the constituent vacancies moving to a neighbouring site. Since the moving vacancy has the other vacancy as a neighbour, the energy barrier the atom jumping into the moving vacancy has to overcome is less than $H_{\text{F}}^\text{V}$, hence nearest-neighbour divacancies have lower enthalpies of migration and become mobile at lower temperatures than monovacancies ($V_1$). Analogous arguments hold also for some of the vacancy clusters containing three or more vacancies. The acceleration of the recovery by the ‘multiple-vacancy effect’ should be smaller after low-temperature quenches (in the present case those from $T_q = 580$ K, 550 K, and 530 K), since the tendency to form multiple vacancies during annealing, and thus to accelerate the recovery, decreases with decreasing vacancy concentration. It appears plausible that in these cases the recovery between 360 K and 420 K is essentially controlled by the annealing out of monovacancies, whereas in the recovery between 250 K and 350 K the migration of divacancies plays a key role. The subject will be taken up again in Sect. 4.5.
4. Discussion

4.1 Comparison with differential dilatometry

If applicable, differential dilatometry is by far the best technique to determine the absolute values of thermal-equilibrium concentrations of vacant sites in metals. Feder and Nowick\(^\text{38)}\) were the first to report a successful application, to Al, of the technique. Figure 5 shows the equilibrium concentrations of vacant sites in metals. Feder and Nowick\(^\text{38)}\) indicated in Sect. 1 and will be discussed further in Sect. 4.3, their concentrations are related according to

\[
C_{2V} = \left(\frac{z}{2}\right) \exp\left(\Delta S_{2V}/k_B\right) \exp\left(H_{2V}^B/k_B T\right) C_{1V}^{\text{eq}},
\]

where the ‘divacancy association entropy’

\[
\Delta S_{2V} = S_{2V}^F - 2S_{1V}^F
\]

is the difference between the entropy of formation of a divacancy, \(S_{2V}^F\), and twice that of two isolated vacancies. Similarly, the divacancy binding enthalpy,

\[
H_{2V}^B = 2H_{1V}^F - H_{2V}^F,
\]

denotes the difference between the enthalpies of formation of two isolated vacancies and a divacancy. In eq. (10), \((z/2)\) is the number of crystallographically distinct possible orientations of a divacancy. For a nearest-neighbour divacancy in an fcc metal, \(z = 12\). Physical intuition as well as calculations indicate that \(\Delta S_{2V} > 0, H_{2V}^B > 0\).

If vacancy agglomerates larger than divacancies may be neglected, for a given total concentration \(C_V\) of vacant sites the monovacancy/divacancy ratio is

\[
\frac{C_{2V}}{C_{1V}} = \frac{1}{4} \left[1 + AC_V\right]^{1/2} - 1
\]

with the abbreviation

\[
A = 4z \exp(\Delta S_{2V}/k_B) \exp(H_{2V}^B/k_B T).
\]

In global thermal equilibrium, i.e., if eq. (5) holds in addition to eq. (10), the effective enthalpy of vacancy formation is given by

\[
H_{\text{eff}}^F = -\left.\frac{\partial \ln C_V}{\partial (1/k_B T)}\right|_{p=\text{const}} = H_{1V}^F + (H_{1V}^F - H_{2V}^B) \left[1 + A\right]^{1/2} - 1
\]

\[
= H_{1V}^F + \frac{1}{2} (H_{1V}^F - H_{2V}^B) \frac{AC_V}{1 + (AC_V/2) + [1 + AC_V]^{1/2}}.
\]

In metals, \(A\) is large compared with unity. Since \(H_{2V}^F > H_{1V}^F\), according to eqs (12) and (15) we have \(H_{\text{eff}}^F > H_{1V}^F\). Hence, the excess of \(H_{\text{eff}}^F\) over \(H_{1V}^F\) increases strongly with increasing \(C_V^{\text{eq}}\) (cf. Sect. 4).

The comparison of the preceding with experiment requires some further considerations.

(1) The scattering cross section of a divacancy for conduction electrons, averaged over all possible orientations, is smaller than that of two independently scattering monovacancies. Hence we expect the specific resistivity of divacancies, \(\rho_{2V}\), to be less than that of two isolated monovacancies, \(2\rho_{1V}\). Therefore, the proportionality factor connecting the resistivity caused by vacancies to the vacancy concentration decreases as the ratio \(C_{2V}/C_{1V}\) increases.

(2) According to eq. (13), as long as local thermal equilibrium between mono- and divacancies obtains, the diva-
vanity fraction of a fixed concentration \( C_V \) of vacant sites increases with decreasing temperature. This means that during quenching, monovacancies tend to form divacancies and that in fcc metals, where the divacancies are more mobile than monovacancies, vacancy agglomeration may ensue. Therefore, even if there is no loss of vacant sites to surface or internal sinks, the quenched-in size distribution of the agglomerates may be quite different from that at the quenching temperature. This effect increases with increasing vacancy concentration and thus with increasing quenching temperature. As indicated in Sect. 3.2, it is responsible for the huge difference between the recovery after the 'low-'\( T_q \) quenches' (\( T_q=530 \) K, 550 K, 580 K) and the 'high-'\( T_q \) quenches' (\( T_q=780 \) K, 700 K). In the latter case, the recovery is shifted to lower temperatures by much more than might be accounted for by higher \( C_V(T_q) \) values and the accompanying increase of \( C_{eq}^{\infty}/C_{eq}^{0} \).

(3) Since the resistivity per vacancy in small vacancy agglomerates is less than that of an isolated vacancy (see the argument given above for \( V_2 \)), it follows from the preceding consideration that the ratio \( \rho_V/C_{eq}^{0} \) decreases with increasing \( T_q \). At low quenching temperatures, at which both the loss and the agglomeration of vacancies during the quenching are negligible, the relationship (8) between the quenched-in resistivity \( \rho_q \) and the vacancy concentration \( V_{eq} \) as determined by dilatometry holds. At the high-temperature end of the present \( T_q \) range, however, eq. (8) is no longer valid. By the above argument, the quenched-in resistivity is less than \( \rho_{1V}C_{eq}^{0}(T_q) \), but it is difficult to determine by how much. Of help is the fact that if \( \rho_{1V} \) is adjusted correctly, the \( C_{eq}^{0} \) values derived from \( \rho_q \) should fit smoothly to those obtained by dilatometry. A schematic drawing of the situation, exaggerated for clarity, is shown in Fig. 6. It demonstrates that the three 'formation' enthalpies introduced above satisfy the inequalities

\[
H_{eff}^F > H_{1V}^F > H_q^F \quad (16)
\]

The first of them results from the fact that in practice eq. (15) gives reasonably accurate \( H_{eff}^F \)-values only at temperatures at which \( C_{eq}^{\infty} \) is not negligible.

4.3 Monovacancy–divacancy analysis of the high-temperature data

A similar high-temperature curvature as in the \( \ln C_{eq}^{0} \)-vs.-\( T^{-1} \) plot was first discussed for Arrhenius plots of the tracer self-diffusivity of fcc metals.43, 44 In both cases there are essentially two alternative explanations, viz. a temperature dependence of the enthalpies and entropies of formation and migration, or contributions from defects other than monovacancies. The matter was discussed in detail elsewhere45, 46 with the conclusion45 that in most fcc metals (including Al47) showing strongly curved Arrhenius (or Boltzmann) plots, the curvatures are mainly due to divacancies present in high-temperature thermal equilibrium. (An analogous statement would presumably not be true for bcc metals.16)

In the following the assumption is made that in the analysis of the \( C_{eq}^{0}(T) \) data the \( T \)-dependence of the formation enthalpies may be disregarded. A temperature dependence that is weak enough to be physically reasonable would reduce \( H_{2V}^B \) slightly but leave \( H_{1V}^F \) virtually unchanged. In Sect. 4.6 it will be shown that the assumption23 of a much stronger \( T \)-dependence of \( H_{1V}^F \) is unphysical. Furthermore, such an assumption would destroy the agreement between the \( H_{1V}^F \) to be derived from high-temperature data with the 'low-temperature' value deduced from annealing experiments by Doyama and Koehler48 and by Levy, Lanore, and Hillairet49, 50 to be referred to presently.

Our analysis followed the Seeger-Mehrer45, 46 procedure. By averaging the data of Simmons and Balluffi,39 Bianchi et al.,40 von Guérard et al.,41 and Mosig42 \( C_{eq}^{0}(878 \) K) = 4.72 \times 10^{-4} was obtained. Least-square fitting of the \( V_1–V_2 \) model to Mosig's data42 for selected \( S_{1V}^F–S_{2V}^F \) pairs resulted in Fig. 7. With the plausible assumption \( 0.5 \leq \Delta S_{2V}/K_B \leq 1.5 \), eq. (7) restricts the \( H_{1V}^F – H_{2V}^B \) pairs that are compatible with the experimental data to the quadrangular area in Fig. 7 surrounded by full lines. Since too low \( S_{1V}^F \) values are implau-
sible, we consider
\[ S_{1V}^F = (0.8 \pm 0.1) k_B \] (17)
to be a good estimate for the monovacancy formation entropy in Al. Thus, Fig. 7 gives us
\[ 0.15 \text{ eV} \leq H_{1V}^B \leq 0.20 \text{ eV}, \] (18)
in good agreement with \( H_{1V}^B = (0.17 \pm 0.05) \text{ eV} \) obtained by Doyama and Koehler\(^{(48)}\) and with \( H_{1V}^B = 0.18 \text{ eV} \) obtained by Levy et al.\(^{(50)}\) from the analyses of their annealing data after quenching. The agreement is highly significant, since eq. (18) and the last-mentioned numerical values are based on quite different approaches. While the results for \( H_{1V}^F \) and \( S_{1V}^F \) agree with those obtained earlier,\(^{(45)}\) the present \( H_{1V}^M \) value is distinctly lower than the previous one.\(^{(45)}\)

### 4.4 Comparison with self-diffusion data

Aluminium possesses only one long-lived radioactive isotope, \(^{26}\)Al, with a half life of \( 7.1 \times 10^5 \text{ yrs} \) and therefore not very convenient for measurements of the tracer self-diffusivity \( D^T(T) \). As a consequence, radiotracer measurements of \( D^T \) using \(^{26}\)Al are available only over a limited temperature range near the melting temperature. Here, divacancies are likely to contribute substantially to \( C_{1V}^{SV} \) and hence to \( D^T(T) \), making it impossible to obtain \( H_{1V}^{SD} \) from the radiotracer data alone. Fortunately, the 100%-abundant stable isotope \(^{27}\)Al is well suited for NMR investigations of the self-diffusivity by measuring the spin-lattice relaxation rate in a rotating frame (\( T_1 \)).\(^{(11)}\) The extension of these measurements to temperatures as low as \( 515 \text{ K} \)\(^{(11,12)}\) allowed \( H_{1V}^{SD} \) to be determined quite accurately, giving us
\[ H_{1V}^F + H_{1V}^M = (1.26 \pm 0.02) \text{ eV}. \] (19)

In view of the following discussion, note that the error estimate in eq. (19) is conservative. While it is true that the relationship between the quantity furnished by the NMR measurements, \( \Gamma_{1V} \), and the tracer self-diffusivity, \( D^T \), is model-dependent, this does not affect the determination of \( H_{1V}^F + H_{1V}^M = H_{1V}^{SD} \). \( (\text{For details see, e.g., Seeger, Wolf, and Messer}^{(47)} \text{ or Dais, Messer, and Seeger}^{(11)}).) \) In a detailed analysis, taking into account also the radiotracer data,\(^{(51,52)}\) Dais et al.\(^{(11)}\) deduced for the pre-exponential factor in the Arrhenius relationship of the tracer self-diffusivity by the monovacancy mechanism,
\[ D_{1V}^T = D_{1V,0}^T \exp(-H_{1V}^{SD}/k_B T), \] (20)
the numerical value
\[ D_{1V,0}^T = 1.0 \times 10^{-5} \text{ m}^2 \text{s}^{-1}. \] (21)
Together with eq. (7), eq. (19) allows us to derive the range of possible \( H_{1V}^M \) values by the construction of Fig. 8, which shows, in the \( H_{1V}^F, H_{1V}^M \)-plane, the bands corresponding to eqs (7) and (19). The intersection of the allowed bands, marked as an empty parallelogram and enlarged in the inset, gives us
\[ H_{1V}^F = (0.61 \pm 0.02) \text{ eV}. \] (22)

Further information may be obtained from the pre-exponential factor in eq. (20),
\[ D_{1V,0}^T = f_{1V} D_{1V}^0 \exp(S_{1V}^F/k_B) = f_{1V} \alpha_{1V} \gamma_{1V} \exp(S_{1V}^F/k_B), \] (23)
where \( \alpha_0 = 4.4 \times 10^{-10} \text{ m} \) is the edge length of the elementary cube, \( f_{1V} = 0.78 \) the self-diffusivity correlation factor for nearest-neighbour jumps of monovacancies in the fcc structure, and \( \gamma_{1V} \) the effective frequency of these jumps. As is obvious from Fig. 8, the numerical values of \( H_{1V}^M \) and \( H_{1V}^F \) are correlated. Because of this, it is unlikely that the extreme values of eqs (7) and (22) are assumed simultaneously. Table 1 reports the results of the analysis of the pre-exponential factor in eq. (23) based on different assumptions for \( H_{1V}^F \) and \( H_{1V}^M \) (first two columns of Table 1), which in turn correspond to different values of \( H_{1V}^{SD} \) (third column of Table 1). The fourth column of Table 1 gives, for fixed \( D_{1V}^T (590 \text{ K}) \), the pre-exponential factors \( D_{1V,0}^T \) that are associated with the different \( H_{1V}^{SD} \) values. Making use of \( C_{1V}^{S_0} (800 \text{ K}) = 1.75 \times 10^{-4} \) (cf. Fig. 5), we obtain from eq. (4) the monovacancy formation entropies \( S_{1V}^F \) listed in the fifth column. Finally, columns six and seven contain the numerical values of the pre-exponential factor and the attempt frequency of the monovacancy diffusivity. The bold entries are the ‘best values’ following from the preceding analysis. The other two lines of Table 1 are also compatible with the experimental data and with the intuitive requirement \( S_{1V}^F > 0 \). However, since in the lower line the entropy of monovacancy formation comes out lower and the attempt frequency of the monovacancy higher than might be expected on theoretical grounds (in the latter case theory predicts a small multiple of the Debye frequency \( \nu_D = 0.8 \times 10^{13} \text{ s}^{-1} \)), we believe that if a significant deviation from the ‘best values’ exists, it is likely to be in the direction of the upper line. If we use the ‘best values’ of Table 1 to estimate the fraction of \( C_{1V}^{S_0} (800 \text{ K}) \) that is lost to surface sinks during quenching (cf. Appendix A), we find \( 6 \times 10^{-3} \). This value is small enough to be negligible.
Table 1 Monovacancy migration properties following from different assumptions (see text). The ‘best’ data are printed in bold.

<table>
<thead>
<tr>
<th>$H^F_{1V}$ [eV]</th>
<th>$H^M_{1V}$ [eV]</th>
<th>$H^D_{1V}$ [eV]</th>
<th>$D_{1V}^{0}$ ([m^2s^{-1}])</th>
<th>$S_{1V}^F/k_B$</th>
<th>$D_{1V}^{1}$ ([m^2s^{-1}])</th>
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<td>$4.25 \times 10^{-6}$</td>
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<tr>
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<td>0.63</td>
<td>1.27</td>
<td>$1.2 \times 10^{-5}$</td>
<td>0.61</td>
<td>$8.2 \times 10^{-6}$</td>
<td>$5.0 \times 10^{15}$</td>
</tr>
</tbody>
</table>

4.5 Resistivity recovery

A preliminary discussion of the recovery of the quenched-in electrical resistivity of high-purity Al during annealing has already been given Sect. 3.2. Qualitatively, our results agree with the more detailed measurements of Doyama and Koehler\(^{48}\) and of Levy et al.\(^{49}\) Their results on $H_{2V}^B$ have been reported in Sect. 4.4. In addition, in an analysis allowing for triple and quadruple vacancies, Levy et al.\(^{50}\) determined the $V_2$ migration enthalpy as $H_{2V}^M \approx 0.5\, \text{eV}$. Within the experimental uncertainties, their value of the $V_1$ migration enthalpy, $\approx (0.65 \pm 0.03)\, \text{eV}$, agrees with that derived in the present work by a quite different approach. After low-temperature particle irradiation of pure Al, during 600 s anneals the recovery stage III is observed at about 200 K (cf. Ref. 7). It exhibits the characteristics of a self-interstitial–vacancy annihilation reaction. The activation energy $E_{III}^* = (0.59 \pm 0.02)\, \text{eV}$ is compatible with eq. (22). However, as emphasized in Sect. 1, the relationship $E_{III} \approx H_{2V}^M$ is only a necessary condition for the assignment of Stage III to monovacancy migration. The comparison with the quenching data shows clearly that the assignment $E_{III} = H_{2V}^M$ cannot be correct. At similar or even larger defect concentrations, the recovery somewhat above 200 K after high-temperature quenches is not controlled by the migration of monovacancies but by that of divacancies or possibly of larger highly mobile vacancy clusters. Monovacancy migration takes place at temperatures that are about 100 K higher than Stage III, in what is conventionally called Stage IV. An attempt to assign the recovery observed after high-temperature quenches just above 200 K to monovacancy migration would lead to the contradiction that the measured activation enthalpies are much less than $H_{2V}^M$. The conclusion can only be that in Stage III of Al the migrating defect is not the monovacancy, the only serious candidate being a dumbbell-type self-interstitial as demonstrated for Zn and Cd (cf. Sect. 1) and indeed all other fcc metals investigated in detail.

4.6 The Carling–Wahnström claim

As mentioned in Sect. 1, Carling et al.\(^{23}\) have recently claimed, on the basis of their GGA computations, ‘that the divacancy in Al is energetically unstable’ and ‘that anharmonic atomic vibrations explain the non-Arrhenius temperature dependence of vacancy concentrations’. This claim is in clear conflict with the present and most previous work. Carling et al.\(^{23}\) realize that a negative binding enthalpy of nearest-neighbour divacancies in metals with free-electron-like electronic structure, such as Al, is ‘counterintuitive’. Indeed, as was shown a long time ago,\(^{23}\) the binding enthalpy of divacancies in metals may be understood as follows. The negative effective electric charge resulting form the removal of an ion core from its lattice site when a vacancy is formed in a metal must be screened by a shift of conduction-electron density away from the site. (Figure 1 of Carling et al.\(^{23}\) is in agreement with this.) The accompanying increase of the kinetic energy of the electrons is the most important contribution to the vacancy formation energy.\(^{54}\) If two vacancies are brought together on adjacent sites, their effective charges will be screened by a common ‘screening cloud’ that is more extended than that of an isolated vacancy. The greater spatial extension leads to a reduction of the electronic kinetic energy compared with that of two isolated vacancies and hence to $H_{2V}^B > 0$. The $H_{2V}^B$ values of monovalent metals are of the right order of magnitude (0.1 to 0.2 eV). The underlying physical picture should be applicable to Al, too.

Since Carling et al.\(^{23}\) do not give details of their computations, one can only speculate about the origin of their unphysical result. They state that for the divacancy computation they used supercells of 80 sites, equivalent to 20 cubic unit cells. The average half-length of a supercell was thus 1.36a0. The nearest-neighbour separation in the fcc structure is 0.7a0, the next nearest-neighbour distance is 1.0a0. The cell size may therefore not have been big enough to treat the screening effects in the divacancy case correctly.

Another possible source of error may lie deeper. The basic GGA computation\(^{23}\) gives $H_{1V}^B = 0.54\, \text{eV}$, an unacceptably low value. The final value of 0.69 eV involves a 30% correction that appears, at least to the present writers, rather unconvincing. It is based on the free-electron model, which, as outlined above, gives a divacancy binding enthalpy that is far from the zero value of Carling et al.\(^{23}\) One might suspect that in the monovacancy case the approximate agreement with the experimental $H_{1V}^F$ is fortuitous and that it is the assumptions made in the ‘correction’ that are responsible for the unphysical binding enthalpy. Note that in the approach of Carling et al.\(^{23}\) the divacancy binding enthalpy is the result of adjusting (because of the different sizes of the supercells involved) and subtracting two large numbers in order to find a tiny difference.

There are also empirical arguments that force us to reject the Carling–Wahnström result. Even if their claim of ‘excellent agreement between experiment and theory’ were correct, it would not prove that their theory was correct, since alternative interpretations of the experimental data might do as well if not better. In fact, it is not difficult to show that the Carling–Wahnström interpretation leads (i) to an unphysical result in stage III of Al if not better. In fact, it is not difficult to show that the Carling–Wahnström result. Even if their claim of ‘excellent agreement between experiment and theory’ were correct, it would not prove that their theory was correct, since alternative interpretations of the experimental data might do as well if not better. In fact, it is not difficult to show that the Carling–Wahnström interpretation leads (i) to an unphysical result in stage III of Al
and $H_{1V}^F(0) = 0.68$ eV the monovacancy formation enthalpy at $T = 0$ K. Inserting $f(900)$ = 1.13 and $C_{1V}^F(900)$ = $9 \times 10^{-4}$ gives us $S_{1V}^F = 2.9k_b$. For a close-packed metal such as Al this value is too large unless the vacancies are smeared out in a liquid-like fashion. There is no experimental evidence, e.g. from positron annihilation, that could be interpreted in this way, however. Moreover, as will be explained at the end of item (ii), another discrepancy would be enhanced by the assumption of smeared-out vacancies.

Again, for lack of detail it is not possible to locate the origin of the unphysical behaviour of $f(T)$ at high temperatures. The function $f(T)$ emerges from molecular-dynamics simulations based on a potential that was derived from the local-density approximation (LDA) to the functional density theory (FDT), i.e. the approach that Carling et al.\(^23\) dismiss in favour of their GGA approach. Furthermore, it is well known that for defect properties of metals, potential-based molecular-dynamics simulations give poorer results than the FDT-based computations. (If this was not so, there would be no incentive to develop the FDT computations.)

(ii) At high temperatures, the Arrhenius plot of the tracer self-diffusivity, $D^T(T)$, of Al is about as strongly curved as that of $C_{1V}^F(T)$ (see, e.g., Refs. 11 and 12)). This has been attributed to the contribution of multiple vacancies to $D^T(T)$, in particular to the presence of divacancies in thermal equilibrium (cf. Sect. 4.4). The interpretation is supported by measurements of the activation volumes

$$ V = \frac{\partial G}{\partial p}|_{T=const} = \frac{\partial H}{\partial p}|_{S=const}. \quad (25) $$

where the free enthalpy $G$ and the enthalpy $H$ may refer to self-diffusion (SD), defect formation (F), or defect migration (M). From the effect of the hydrostatic pressure $p$ on the electrical resistance quenched-in from about 700 K, Emrick and McArdrle\(^5\) determined $V^F = (0.62 \pm 0.01)\,\text{cm}^3$, where $V_A = a^3/4$ is the atomic volume. A slightly larger value is obtained if the length changes due to quenching of Al from elevated temperatures observed by Harrison and Wilkes\(^6\) are compared with $C_{1V}^F(T)$. The computed value $V_{1V}^F = 0.67\,\text{cm}^3$ of Carling et al.\(^23\) is in agreement with these experimental results. The conclusion that vacancies in Al show considerable inward relaxation of the neighbouring atoms is supported by the lattice parameter measurements of Babić et al.\(^5\) on Al that was quenched from the melt.

Buescher and Emrick\(^8\) obtained migration volumes $V^M = (0.17 \pm 0.02)\,\text{cm}^3$ and $(0.18 \pm 0.02)\,\text{cm}^3$ from the resistivity recovery of Al wires that had been quenched from 833 K or 604 K. The first of these two $V^M$ values does certainly not reflect entirely monovacancy migration but may well be characteristic of divacancy migration. Since, however, in fcc metals divacancy migration occurs by essentially the same mechanism as monovacancy migration, we are justified in identifying the preceding values with $V_{1V}^M$. It follows that the activation volume for self-diffusion by the monovacancy mechanism,

$$ V_{1V}^{SD} = V_{1V}^F + V_{1V}^M, \quad (26) $$

is about $0.8\,V_A$ and certainly less than $0.9\,V_A$. However, the radioactive tracer measurements of Beyeler and Adda\(^22\) resulted in self-diffusion activation volumes $V_{1V}^{SD}$ between $(1.35 \pm 0.07)\,\text{cm}^3$ and $(1.23 \pm 0.07)\,\text{cm}^3$ at temperatures between 883 K and 800 K, i.e. under conditions where, according to the present analysis, $V_2$ contribute to self-diffusion. The fact that at high temperatures $V_{1V}^{SD}$ definitely exceeds $V_{1V}^{SD}$ agrees with our analysis but is in striking contrast to the Carling–Wahnström claim. (Note that if at elevated temperatures a stronger inward relaxation of the atoms adjacent to the monovacancies occurred, the ensuing increase of $S_{1V}^F$ would be accompanied by a decrease of $V_{1V}^{SD}$ with increasing temperature. Hence an even stronger discrepancy between experiment and the Carling–Wahnström claim would result.)

### 4.7 Positron annihilation

As explained in Sect. 1, positron annihilation is one of the main methods that allow us, if the circumstances are right, to determine $H_{1V}^F$. Nevertheless, we have so far not made use of it, the reason being that the present quenching experiments are capable of giving us $H_{1V}^F$ with smaller error bars than positron annihilation.

The various positron annihilation techniques have recently been discussed elsewhere\(^16\) and will therefore not be treated here. The $H_{1V}^F$ values derived up to 1987 by these techniques have been listed in Ref. 7); inclusion of more recent work would not change the picture substantially. The $H_{1V}^F$ values range from 0.62 to 0.71 eV with a slight tendency towards higher values than eq. (7). However, the excess is not large enough to conclude that $H^+ > 0$ (cf. Sect. 1). Irrespective of this, the fairly accurate determinations of $\sigma_v C_{1V}^F$ in the middle of the ‘concentration window’ may be used, in conjunction with eq. (4) and Table 1, to derive $\sigma_v$. E.g., from $\sigma_v C_{1V}^F = 4.2 \times 10^8\,\text{s}^{-1}$ at 625 K\(^6\) follows $\sigma_v(625\,\text{K}) = 3.4 \times 10^{14}\,\text{s}^{-1}$. If the capture of positrons by vacancies is limited by the positron diffusivity $D^+$, we may write

$$ \sigma_v = 4\pi r_0 D^+ / V_A, \quad (27) $$

where $r_0$ denotes the positron–vacancy capture radius. Using the theory of the positron diffusivity as limited by phonon scattering\(^{60,61}\) to extrapolate the experimentally determined $D^+$ in Al\(^22\) to higher temperatures gives us $D^+(625\,\text{K}) = 9.6 \times 10^{-2}\,\text{m}^2\text{s}^{-1}$ and, with eq. (27),

$$ r_0 = 1.2\,a_v. \quad (28) $$

From the numerical factor in eq. (28) we may conclude that in Al the positron capture is indeed limited by the positron diffusivity and not by the quantum-mechanical transition rate into a positron bound state at the vacancies.

### 4.8 Ab-initio computations

The literature on *ab-initio computations* on vacancies in metals is so vast that it cannot be fully covered in this review. We confine ourselves to a few examples. Computations based on model potentials often use $H_{1V}^F$ to adjust the potential. Such computations are of interest here only as far as their results may depend critically on both the accurate calculation of $H_{1V}^F$ for a range of model potentials and the correct choice of the numerical value of $H_{1V}^F$ (cf. Sect. 1).

The GGA computation of Carling et al.\(^23\) discussed in Sect. 4.6, does not enhance the confidence in this approach.
The basic $H_{1V}^E$ value came out definitely too low and was brought up to the experimental value only by a ‘non-ab-initio’ correction, not to speak of the unacceptable result for the divacancy binding enthalpy.

As an example of the LDA approach we mention an unpublished frozen-core pseudopotential computation of $H_{1V}^E$ in Al by Furthmüller and Finnis, which has been reviewed elsewhere. Working with the lattice parameter as calculated by LDA and using supercells with $N = 27, 64$ and 125 lattice sites and extrapolating to $N \to \infty$, Furthmüller and Finnis obtained $H_{1V}^E = 0.69 \text{eV}$. Nearest-neighbour relaxation contributed $-0.09 \text{eV}$ to this result and led to $V_{1V} = (0.65 \pm 0.04)\beta a$, in good agreement with the experimental result (cf. Sect. 4.6). Allowing more distant neighbours to relax would lower $H_{1V}^E$ further and might bring the computed vacancy formation enthalpy closer to the experimental value.

Using a computational technique different from that of Furthmüller and Finnis (the full-potential Korringa–Kohn–Rostoker Green-function method), Hoshino and Dimars have recently investigated monovacancies in Al and Cu with emphasis on the choice of the lattice parameter (see Sect. 1) and the relative merits of the LDA and the GGA approach. With regard to the last-mentioned item, their Al results are in agreement with our preceding conclusions. If the lattice relaxation is disregarded, the Al monovacancy formation enthalpy computed by LDA is too high ($0.73 \text{eV}$) and that furnished by GGA ($0.59 \text{eV}$) too low. Since allowing for the lattice relaxation may decrease $H_{1V}^E$ by up to $0.1 \text{eV}$, it is fairly clear that in this case LDA is superior to GGA. The situation appears to be different in Cu, however. Here the LDA values computed for various lattice parameters exceed the corresponding $H_{1V}^E$ values as obtained by GGA by about $0.2 \text{eV}$, but, in contrast to Al, in Cu the GGA result for the computed lattice parameter is not smaller than the experimental value. (A statement to the contrary is due to a misinterpretation of experimental results; see, e.g., Ref. 16.) Since owing to 3d-shell effects the inward relaxation of the neighbouring atoms is expected to be smaller than in Al, the GGA computation may well give a good result for the monovacancy formation enthalpy of copper. Thus, it appears that the question whether LDA or GGA gives better $H_{1V}^E$ results does not have a unique answer.

5. Conclusions

(1) Measurements of the quenched-in residual electrical resistivity of aluminium rapidly cooled from temperatures below about $800 \text{K}$ with initial quenching rates of $2 \times 10^5 \text{K s}^{-1}$ give the enthalpy of formation of monovacancies $H_{1V}^E = (0.65 \pm 0.01)\text{eV}$.

(2) Comparison of the quenching data with high-temperature differential-dilatometry data gives the monovacancy formation entropy $S_{1V}^E = (0.76 \pm 0.4)\text{K} (8 \text{K} = \text{Boltzmann’s constant})$ and the low-temperature resistivity per unit concentration of vacancies $\rho_{1V} = (1.9 \pm 0.1)\text{m} \Omega \text{cm}$.

(3) The binding enthalpy of divacancies in Al is $H_{2V}^F = (0.17 \pm 0.02)\text{eV}$. This is in agreement with earlier experimental determinations by Doyama and Koehler and by Levy et al., but in marked contrast to the claim of Carling et al., based on computations with the generalized gradient approximation, that in Al $H_{2V}^F$ is zero or even negative and therefore the contribution of divacancies to the thermal-equilibrium concentration of vacant sites is negligibly small.

(4) The monovacancy formation enthalpies obtained by positron annihilation show a relatively large scatter but are compatible with the result stated in conclusion (1).

(5) At high temperatures, the capture radius of monovacancies in Al for positrons is $r_0 = 1.2\text{nm}$. The data support the view that at high temperatures the positron capture is diffusion-limited and that the positron diffusivity is limited by phonon scattering.

(6) Combination of conclusion (1) with self-diffusivity data gives the monovacancy migration enthalpy $H_{1V}^F = (0.61 \pm 0.02)\text{eV}$.

(7) Specific-heat measurements by Shukla, Plint and Dimar are compatible with conclusions (1), (2) and (3).

(8) In the case of aluminium, ab-initio computations based on the local-density approximation give better results for $H_{1V}^F$ than computations based on the generalized gradient approximation but, as the counterexample of copper, shows, this is not a generic result.

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The authors would like to thank Professor M. Fähnle for numerous thorough discussions on ab-initio calculations on defects in metals and Professor H. D. Carstanjen and Professor W. Frank for their critical reading of the paper. One of the authors (A. S.) gratefully acknowledges the hospitality of the Structure/Property Relations Group at Los Alamos National Laboratory, Los Alamos, N. M., where part of the present work was done.

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Appendix: A. Estimation of the Defect Losses to Surface Sinks During Quenching

We make the assumption that the quench from the temperature \( T \) to the surfaces is a unique function \( T = T(t) \) of the time \( t \) since the beginning of the quench at \( t = 0 \) and \( T = T_q \). It is then expedient to replace the independent variable \( t \) by

\[
s(t) = \int_{t=0}^{t} D(T(t'))\,dt' = \int_{T=0}^{T=T_q} D(T')\,dt'/T'
\]

where \( D(T) \) is the diffusivity of the defects. In terms of \( s \), the one-dimensional diffusion equation for the defect concentration \( C(x, t) \) may be written as

\[
\frac{\partial C}{\partial s} = \frac{\partial^2 C}{\partial x^2}.
\]

We make the further assumption that the specimen surface at \( x = 0 \) acts as a perfect sink, hence \( C(0, t) \equiv 0; \forall t > 0 \), and that the quench is fast enough for only one specimen surface to be taken into account at a time. (If the second assumption is not satisfied, the loss problem can no longer be handled by a simple correction procedure but requires a much more elaborate treatment.) The solution of (A.2) describing this situation is well known to be

\[
C(x, t) = C^{eq}(T_q)\text{erf}(s^{-1/2}x/2) \quad (x \geq 0, t > 0),
\]

where \( C^{eq}(T_q) \) is the equilibrium concentration at the quenching temperature, \( T_q \), and

\[
\text{erf}(z) := \frac{2}{\pi^{1/2}} \int_0^z \exp(-z^2)\,dz
\]

denotes the error function.

The rate of defect loss to the surface sinks is proportional to

\[
D\frac{\partial C(x, t)}{\partial x}{\bigg|}_{x=0} = DC^{eq}(T_q)(\pi s^{-1/2})\]

\[
= 2C^{eq}(T_q)\frac{d}{dt}(s/\pi)^{1/2}.
\]

We may integrate (A.5) without having to specify \( s(t) \). For the total loss we obtain

\[
\int_0^\infty D \frac{\partial C(x, t)}{\partial t} \,dt = 2C^{eq}(T_q)[s(\infty)/\pi]^{1/2}.
\]

The preceding result means that the total loss to one specimen surface is equivalent to the complete depletion of a layer of width

\[
L_{depth} = 2[s(\infty)/\pi]^{1/2}.
\]

In a slab of width \( L \), the fraction of defects lost to the two surfaces is therefore

\[
2L_{depth}/L = 4[s(\infty)/\pi]^{1/2}/L.
\]
ing losses are based on the highest quenching temperature $T_q$ employed. $L$ denotes the specimen thickness; for the initial quenching rates $\alpha T_q$ see text.

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<th>$L$ [m]</th>
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<th>$\alpha$ [s$^{-1}$]</th>
<th>$s(\infty)$ [10$^{-13}$ m$^2$]</th>
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<td>10.4</td>
<td></td>
</tr>
<tr>
<td>5 $\times$ 10$^{-5}$</td>
<td>823</td>
<td>1 $\times$ 10$^3$</td>
<td>121.5</td>
<td>104</td>
<td>4.6 $\times$ 10$^{-2}$</td>
<td>Berger et al.$^{27}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 $\times$ 10$^4$</td>
<td>12.1</td>
<td></td>
<td>14.5 $\times$ 10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>1 $\times$ 10$^{-4}$</td>
<td>800</td>
<td>2 $\times$ 10$^6$</td>
<td>2.5 $\times$ 10$^5$</td>
<td>1.10</td>
<td>7.5 $\times$ 10$^{-3}$</td>
<td>Present work</td>
</tr>
</tbody>
</table>

and

$$T = T_q \exp(-\alpha t), \quad t = \alpha^{-1} \ln(T_q/T), \quad (A.10)$$

where

$$\alpha T_q \equiv -dT/dt|_{t=0} \quad (A.11)$$

is the initial quenching rate (cf. Sect. 2.2). The integral resulting from the insertion of (A.9) and (A.10) into (A.1) may be evaluated in terms of the exponential integral

$$Ei(-z) = \int_{z=\infty}^{\infty} \xi^{-1} \exp(-\xi) d\xi$$

$$= \exp(-z) \sum_{k=1}^{n} (-1)^k (k-1)! z^{-k} + R_n. \quad (A.12)$$

In (A.12), the right-hand expression is an asymptotic series with the residual term $|R_n| < n!|z^{-(n+1)}|$ (for real z). We thus obtain

$$s(\infty) = (D_0/\alpha) Ei(-H^M/k_B T_q) \approx D(T_q)(k_B T_q/\alpha H^M) \left(1 - \frac{k_B T_q}{H^M} + 2 \left(\frac{k_B T_q}{H^M}\right)^2 + \cdots\right) \quad (A.13)$$

With the initial cooling rate $\alpha T_q = 2.0 \times 10^6$ K s$^{-1}$ (Section 2.2), the monovacancy diffusion $D_{1V} = 6.0 \times 10^{-6}$ m$^2$s$^{-1}$ exp(−0.61 eV/k_B T) and the highest quenching temperature of the present experiments, $T_q = 800$ K, (A.13) gives $s(\infty) = 1.1 \times 10^{-13}$ m$^2$. It follows from (A.8) that in the present work the vacancy fraction lost to the specimen surface during the quench was at most about $4(1.1 \times 10^{-13}/\pi)^{1/2} = 7.5 \times 10^{-3}$. The losses to the surface may thus be disregarded in the present work.

Table A.1 compares the present results with those pertaining to earlier quenching work. All estimates of the quenching losses are based on the highest quenching temperature $T_q$. Tzanetakis et al.$^{360}$ state that their initial quenching rates were between 9 $\times$ 10$^3$ K s$^{-1}$ and 12 $\times$ 10$^3$ K s$^{-1}$. Berger et al.$^{27}$ do not give quenching rates. We have estimated their relative quenching losses by assuming $\alpha T_q = 1 \times 10^5$ K s$^{-1}$ or 1 $\times$ 10$^6$ K s$^{-1}$. Since the quenching in superfluid helium (Rinderer and Schultz$^{66}$) employed by Berger et al.$^{27}$ is known to result in rather low quenching rates, the second assumption may be more realistic than the first.

**Appendix: B. Specific-heat measurements**

Mono- and divacancies in thermal equilibrium increase the enthalpy per atom of a metal by $H_{1V}^{eq} C_{1V}^{eq} + H_{2V}^{eq} C_{2V}^{eq}$. Their contribution to the specific heat per atom at constant pressure, $\Delta c_p$, is thus given by

$$\Delta c_p/k_B = (k_B T)^{-2} [1^2 C_{1V}^{eq} + 2^2 C_{2V}^{eq}]$$

$$= (H_j/k_B T)^2 [C_{jV}^{eq} + [(H_{j}^{eq}/H_{j}^2) - 2] C_{jV}^{eq}], \quad (B.14)$$

where for simplicity we have written $H_j := H_{jV}^2$ ($j = 1, 2$). Provided

$$H_{2V}^{eq}/H_{1V}^{eq} < 2 - \sqrt{2} = 0.59 \quad (B.15)$$

holds, it follows from (B.14) that the presence of divacancies enhances the specific heat per atom over the value it would have if $C_{2V}^{eq} = C_{1V}^{eq}$, i.e. if there were no divacancies. Since (B.15) is realistic (in aluminium the left-hand side is about 0.27), specific-heat measurements are more sensitive against divacancies in thermal equilibrium than differential dilatometry.

Shukla, Plint, and Ditmars$^{67}$ analyzed, in terms of the specific heat at constant volume, their measurements of the specific heat of Al at constant pressure, $c_p$, in the temperature range 273 to 933 K$^{68}$ as well as the data of other authors. Beyond 780 K, $c_p$ (the specific heat per atom at constant volume) exceeds 3k_B. This is a strong indication of a contribution that is not due to phonons. Shukla et al.$^{67}$ calculate the effects of phonon anharmonicities using different models and conclude that the extra specific heat is mainly due to vacancies in thermal equilibrium. In the next paragraph we refine their analysis by taking into account $V_1$ and $V_2$.

From Fig. 4 of Shukla et al.$^{27}$ and eq. (7) we deduce

$$\Delta c_p(900 K)/k_B = (5.3 \pm 0.3) \times 10^{-2}, \quad (B.16)$$

where the uncertainty results mainly from the (small) correction for anharmonic effects other than those already included in the difference $c_p - c_V$. From (B.16) we obtain for the curly brackets on the right-hand side of (B.14) the numerical value (7.5 $\pm$ 0.4) $\times$ 10$^{-4}$. On the other hand, Fig. 5 gives us $C_{1V}^{eq}(900 K) = 8.5 \times 10^{-4}$. With $[(H_{2}^{eq}/H_{1}^2) - 2] \approx 1.0$, this indicates that $C_{2V}^{eq} > 0$ and that not only the total thermal-equilibrium concentration but also the $V_2$ fraction deduced in Sect. 4.4 is compatible with the calorimetric measurements of Ditmars et al.$^{68}$