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Atomic Defects and Diffusion in Metals*

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Atomic Defects and Diffusion in Metals

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The tracer self-diffusion data for fcc and refractory bcc metals are briefly reviewed with respect to (i) the available monovacancy formation and migration properties and (ii) the high-temperature diffusion enhancement above that expected for mass transport via atomic exchange with monovacancies. While the atomic-defect mechanism for low-temperature self-diffusion can be reliably attributed to monovacancies, the mechanisms responsible for high-temperature mass transport are not so easily defined at this time; both divacancies and interstitials must be seriously considered. Possibilities for improving our understanding in this area are discussed.

I. INTRODUCTION

Precise tracer self-diffusion data over a wide range of temperatures have recently become available for the refractory bcc metals. These data generally exhibit a temperature dependence similar to that found in the tracer self-diffusion data for the fcc metals, and the bcc alkali metals; the tracer-diffusion coefficient follows a linear Arrhenius behavior at low temperatures, but is enhanced with increasing magnitude as one approaches the melting temperature. Since the observed diffusion behavior is rather similar for these metals, it has become rather common [1,2] to think that the atomic-defect mechanisms for such mass transport are also similar. These mechanisms are usually thought to be atomic exchange with monovacancies at low temperatures, enhanced by the additional exchange with increasing concentrations of divacancies as the melting temperature is approached [3]. However, the data regarding atomic-defect properties that have become available in the past few years suggest the need to reconsider this commonly held, and most probably oversimplified, picture of self-diffusion in metals.

II. TRACER SELF-DIFFUSION

The tracer self-diffusion (D_T) data for the fcc metals Al, Ag, Au, Cu, and Ni are shown in Fig. 1, along with single-exponential fits to the low-temperature data, indicating the respective activation enthalpies Q_1 , and the "best" available values for the enthalpies of monovacancy formation (H_{1v}^F) and migration (H_{1v}^M). These vacancy properties have resulted from a combination of equilibrium positron-annihilation studies and nonequilibrium quenching investigations (Al [21,22], Ag [23,24], Au [25], Cu [26,27], Ni [28]). The low-temperature diffusion behavior has been linearly extrapolated to the respective melting temperatures (T_m) of these metals to indicate the enhancement of D_T over that expected from tracer exchange with monovacancies having temperature-independent properties. The enhancement at T_m is indicated by the shaded bar for each metal in Fig. 1. Similarly, the tracer self-diffusion data for the refractory bcc metals V, Nb, Ta, Cr, Mo, and W are shown in Fig. 2, in which the straight lines shown are those dominating the low-temperature

Fig. 1. Tracer self-diffusion in fcc metals. $\ln D_T$ versus reciprocal temperature for Al [4,5], Ag [7,8], Au [5,9-14], Cu [15-18], and Ni [19,20].

Fig. 2. Tracer self-diffusion in refractory bcc metals. $\ln D_T$ versus reciprocal temperature for V [29], Nb [30], Ta [31,32], Cr [33,34], Mo [35], and W [36].

behavior, deduced from two-exponential fits to the data, with the exception of Cr. For Cr, only a single-exponential fit appears to be appropriate, corresponding to the high-temperature diffusion regions in the other refractory bcc metals (See [34] for a discussion). In general, the tracer self-diffusion (D_T) enhancement at T_m for the refractory bcc metals is considerably greater than that for the fcc metals, amounting to from ~ 85 to almost 100% of the tracer current at T_m compared with from 20 to 75% in the case of the fcc metals. The activation enthalpies Q_1 and Q_2 for the low- and high-temperature parts of the $\ln D_T$ versus T^{-1} plots, respectively, are presented in Fig. 2, along with the "best" (i.e., most reliable) values for the monovacancy formation and migration enthalpies in W [37] and Mo [38], available from quenching studies and consistent with positron annihilation equilibrium results [39].

It should be noted in relation to Figs. 1 and 2, that such displays of enhancement, or Arrhenius-plot curvature (as it is usually referred to), are related to that of actual self-diffusion through the effective correlation factor f , which is temperature dependent if more than one atomic-defect mechanism is operative over the temperature range of the measurements. Thus, for example, if either a divacancy (2v) or interstitialcy (I) mechanism, or a combination of these, contributes to the observed high-temperature enhancement in D_T , then the actual enhancement of the self-diffusion coefficient (D_S) would be greater than that indicated in Figs. 1 and 2, since both $f(2v)$ and $f(I)$ are less than $f(1v)$ in both the fcc and bcc lattices (see Table 1). Thus, highly correlated (i.e., very low f values) tracer or impurity jumps at high temperatures may suggest considerably less enhancement near T_m than might be observable if true (random) self-diffusion were itself being monitored.

Tracer-diffusion isotope-effect measurements have been performed in a number of fcc and bcc metals in order to investigate the temperature dependence of the effective correlation factor for tracer diffusion and, thereby, the atomic-defect mechanisms responsible for mass transport. The results for recent measurements in Cr [33] and Nb [41] are shown in Fig. 3 along with those from Na [42], Cu [15], and Ag [7]. Isotope-effect measurements have been useful in indicating that monovacancies are primarily responsible for mass transport in Cu and Ag. For Ag, they also suggest that a more highly correlated jump process makes an increasingly important contribution at higher temperatures. However, their contribution to understanding the atomic-defect mechanisms for self-diffusion in the

Table 1. Correlation factors for tracer self-diffusion by monovacancy, divacancy [2], and dumbbell interstitialcy mechanisms [40].

Correlation factor	fcc	bcc
$f(1v)$	0.78	0.73
$f(2v)$	0.49	0.35 [†]
$f(I)$	0.44	0.41

[†]Value for $2n+4n+2n$ jump sequence; $f(2v)=0.43$ and 0.49 for $1n+2n+4n$ and $1n+2n+1n$ jumps, respectively.

Fig. 3. Isotope-effect ($f\Delta K$) versus (T_m/T) for Cu, Ag, Cr, Nb, and Na.

bcc metals can now be seen to be minimal. This is a result of (i) the rather low values of fAK that have been measured, (ii) the current intractability of estimating AK values theoretically, and (iii) the fact that the correlation factors for tracer diffusion via divacancy (2v) and interstitialcy (I) jumps are rather similar [40]. Thus, even within the low-temperature diffusion regime in Nb and Na, where monovacancies are thought to dominate the diffusion process, the expected value for $f(1v) = 0.73$ would demand from the measured fAK values that $AK \approx 0.6$; but this is undistinguishable from some of the 2v cases with AK of unity or slightly less, or the I case with $AK \approx 0.5$. (Note: The isotope effect (fAK) plotted in Fig. 3 assumes single-atom jumps for all mechanisms involved; the contribution from a two-atom jump process, such as the I mechanism, would reduce the indicated fAK values by up to a factor of ~ 2). Thus, although the results of the isotope-effect measurements will eventually have to be shown to be consistent with those from more direct studies of the atomic-defect mechanisms for self-diffusion, they are of limited value at present in determining such mechanisms. A similar situation exists for essentially any technique that focuses upon tracer correlation (e.g., quasielastic neutron scattering), since although the 1v mechanism may be distinguishable from the 2v or I mechanism, as recently shown for Na [40], these latter two mechanisms would remain indistinguishable in such measurements. This may now be a rather important consideration, especially, but possibly not uniquely so, for the refractory bcc metals.

III. ATOMIC-DEFECT MECHANISMS

It must be emphasized that Arrhenius-plot curvature, as almost ubiquitously results from careful tracer-diffusion studies over a sufficiently wide range of temperatures, does not in itself indicate that more than one diffusion mechanism is operative. Ancillary measurements, preferably dealing directly with the atomic defects themselves, are required to elucidate the atomic-defect mechanisms of diffusion. The case of Al is particularly interesting in this regard, since a controversy over its self-diffusion behavior has existed [1,3], primarily because no suitable radiotracer of Al is available for standard tracer self-diffusion studies at temperatures below ~ 650 K. As such, a representation of the lower-temperature NMR data from [6] is shown along with the available tracer data for Al in Fig. 1. Taken together, these indicate rather strong diffusion enhancement at high temperatures, but the results of neither technique alone show this. The source of this controversy was a number of impurity diffusion measurements [43-45] in Al, carried out over a wide range of temperatures, which indicated no such enhancement; these were taken as a tacit indication that the apparent enhanced self-diffusion at high temperatures in Al was largely a result of combining data from two separate techniques, a procedure which had been unnecessary for other metals. However, considerable information regarding the vacancy defects in Al has become available [46,47] which is consistent with the strongly enhanced self-diffusion behavior indicated by the combination of tracer-diffusion and NMR data shown in Fig. 1, and indicates that this enhancement is due to divacancies. Thus, observations [21] of selective interaction of Fe with the 2v in dilute Al(Fe) would allow for a rather natural explanation of the lack of observed Arrhenius-plot curvature in the Fe-diffusion measurements in Al, and in the other cases as well if the 2v-solute interactions were similarly strong, since the resulting highly correlated impurity jumps via exchange with divacancies would be expected to suppress the diffusion enhancement at high temperatures.

The combination of precise low-temperature tracer-diffusion measurements of Q_1 and independent measurements of H_{1v}^F and H_{1v}^M by post-quench resistometry and positron annihilation have now clearly shown, by the theoretically expected equality of Q_1 and $(H_{1v}^F + H_{1v}^M)$, that atomic exchange with monovacancies is the dominant mechanism for self-diffusion at low temperatures in a number of fcc and, most recently, refractory bcc metals (see Figs. 1 and 2 and their associated References). The evidence that these dominant defects are vacancies comes from a number of investigations using "vacancy-specific" techniques, such as differential dilatometry, positron annihilation, or direct observations of vacancies with field ion microscopy (FIM) and of vacancy precipitates with transmission electron microscopy (TEM) [46].

It is probably safe to conclude that in all so-called "normal" metals self-diffusion at low temperatures takes place via atomic exchange with monovacancies. In contrast, however, the explanation of the mechanisms responsible for high-temperature diffusion is presently not so clear. The high-temperature diffusion enhancements seen in Figs. 1 and 2 could, in principle, be due either to temperature-dependent properties of the monovacancies, or to the additional contributions from other atomic-defect mechanisms, or to a combination of these.

What is the available evidence for additional defect mechanisms? In the fcc metals, three clear and incontrovertible cases would seem to exist, Al, Au, and Pt. For Al, post-quench resistivity annealing studies [47,21] have demonstrated the existence of two types of mobile defects, which anneal out at two different temperatures and whose relative proportions change with varying quench temperature, as shown in Fig. 4. Such post-quench annealing behavior cannot be explained by any of the single-defect models for Arrhenius-plot curvature [48-50]. The post-quench annealing behavior [47,21], the total vacancy concentration and formation enthalpy data [46], and the tracer [4,5] and NMR [6] diffusion data are consistent with a description in terms of an equilibrium vacancy ensemble that is enhanced with increasing temperature by an increasing concentration of divacancies, which are more mobile than the monovacancy, and which are responsible for the high-temperature diffusion enhancement. Direct experimental evidence for the divacancy and its greater mobility has not yet been obtained for Al. However, divacancies have been directly observed in a FIM investigation of quenched Pt [51], which also showed via an anneal that the divacancy (2v) is more mobile than the monovacancy (1v); these results thus lend significant support to the 1v-2v model for self-diffusion in the fcc metals.

Further strong evidence for divacancy contribution to diffusion enhancement at elevated temperatures comes from extensive investigations of quenched Au and the self-consistent modeling of the tracer-diffusion data, the vacancy concentration information, and the post-quench annealing behavior (see [25] and references therein). Of particular importance with regard to the evidence for divacancy contributions in Au is the vacancy-concentration dependence of the effective migration enthalpy of the quenched-in vacancy ensemble, shown in Fig. 5; the data of [52] were obtained from TEM observations of the growth of stacking-fault tetrahedra at various temperatures in a given sample. These data, as in the case of the Al results, cannot be explained on the basis of a single mobile defect alone, but require increasing contributions from more mobile defects for increasing C_V values. This conclusion similarly applies to the case of Pt, in which the effective migration

Fig. 4. Isochronal resistivity (ρ) annealing in Al quenched from various temperatures, T_0 [47].

Fig. 5. Vacancy-concentration (C_V) dependence of the effective migration enthalpy (H_{eff}^M) in quenched Au [52]. The shaded area represents data from resistivity annealing studies (see [25]).

enthalpy was also found [53] to decrease with increasing concentration of quenched-in vacancies, and for which the available tracer-diffusion [54] and vacancy defect [55] data are consistent with a 1v-2v model. This is essentially the evidence for the divacancy and its contribution to high-temperature diffusion enhancement; it is limited, somewhat indirect, but nevertheless compelling, at least for these three fcc metals. However, one must ask: How general is such an explanation; can it be comfortably extended to other fcc metals, and also to the bcc metals?

Attempts have been made to deduce information regarding divacancies from the fitting of 1v-2v models to the measured temperature dependence of positron annihilation data in other fcc metals, such as Cu and Ni [56,57]. Although two-defect fits to these data can be made, they lack uniqueness in much the same manner as do fits to curved Arrhenius plots using either two-defect models [18] or single-defect models with strongly temperature-dependent properties [49,50]. A recent detailed study of positron annihilation Doppler-broadening data for Cu [27], shown in Fig. 6, concluded that no unique divacancy information could be obtained from this type of positron data using parametric trapping-model fits, at least for Cu which has a rather low vacancy concentration at T_m . This difficulty results from a lack of knowledge regarding the temperature-dependent annihilation characteristics for 1v- and 2v-trapped positrons. If these characteristics were known, from either theory or experiment, the high-temperature lineshape parameter variation could be deconvoluted into its component, defect-specific (1v,2v) parts. Otherwise, only fits yielding model-dependent results for the highest-temperature region (see Fig. 6) are obtained. The results of this positron annihilation study of Cu [27], taken together with those of a low-temperature quenching study [26] and complementary higher-temperature differential dilatometry [58] and quenching [59] investigations, give no indication of the presence of divacancies in the total vacancy ensemble, even though the observed high-temperature diffusion enhancement is significant (see Fig. 1). An alternative explanation has been suggested [60] for this diffusion enhancement in terms of a contribution to atomic transport via a dumbbell interstitialcy mechanism; this defect is known [61] to be highly mobile from very low-temperature post-irradiation annealing measurements, and thus only very low equilibrium concentrations of the interstitial would be required. The sum of the values for the formation (~ 2.2 eV) and migration (~ 0.1 eV) enthalpies of the dumbbell interstitial in Cu would be consistent with the limiting high-temperature activation enthalpy for self-diffusion Q_2 (2.47 eV), within the experimental uncertainties. It would appear that a model for the high-temperature diffusion enhancement in Cu based upon either the 2v or 1 mechanism, or a combination of these, could be consistent with the available diffusion and defect data.

The possibility for significant contributions to high-temperature mass transport from an interstitialcy mechanism becomes even more intriguing when one considers the data on both tracer self-diffusion and atomic-defect properties that have recently become available for the refractory bcc metals. In the case of the bcc metals, especially, the possible contribution of self-interstitials to high-temperature diffusion cannot be taken lightly for a number of reasons: (1) The equilibrium

Fig. 6. Doppler-broadening lineshape parameter $F(T)$ for Cu as a function of T , and four statistically indistinguishable trapping-model fits to the data [27]. The $F_v(T)$ deduced from these fits (1v or 1v-2v) are seen to accommodate to the uncertainties regarding the vacancy ensemble.

concentration ratio of interstitials to vacancies may be expected to be higher in the more open bcc lattice than in the close-packed fcc lattice; the mobilities of the dumbbell interstitials in the fcc and bcc metals are rather similar and large [62]. (ii) The divacancy in fcc metals, in which the vacancies sit on nearest-neighbor sites, is known to be more mobile than the monovacancy; this leads to a combination of defect-concentration and mobility enhancement at high temperatures to account for the observed diffusion enhancement in the fcc metals. In bcc metals, on the other hand, the divacancy, in which the vacancies are theoretically predicted to sit on sites that are second-nearest-neighbors to one another [62], is most likely to be similarly or somewhat less mobile than the monovacancy; this would require a defect-concentration enhancement alone to account for the even greater high-temperature diffusion enhancement found in these metals compared with the fcc metals. (iii) The vacancy-defect data that have recently become available for the bcc refractory metals W and Mo do not seem to allow for the divacancy to account for the observed high-temperature diffusion enhancement.

The most completely studied refractory bcc metal is W, for which reliable tracer-diffusion and vacancy-defect property measurements have recently become available. The sum of the measured [37] $H_{1v}^F = 3.6$ eV and $H_{1v}^M = 1.8$ eV agrees well with the $Q_1 = 5.4$ eV from the low-temperature diffusion data [36]. This result, along with direct observations of quenched-in vacancy precipitates with TEM [37] and positron annihilation measurements of trapping at vacancies [39], indicate clearly that, as expected, monovacancies are responsible for the low-temperature diffusion. A similar conclusion can be drawn for Mo, since the sum of the measured [38] $H_{1v}^F = 3.2$ eV and $H_{1v}^M = 1.3$ eV also agrees well with the $Q_1 = 4.5$ eV from tracer-diffusion studies [35], and equilibrium positron annihilation measurements [39] support this view. However, the explanation for the high-temperature diffusion enhancement found in both of these metals is not so easily found. A divacancy (2v) model for this enhancement would require that $Q_2 = 2H_{1v}^F - H_{2v}^b + H_{2v}^M$, assuming one 2v configuration and jump sequence to be dominant. As pointed out elsewhere [37] for W, the value [36] of $Q_2 = 6.9$ eV is not easily accommodated to a 2v model, since it, along with the quenching results [37], would require a rather strongly bound ($H_{2v}^b \geq 2$ eV) divacancy with a mobility similar to that of the monovacancy to account for the observed enhancement. Recently [63], direct observations of both mono- and divacancies in quenched W using FIM have been analyzed to obtain a value for the divacancy binding enthalpy; the result is $H_{2v}^b = 0.7$ eV, which confirms the inability to explain the observed value of Q_2 in W on the basis of a 1v-2v model. Also, recent calculations [64] of the divacancy properties in W have yielded a value for $H_{2v}^b = 0.8$ eV, obtained for the most stable relaxed configuration with second-nearest-neighbor vacancies, and a value for $H_{2v}^M = 1.95$ eV ($\approx H_{1v}^M$) for the easiest $2n+4n+2n$ jump sequence, in good agreement with [37,63] and the conclusions drawn here. The recent results [35,38] for Mo suggest that the high-temperature diffusion enhancement for this metal is similarly difficult to explain. For Mo, $Q_2 = 5.7$ eV; the condition $H_{2v}^M \geq H_{1v}^M$ would then require that $H_{2v}^b \geq 2$ eV, or more than 60% of its monovacancy formation enthalpy, an unlikely value, if its high-temperature diffusion were to be explained on the basis of a divacancy mechanism.

If not divacancies in these metals, then what? As suggested elsewhere [37] for W, the self-interstitial dumbbell would provide a relatively easy solution to the dilemma at hand, since its extremely high mobility would allow an exceedingly small equilibrium concentration of these defects to contribute in a very substantial way to mass transport at high temperatures. Thus, if one assumes that $Q_2 = H_I^F + H_I^M$, the sum of the formation and migration enthalpies of the interstitial, then the ratio (H_I^F/H_{1v}^F) would have to be ~ 1.9 for W and ~ 1.8 for Mo, hardly unreasonable values for the rather open bcc structure, and rather similar to the known ratio for Cu [27,60] of (H_I^F/H_{1v}^F) ≈ 1.7 . Clearly, although the reality of divacancies has now also been established in the refractory bcc metals [63], their presence does not appear to explain the strong high-temperature enhancement of self-diffusion observed in these metals. — A simpler and quite reasonable, but as yet unproven, alternative atomic-defect mechanism for this enhancement would be the interstitialcy migration of

the dumbbell interstitial. One cannot exclude the possibility that these two mechanisms act in concert, in varying degrees in different metals, to enhance the observed diffusion over that expected from atomic exchange with monovacancies.

The above discussion has assumed that (i) the properties of the various atomic defects are not strongly temperature dependent and (ii) the observed diffusion behavior is intrinsic and unaffected by impurities. Although small temperature dependences may be expected, the weight of the experimental and theoretical evidence to date appears to mitigate the arguments for strongly temperature-dependent defect properties. An example of this type of evidence is the excellent agreement between the theoretically expected $Q_1 = H_{1v}^F + H_{1v}^M$ for atomic transport via exchange with monovacancies and the values of these parameters, with Q_1 and H_{1v}^F measured at high temperatures and H_{1v}^M often measured at temperatures several hundred degrees lower. The likelihood that impurities are significantly responsible for the observed temperature-dependent diffusion behavior is reduced by the demonstrated reproducibility (e.g., see [30,36]) of D_T measurements.

IV. FUTURE PROSPECTS

Finally, it seems appropriate to consider which directions might be the most fruitful in further elucidating the atomic-defect mechanisms responsible for the high-temperature diffusion enhancement in both the fcc and refractory bcc metals, but especially in the latter owing to the magnitude of the effect and the future technological importance of these metals. Two parallel avenues of approach to the problem will have to be taken, one focused on determining the nature of the high-temperature vacancy-defect ensemble, the other focused on measuring the contribution to mass transport via the interstitialcy mechanism.

The first of these may have a solution close at hand in positron annihilation spectroscopy [65]. The full information available from two-dimensional angular correlation, previously used for electronic structure investigations of defect-free metals [66], can be used for the investigation of positrons annihilating from vacancy-defect-trapped states within the high-temperature equilibrium vacancy ensemble. By comparing such experimental results with those from realistic theoretical calculations (based upon a fully self-consistent formalism [67]) of the positron-annihilation characteristics from 1v- and 2v-trapped states, it should be possible for the first time to directly specify the components of the equilibrium vacancy ensemble in a metal. Such a combined experimental and theoretical investigation of Al is now in progress; the results will be reported elsewhere [68]. Neither the experimental nor the theoretical techniques being used for the Al investigation are limited with respect to the type of metal that can be studied in the future. Considerable information, including that unique to divacancies, is expected to be present in the experimental two-dimensional angular correlation spectra. Comparison of these spectra with the theoretical spectra, which exhibit distinctly different shapes for mono- and divacancies as shown in Fig. 7, should provide a new method for elucidating the nature of the equilibrium vacancy ensemble in a metal. This is nevertheless only one of the avenues that must be explored in trying to understand the high-temperature diffusion behavior in metals.

Fig. 7. Calculated two-dimensional angular correlation surfaces in the (001) plane of Al for positrons annihilating from (a) the lattice [67], (b) the monovacancy-trapped state, and (c) the divacancy-trapped state [68].

The second avenue may be more difficult, since the equilibrium concentration of interstitials necessary to account for the diffusion enhancement at elevated temperatures is below the detection limit of any presently available technique. Therefore, investigations regarding the interstitial will have to focus on mass transport via this high-diffusivity path. It is hoped that some clever ideas for such studies will arise in the future. For the present, a plan of attack that may be productive would be a set of careful investigations of solute diffusion over a wide range of temperatures, based upon prior studies of solute-interstitial interactions after low-temperature irradiation to determine the binding and configurations of the solute-interstitial pair. For example, if it could be determined for impurity elements A and B in a given metal host that A formed a mixed dumbbell, while B remained substitutional, then tracer-diffusion studies of A and B in the host metal should indicate whether the high-temperature diffusion enhancement were due to dumbbell interstitials or not, depending on the relative enhancements seen in $D_A(T)$ and $D_B(T)$. In conclusion, while it is clear that the atomic-defect mechanism for low-temperature self-diffusion can be reliably attributed to atomic exchange with monovacancies, it is equally clear that the atomic-defect mechanisms responsible for high-temperature mass transport are not so easily defined at this time. This may be especially the case for the refractory bcc metals, but not exclusively so. Both divacancies and interstitials need to be seriously considered in the future planning of experiments to elucidate the high-temperature diffusion behavior in metals.

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REFERENCES

- [1] N. L. Peterson, *J. Nucl. Mater.* **69 & 70**, 3 (1978).
- [2] H. Mehrer, *J. Nucl. Mater.* **69 & 70**, 38 (1978).
- [3] A. Seeger and H. Mehrer, in *Vacancies and Interstitials in Metals*, edited by A. Seeger et al. (North-Holland, Amsterdam, 1970) p. 1.
- [4] T. S. Lundy and J. F. Murdock, *J. Appl. Phys.* **33**, 1671 (1962).
- [5] M. Beyeler and Y. Adda, *J. Physique* **29**, 345 (1968).
- [6] S. Dais, Diplomarbeit, Universität Stuttgart, 1974 (unpublished).
- [7] S. J. Rothman, N. L. Peterson, and J. T. Robinson, *phys. stat. sol.* **39**, 635 (1970).
- [8] N. Q. Lam, S. J. Rothman, H. Mehrer, and L. J. Nowicki, *phys. stat. sol. (b)* **57**, 225 (1973).
- [9] S. M. Makin, A. H. Rowe, and A. D. LeClaire, *Proc. Phys. Soc.* **70**, 545 (1957).
- [10] H. M. Gilder and D. Lazarus, *J. Phys. Chem. Solids* **26**, 2081 (1965).
- [11] A. Gainotti and L. Zecchina, *Nuovo Cim.* **40B**, 295 (1965).
- [12] W. Rupp, U. Ermert, and R. Sizmann, *phys. stat. sol.* **33**, 509 (1969).
- [13] D. Gupta and R. T. C. Tsui, *Appl. Phys. Lett.* **17**, 294 (1970).
- [14] Chr. Herzig, H. Ecksele, W. Bussmann, and D. Cardis, *J. Nucl. Mater.* **69 & 70**, 61 (1978).
- [15] S. J. Rothman and N. L. Peterson, *phys. stat. sol.* **35**, 305 (1969).
- [16] K. Maier, C. Bassani, and W. Schüle, *Phys. Lett.* **44A**, 539 (1973).
- [17] N. Q. Lam, S. J. Rothman, and L. J. Nowicki, *phys. stat. sol. (a)* **23**, K35 (1974).
- [18] D. Bartdorff, G. Neumann, and P. Reimers, *Phil. Mag. A* **38**, 157 (1978).
- [19] H. Bakker, *phys. stat. sol.* **28**, 569 (1968).
- [20] K. Maier, H. Mehrer, E. Lessmann, and W. Schüle, *phys. stat. sol. (b)* **78**, 689 (1976).
- [21] A. S. Berger, S. T. Ockers, M. K. Chason, and R. W. Siegel, *J. Nucl. Mater.* **69 & 70**, 734 (1978).
- [22] M. J. Fluss, L. C. Smedskjaer, M. K. Chason, D. G. Legnini, and R. W. Siegel, *Phys. Rev. B* **17**, 3444 (1978).
- [23] Y. C. Jean, K. G. Lynn, and J. E. Dickman, *Phys. Rev. B* **21**, 2655 (1980).
- [24] M. Doyama and J. S. Koehler, *Phys. Rev.* **127**, 21 (1962).

- [25] R. P. Sahu, K. C. Jain, and R. W. Siegel, *J. Nucl. Mater.* **69 & 70**, 264 (1978).
- [26] A. S. Berger, S. T. Ockers, and R. W. Siegel, *J. Phys. F* **9**, 1023 (1979).
- [27] M. J. Fluss, L. C. Smedskjaer, R. W. Siegel, D. G. Legnini, and M. K. Chason, *J. Phys. F* **10**, 1763 (1980).
- [28] L. C. Smedskjaer, M. J. Fluss, D. G. Legnini, M. K. Chason, and R. W. Siegel, *J. Phys. F* **11**, 2221 (1981); see also these Proceedings.
- [29] J. Pelleg, *Phil. Mag.* **29**, 383 (1974).
- [30] R. E. Einziger, J. N. Mundy, and H. A. Hoff, *Phys. Rev. B* **17**, 440 (1978).
- [31] R. E. Pawel and T. S. Lundy, *J. Phys. Chem. Solids* **26**, 937 (1965).
- [32] D. Hönes, Diplomarbeit, Universität Stuttgart, 1979 (unpublished).
- [33] J. N. Mundy, C. W. Tse, and W. D. McFall, *Phys. Rev. B* **13**, 2349 (1976).
- [34] J. N. Mundy, H. A. Hoff, J. Pelleg, S. J. Rothman, L. J. Nowicki, and F. A. Schmidt, *Phys. Rev. B* **24**, 658 (1981).
- [35] K. Maier, H. Mehrer, and G. Rein, *Z. Metallk.* **70**, 271 (1979).
- [36] J. N. Mundy, S. J. Rothman, N. Q. Lam, H. A. Hoff, and L. J. Nowicki, *Phys. Rev. B* **18**, 6566 (1978).
- [37] K.-D. Rasch, R. W. Siegel, and H. Schultz, *Phil. Mag. A* **41**, 91 (1980); H_{lv}^F from data of Fig. 6 [37] using a revised $\rho(T)$ scale from J. N. Mundy, *Phil. Mag. A*, to be published (1982).
- [38] I. A. Schwirtlich and H. Schultz, *Phil. Mag. A* **42**, 601 (1980).
- [39] K. Maier, M. Peo, B. Saile, H.-E. Schaefer, and A. Seeger, *Phil. Mag. A* **40**, 701 (1979).
- [40] D. Wolf, *Phil. Mag. A*, to be published (1982).
- [41] W. Bussmann, Chr. Herzig, H. A. Hoff, and J. N. Mundy, *Phys. Rev. B* **23**, 6216 (1981).
- [42] J. N. Mundy, *Phys. Rev. B* **3**, 2431 (1971); J. N. Mundy, L. W. Barr, and F. A. Smith, *Phil. Mag.* **14**, 785 (1966).
- [43] N. L. Peterson and S. J. Rothman, *Phys. Rev. B* **1**, 3264 (1970).
- [44] W. B. Alexander and L. M. Slifkin, *Phys. Rev. B* **1**, 3274 (1970).
- [45] S. Fujikawa and K. Hirano, *Trans. Japan Inst. Met.* **17**, 809 (1976).
- [46] R. W. Siegel, *J. Nucl. Mater.* **69 & 70**, 117 (1978).
- [47] V. Levy, J. M. Lanore, and J. Hillairet, *Phil. Mag.* **28**, 373 (1973).
- [48] H. M. Gilder and D. Lazarus, *Phys. Rev. B* **11**, 4916 (1975).
- [49] P. Varotsos, W. Ludwig, and K. Alexopoulos, *Phys. Rev. B* **18**, 2683 (1978).
- [50] A. DaFano and G. Jacucci, *J. Nucl. Mater.* **69 & 70**, 549 (1978).
- [51] A. S. Berger, D. N. Seidman, and R. W. Balluffi, *Acta Met.* **21**, 123, 137 (1973).
- [52] K. C. Jain, Ph.D. Thesis, S.U.N.Y. at Stony Brook, 1972 (unpublished); K. C. Jain and R. W. Siegel to be published; see also [22].
- [53] J. Polák, *phys. stat. sol.* **21**, 581 (1967).
- [54] G. Rein, H. Mehrer, and K. Maier, *phys. stat. sol. (a)* **45**, 253 (1978).
- [55] R. W. Balluffi, *J. Nucl. Mater.* **69 & 70**, 240 (1978).
- [56] G. Dlubek, O. Brümmer, and N. Meyendorf, *Appl. Phys.* **13**, 67 (1977).
- [57] S. Nanao, K. Kuribayashi, S. Tanigawa, and M. Doyama, *J. Phys. F* **7**, 1403 (1977).
- [58] R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963).
- [59] R. R. Bourassa and B. Lengeler, *J. Phys. F* **6**, 1405 (1976).
- [60] W. Schilling, *J. Nucl. Mater.* **69 & 70**, 465 (1978).
- [61] F. W. Young, Jr., *J. Nucl. Mater.* **69 & 70**, 310 (1978).
- [62] R. A. Johnson and W. D. Wilson, in *Interatomic Potentials and Simulation of Lattice Defects*, edited by P. C. Gehlen et al. (Plenum, New York, 1974) p. 301.
- [63] J. Y. Park, H.-C. W. Huang, R. W. Siegel, and R. W. Balluffi, *Phil. Mag. A*, to be published (1982).
- [64] R. A. Johnson (private communication).
- [65] R. W. Siegel, in *Advanced Techniques for the Characterization of Microstructures*, edited by F. W. Wiffen and J. A. Spitznagel (TMS-AIME Conf. Proc., 1982) in press.
- [66] S. Berko, M. Haghgoorie, and J. J. Mader, *Phys. Lett.* **63A**, 335 (1977).
- [67] B. Chakraborty, *Phys. Rev. B* **24**, in press (1981).
- [68] M. J. Fluss, S. Berko, B. Chakraborty, K. Hoffman, P. Lippell, and R. W. Siegel, *Proc. Sixth Intl. Conf. on Positron Annihilation, 1982*, to be published.