

Equilibrium vacancy concentrations in copper investigated with the absolute technique

Th. Hehenkamp, W. Berger, J.-E. Kluin, Ch. Lüdecke, and J. Wolff
*Institut für Metallphysik, Abteilung für Metallkunde, Universität Göttingen,
 D-3400 Göttingen, Federal Republic of Germany*

(Received 28 June 1991)

The molar fraction of thermally generated vacant lattice sites N_v has been measured during thermal equilibrium up to temperatures near the melting point in 99.9998%-grade copper with an absolute technique. A high-resolution differential dilatometric experiment is performed. The thermal expansion of the lattice $\Delta a(T)/a_0$ is determined by the Debye-Scherrer technique. The macroscopic expansion $\Delta L(T)/L_0$ is measured with a special laser interferometer simultaneously as a function of temperature in the same specimen. The absolute concentration of equilibrium vacancies is obtained from $N_v(T) = 3[\Delta L(T)/L_0 - \Delta a(T)/a_0]$. The lattice expansion $\Delta a(T)/a_0$ can be determined with a relative accuracy of 2×10^{-5} . At high temperatures the error of the Laser interferometer is 2×10^{-6} for each point, respectively, equivalent to an absolute length variation of $0.04 \mu\text{m}$. An extrapolation of N_v up to the melting point T^m leads to $N_v(T^m) = (0.76 \pm 0.03) \times 10^{-3}$. The usual Arrhenius evaluation gives a formation enthalpy $H_v^f = (1.19 \pm 0.03) \text{ eV}$ and a formation entropy $S_v^f = (3.0 \pm 0.3)k$.

INTRODUCTION

It is well known that important mechanical, electrical, and optical properties of solids are strongly influenced by point defects. In case of substitutional solid solutions diffusion of matter depends on the formation of vacant lattice sites. The vacancy concentration N_v , determined by the minimum of the Gibbs free energy, is given by

$$N_v(T) = \exp \left[\frac{S_v^f}{k} - \frac{H_v^f}{kT} \right], \quad (1)$$

where S_v^f is the formation entropy, H_v^f the formation enthalpy, T the absolute temperature, and k Boltzmann's constant.

According to Eq. (1) the formation entropy and enthalpy can be determined, respectively, by an Arrhenius plot of the $N_v(T)$ data measured provided a monovacancy formalism is being operative. The measurement of vacancy concentrations is possible by various techniques. In previous thermal equilibrium experiments the temperature dependence of properties like specific heat and electric resistivity have been measured often.¹⁻⁶ The change of these properties due to thermal equilibrium defects is small compared to the thermal contribution of the defect-free crystal. This thermal background cannot be determined by independent measurements unambiguously while vacancies are present. Therefore problematic extrapolation of the measured properties from the lower temperature range is necessary, in which the vacancy concentration is negligible. Anharmonic phonon contributions which cannot be separated from the vacancy effect because they are not observable in the low temperature ranges where vacancies are not being formed thermally may add significantly to the thermal background with increasing temperature. A disagreement at high temperatures is hence possible.

Recently positron annihilation spectroscopy has be-

come a suitable tool for the study of vacancies in thermal equilibrium (for a review, see Ref. 7). Here the same kind of background problem does not arise, but the evaluation of the absolute vacancy concentration is again not possible because of other background problems and the uncertainty in the trapping rate of positrons. The basic idea of the absolute technique was described by Wagner and Beyer.⁸ They pointed out, that the expansion of the macroscopic volume of the sample should increase more rapidly than the one of the unit cell of the investigated material as function of temperature in case of vacancy formation. First coordinated measurements of both the relative macroscopic expansion and of x-ray lattice parameter variation were carried out by Gott (1942)⁹ in aluminum, but the accuracy of the equipment used was insufficient for observing a deviation of both curves at that time known to be very small today. Later the thermal variations of macroscopic and microscopic expansion were investigated in aluminum and lead by Feder and Nowick (1958).¹⁰ These authors determined the absolute concentration of vacancies $N_v(T)$ in thermal equilibrium applying an approach of Eshelby (1954),¹¹ which leads to

$$N_v(T) - N_I(T) = 3 \left[\frac{\Delta L(T)}{L_0} - \frac{\Delta a(T)}{a_0} \right]. \quad (2)$$

Here L is the macroscopic length, a the lattice parameter, and T the absolute temperature. L_0 and a_0 are the respective values at a low reference temperature. The concentration of thermally generated self-interstitials $N_I(T)$ is supposed to be negligible in fcc metals because of their high formation enthalpy.¹² It is important to note that the result of Eq. (2) is independent of the state of aggregation of the thermally generated defects and also of any detailed knowledge of the lattice relaxation around them.

In the early 1960s Simmons and Balluffi¹³⁻¹⁶ carried

out several well-known measurements in aluminum, silver, copper, and gold employing this technique. Further vacancy-formation measurements are known of Feder and Nowick¹⁷ in dilute lead alloys, of Feder¹⁸ in lithium and of Guérard¹⁹ in aluminum. Recently Trost *et al.*²⁰ tried to determine the equilibrium vacancy concentration in copper and gold using neutron instead of x-ray diffraction but, as reported by these authors, their results were only of preliminary character, since the experimental conditions were not optimal yet. The main difficulty of the absolute technique is the extremely high accuracy required in $\Delta L(T)/L_0$ and $\Delta a(T)/a_0$ in the order of a few 10^{-6} , which is necessary to separate the small contribution of vacancy formation from the thermal expansion effect to determine vacancy concentrations down to some 10^{-5} with some precision. Consequently the temperature difference between both, the $\Delta L(T)/L_0$ and $\Delta a(T)/a_0$ measurements has to be kept to less than 0.2 K. This requires a simultaneous measurement of both quantities in one and the same sample. Because of these difficulties, the absolute concentration of equilibrium vacancies in many metals and particularly alloys is still not well known. In this paper an apparatus will be described which allows a precise determination of the absolute vacancy concentration as function of temperature with an accuracy of about 2×10^{-6} in $\Delta L(T)/L_0$ and 2×10^{-5} in $\Delta a(T)/a_0$ limited by the x-ray goniometer used currently.

EXPERIMENTAL PROCEDURE

The polycrystalline sample (grain size of the order of mm), which is shown in Fig. 1 was prepared from 99.9998% grade copper supplied by Preussag, Goslar. For a determination of the lattice parameter according to the Debye-Scherrer technique a powder specimen of the same material was pressed and sintered exactly at the central axis of the sample in order to guarantee good thermal contact. At the back side of the sample, a differential thermocouple was mounted. It controlled an additional heater (fixed at the upper end of the sample holder) to reduce temperature gradients in the sample to less than 0.08 K/cm at 1000 K. The thermal expansion was measured by a special laser interferometer. As shown in Fig. 2, the top of the sample forms a laser-illuminated slit with the surrounding cage. Provided the coefficient of expansion of the cage is much smaller than that of the sample, the slit width will decrease with increasing temperature. The correction for the thermal expansion of the cage and the parts forming the slit can be calibrated with the same machine and accuracy by replacing the copper sample by an exactly identical one made from high purity molybdenum, which is known to produce no thermal vacancies below 2000 K.²¹ Hence $\Delta L(T)/L_0$ and $\Delta a(T)/a_0$ have to be identical over the entire temperature range covered by the copper measurements. Therefore, after a precise calibration of the system the shifting in the developing diffraction pattern which is registered by a high-resolution multiphotodiode array (supplied by Hamamatsu) allows one to determine length variations of the specimen with an accuracy of

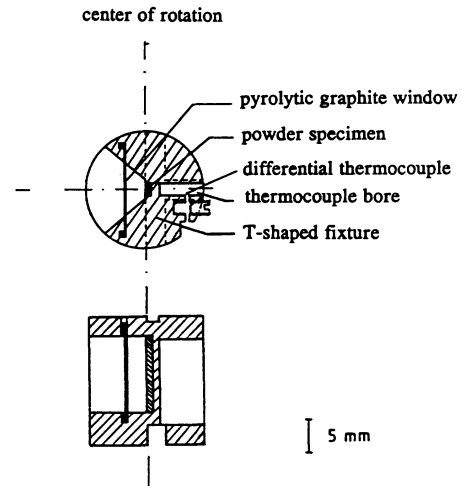


FIG. 1. The polycrystalline specimen.

about 7×10^{-6} in case of low temperatures (large slit width) and 2×10^{-6} in case of high temperatures (small slit width). This leads to a rise of sensitivity with increasing temperature and provides optimum conditions to determine vacancy concentrations in the interesting temperature range.

As shown in Fig. 3, the set-up described above is mounted in a vacuum chamber on a horizontal θ - 2θ goniometer supplied by Seifert (Ahrensburg). The high mechanical stability of the entire system guarantees a precise determination of the lattice parameter with an accuracy of about 2×10^{-5} for each single measurement

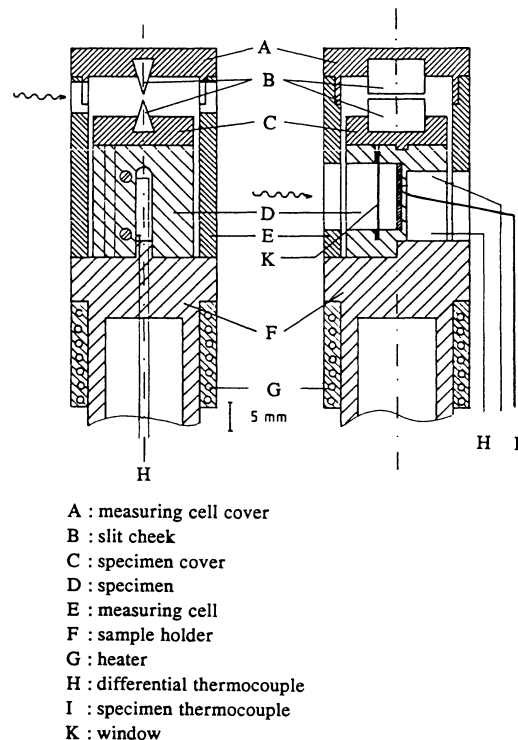


FIG. 2. The sample arrangement.

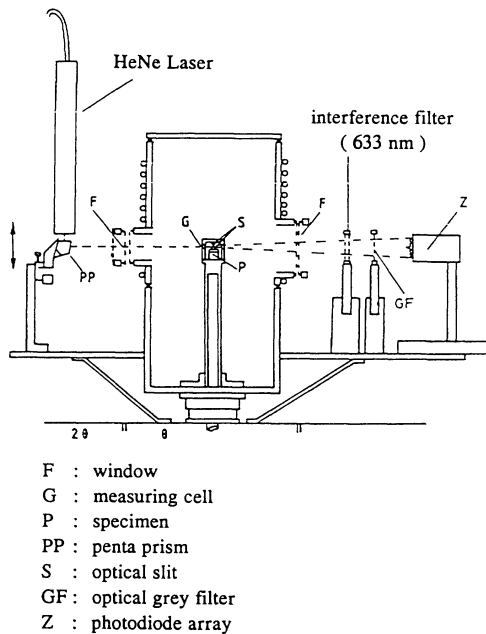


FIG. 3. The complete equipment. For a better general view the furnace is not shown in this figure.

over a wide temperature range in the near backreflection region. In order to obtain a better thermal coupling between sample and furnace and hence a good temperature control of the sample the vacuum chamber is filled with 500-mbar helium during the measurement. The temperature was increased computer controlled by steps of about 15 K between room temperature and close to the melting point of the sample. The accuracy of the temperature control was better than 0.1 K.

As shown in Fig. 4 two different x-ray peaks were used to evaluate the lattice parameter. If both did not give the same value, a poor adjustment of the sample was evident. Therefore a permanent adjustment control of the diffractometer was possible. During a temperature step the laser-diffraction pattern is registered several times to minimize the statistical error and to average possible fluctuations.

Evaporation from the sintered powder for the x-ray measurements was prevented by inserting a thin window made from pyrolytic graphite which is amorphous to

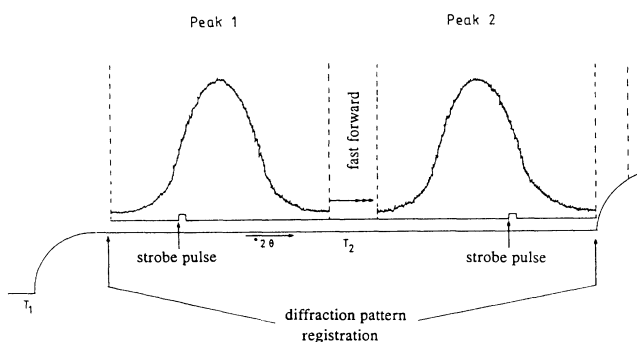


FIG. 4. The measuring scheme.

about 2000 K and hence gives no sharp x-ray reflexions. This material can be thinned in order to avoid substantial x-ray absorption. This feature is particularly useful for the measurement of alloys, where a selective evaporation of the constituents would be completely deleterious to the measurement since under Bragg-reflexion conditions only the very surface is sampled by the x-rays.

RESULTS AND DISCUSSION

A first measurement was performed on a high-purity copper sample in the described manner. Figure 5 shows the thermal increase of the lattice parameter. To reduce the statistical error, the measured data were smoothed by a polynomial fit.

In Fig. 6 the relative thermal expansion of the lattice is shown in the form $\Delta a(T)/a_0(T - T_0)$ versus T because this plot is much more sensitive than a plot of $\Delta t, a(T)/a_0$ versus T even though the sensitivity decreases with increasing temperature as elucidated by the error bars representing errors as stated in the figure caption.

The macroscopic thermal expansion measured simultaneously is depicted in Fig. 7 in the same way as described above. It has to be emphasized that $\Delta L(T)/L_0$ and $\Delta a(T)/a_0$ are found to be identical at temperatures lower than the onset of thermal vacancy formation within experimental accuracy. Therefore, these two curves do not have to be adjusted to each other as it has been the case in all earlier measurements. The equilibrium concentrations of vacancies $N_v(T)$ determined by Eq. (2) are shown in Fig. 8. The usual evaluation of the Arrhenius plot according to Eq. (1) (see Fig. 9) gives a concentration of vacancies at the melting point T^m of

$$N_v(T^m) = (0.76 \pm 0.03) \times 10^{-3}$$

a formation enthalpy of

$$H_v^f = (1.19 \pm 0.03) \text{ eV}$$

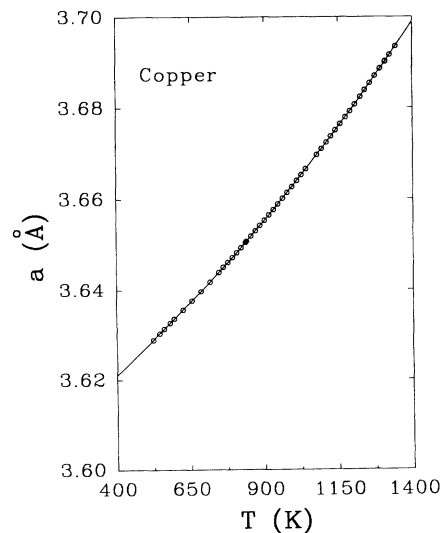


FIG. 5. Thermal variation of the lattice parameter in high-purity copper.

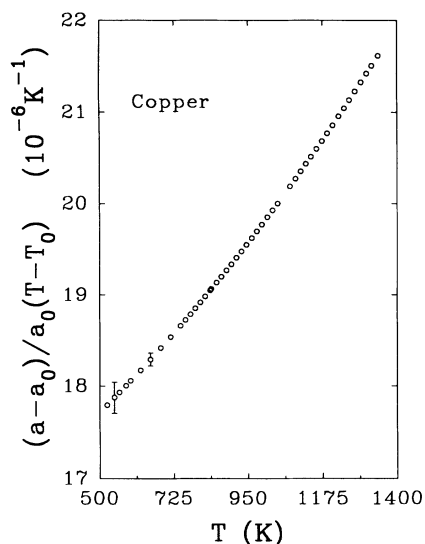


FIG. 6. Relative thermal expansion of the lattice ($T_0 = 500$ K, $\Phi = \pm 7 \times 10^{-6}$).

and a formation entropy of

$$S_v^f = (3.0 \pm 0.3) \text{ k}.$$

For comparison, the reader is referred to the results of Simmons and Balluffi.¹⁵ These authors found $N_v(T^m) = (0.20 \pm 0.05) \cdot 10^{-3}$ and $H_v^f = (1.17 \pm 0.11)$ eV under the assumption of $S_v^f = (1.5 \pm 0.5)$ k. Due to the large scatter of their data an experimental determination of S_v^f was not possible. It is obvious, that the vacancy formation enthalpy is in good agreement with the value determined in this work within the error limits, but there are significant differences in $N_v(T)$ and correspondingly S_v^f . This is not surprising if one takes into account, that Simmons and Balluffi needed samples with a length of

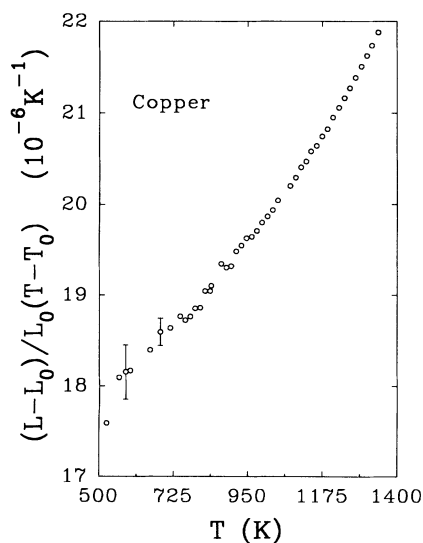


FIG. 7. Relative macroscopic thermal expansion of copper ($T_0 = 500$ K, $\Phi = \pm 5 \times 10^{-6}$).

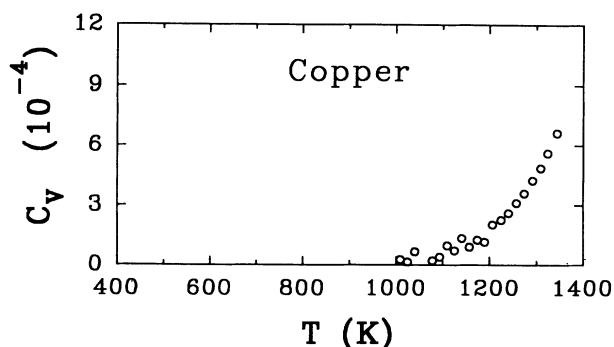


FIG. 8. Equilibrium concentration of vacancies in copper.

about 50 cm in order to obtain sufficient accuracy of the length measurement. This involves certainly problems with the homogeneity of the sample temperature. Additionally the lattice parameter was determined on a powder specimen in the same furnace but not being part of the specimen directly for the measurement of the length change. The insufficient precision of their experiment becomes obvious furthermore by the necessity of an adjustment of both measured curves $\Delta L(T)/L_0$ and $\Delta a(T)/a_0$ in the prevacancy temperature range. This adjustment may affect the determined $N_v(T)$ values as well and is not necessary in the present experiments. It is interesting to note that Trost *et al.*²⁰ who had difficulties with their neutron diffractometer, which made an absolute measurement of the lattice parameter impossible, reproduced the determined values of Simmons and Balluffi with smoothed $\Delta a(T)/a_0$ data fitted to the length measurement. This supports the assumption, that a shift in the $\Delta a(T)/a_0$ baseline which characterizes the thermal expansion of the defect-free crystal may be responsible for the observed differences.

A summary of the most important results measured by various techniques is given in Table I. It is obvious that the formation enthalpy $H_v^f = 1.28$ eV determined by positron annihilation experiments is significantly higher than the result of this work. These differences seem to be real and are being discussed elsewhere²² in detail. For the interpretation of the data the question may be important to what extent divacancies could contribute to the total

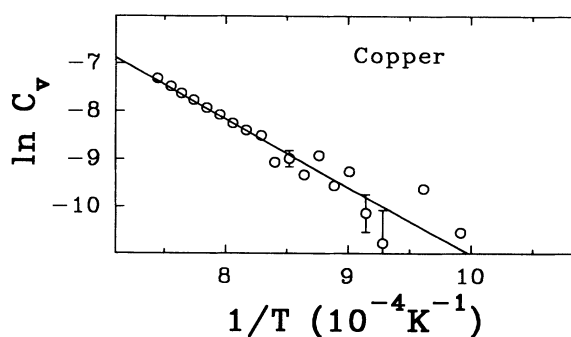


FIG. 9. Arrhenius plot of equilibrium vacancy concentrations in copper.

TABLE I. Vacancy formation data in copper.

Technique	H_v^f (eV)	S_v^f (k)	$N_v(T^m)(10^{-3})$	Ref.
Absolute	1.19 ± 0.03	3.0 ± 0.3	0.76 ± 0.03	This work
Absolute	1.17 ± 0.11	1.5 ± 0.5^a	0.20 ± 0.05	16
Absolute	1.18	1.6	0.21 ± 0.01	20
Electrical resistivity	1.29 ± 0.09	3.5	0.53	1
Specific heat	1.09	2.8	1.7	5
Specific heat	1.05	3.7	5.1	6
Positron annihilation	1.29 ± 0.02			23
Positron annihilation	1.28 ± 0.07			24
Positron annihilation	1.28 ± 0.10			25
Positron annihilation	1.29 ± 0.08			26
Positron annihilation	1.28 ± 0.04			27
Positron annihilation	1.28 ± 0.04			28
Positron annihilation	1.13 ± 0.04^b			29
Positron annihilation	1.19 ± 0.04^c			22

^aFixed value estimated from theory.

^bValue estimated assuming thermal detrapping.

^cValue estimated by consideration of deviations from the simple two-state trapping model.

measured vacancy concentration particularly because the vacancy concentration at the melting point is considerably larger than anticipated and the divacancy contribution is proportional to the square of the monovacancy concentration. In this context the reader is referred to subsequent papers³⁰ which take also results of positron annihilation measurements into account, thus extending the temperature range substantially which is being covered by the combined techniques.

CONCLUSIONS

An apparatus has been designed to measure $\Delta L(T)/L_0$ and $\Delta a(T)/a_0$ precisely enough to determine these quantities better than possible before. The present investigation of the absolute vacancy concentration in copper leads to a vacancy concentration at the melting point $N_v(T^m) = (0.76 \pm 0.03) \times 10^{-3}$. An evaluation of the

Arrhenius plot gives a formation enthalpy $H_v^f = (1.19 \pm 0.03)$ eV and a formation entropy $S_v^f = (3.0 \pm 0.3)$ k. For comparison, Simmons and Balluffi¹⁵ found $N_v(T^m) = (0.20 \pm 0.05) \times 10^{-3}$ and $H_v^f = (1.17 \pm 0.11)$ eV with the assumption of $S_v^f = (1.5 \pm 0.5)$ k. One of the most probable explanations of the differences is the insufficient precision of their lattice parameter experiment which did not allow an accurate determination of the thermal background as well as possible temperature gradients due to their sample size of about 50 cm.

ACKNOWLEDGMENTS

The authors thank Dr. F. Faupel and Dr. W. Lühr-Tanck for many stimulating discussions and Deutsche Forschungsgemeinschaft and Sonderforschungsbereich 126 Göttingen/Clausthal for their financial support.

¹Th. Hehenkamp and L. Sander, *Z. Metallk.* **70**, 202 (1979).

²C. H. Meechan and R. R. Eggleston, *Acta Metall.* **2**, 680 (1954).

³A. Ascoli, T. Guarini, and G. T. Queirolo, *Cryst. Lattice Defects* **1**, 159 (1970).

⁴R. Bourrassa and B. Lengeler, *J. Phys. F* **6**, 1406 (1976).

⁵D. Methfessel, Diploma Thesis, Göttingen, 1980.

⁶Y. A. Kraftmakher, *Fiz. Tverd. Tela. (Leningrad)* **9**, 1458 (1967) [*Sov. Phys. Solid State* **9**, 1137 (1967)].

⁷*Positrons in Solids*, edited by P. Hautöjärvi (Springer, New

York, 1979).

⁸C. Wagner and J. Beyer, *Z. Phys. Chem. B (Leipzig)* **32**, 113 (1936).

⁹A. Gott, *Ann. Phys. (Leipzig)* **41**, 520 (1942).

¹⁰R. Feder and A. S. Nowick, *Phys. Rev.* **109**, 1959 (1958).

¹¹D. J. Eshelby, *J. Appl. Phys.* **25**, 255 (1954).

¹²R. Bauer, W. Maysenhölder, and A. Seeger, *Phys. Lett.* **90A**, 55 (1982).

¹³R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 52 (1960).

¹⁴R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **119**, 600 (1960).

- ¹⁵R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **125**, 862 (1962).
- ¹⁶R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963).
- ¹⁷R. Feder and A. S. Nowick, *Philos. Mag.* **15**, 805 (1967).
- ¹⁸R. Feder, *Phys. Rev. B* **2**, 828 (1970).
- ¹⁹B. von Guérard, H. Peisl, and R. Zitzmann, *Appl. Phys.* **3**, 37 (1974).
- ²⁰W. Trost, K. Differt, K. Maier, and A. Seeger, *Springer Proc. Phys.* **10**, 219 (1986).
- ²¹K. Maier, M. Peo, H. Saile, H. E. Schaefer, and A. Seeger, *Philos. Mag. A* **40**, 701 (1979).
- ²²J.-E. Kluin and Th. Hehenkamp, *Phys. Rev. B* **44**, 11 597 (1991).
- ²³W. Triftshäuser and J. D. McGervey, *Phys. Rev. B* **12**, 4634 (1975).
- ²⁴R. Jank, *Doktor Thesis, Aachen*, 1975.
- ²⁵M. Doyama, K. Kuribayashi, S. Nanao, and S. Tanigawa, *Appl. Phys.* **4**, 1536 (1974).
- ²⁶J. I. Takamura, in *Physical Metallurgy*, edited by R. W. Cahn (North-Holland, Amsterdam, 1974).
- ²⁷Th. Hehenkamp, Th. Kurschat, and W. Lühr-Tanck, *J. Phys. F* **16**, 981 (1986).
- ²⁸M. Ederhof, W. Lühr-Tanck, A. Saager, Th. Kurschat, and Th. Hehenkamp, *Cryst. Res. Technol.* **22**, K177 (1987).
- ²⁹H. E. Schaefer, W. Stuck, F. Banhart, and W. Bauer, *Mater. Sci. Forum* **15-18**, 117 (1987).
- ³⁰J.-E. Kluin, *Philos. Mag.* (to be published).