Diffusion In Wide Grain Boundaries

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in the single-crystal samples, whereas, close to a twin boundary, the diffusion coefficient goes up by a factor of 2.5.

Our investigations on the effect of foreign atoms on the volume diffusion[1,2] demonstrate that many chemical impurities, too, tend to exalt the diffusion in this temperature range.

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Diffusion in Wide Grain Boundaries

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The rigorous solution of the grain-boundary diffusion problem has been approximated by a series expansion method. The calculations show that higher-order terms may be neglected in the bulk adjacent to the grain boundary. Thus, in this region Whipple's and Suzuoka's solutions represent a close approximation to the problem. Inside the grain boundary, however, higher-order approximations have to be taken into account. These approximations gain importance in the case of wide grain boundaries. The solutions obtained for an instantaneous source have been fitted to available grain-boundary diffusion data of Ni^{2+} in MgO at 1200°C. Numerical calculations give for the bulk diffusion coefficient $D=2.9\times10^{-12}$ cm² sec⁻¹, the ratio of diffusion coefficient $\Delta=1.5$ and for the grain-boundary width $a=75\ \mu$.

INTRODUCTION

The solutions of the grain boundary diffusion problem by Whipple[1] and Suzuoka[2] give the two dimensional concentration profile outside the grain boundary for a constant and for an instantaneous source, respectively. Both solutions are approximations for narrow grain boundaries. They describe diffusion profiles in metals and alloys[3] where the grain-boundary width is generally assumed to be of the order of a few Burgers vectors[4,5] fairly well. In alkali halides and oxides, however, there are indications that the high diffusivity paths are of considerable dimensions.[6–8] In these crystals higher-order approximations have to be taken into account. In the present paper higher-order approximations for the solution of the grain-boundary diffusion problem for an instantaneous source are presented. The results are applied to the available grain-boundary diffusion data of Ni^{2+} in MgO[7] on the basis of which diffusion parameters are calculated by a curve fitting process. The solutions for a constant source may be obtained from the expressions presented in this paper by an integration.

THE GENERAL SOLUTION

The grain boundary is represented by a slab of diffusivity D' oriented rectangularly to the surface of the bulk of diffusivity D. The differential equations for this grain-boundary diffusion problem with an instantaneous source of strength γ at the surface are

$$(\partial^2c/\partial x^2)+(\partial^2c/\partial y^2)=D^{-1}(\partial c/\partial t)-(\gamma/D)\delta(y)\delta(t), \qquad |x|>a,$$
$$(\partial^2c'/\partial x^2)+(\partial^2c'/\partial y^2)=(D')^{-1}(\partial c'/\partial t)-(\gamma/D')\delta(y)\delta(t), \qquad |x|<a. \tag{1}$$

The boundary conditions are given by

$$c'=c, \qquad D'(\partial c'/\partial x)=D(\partial c/\partial x), \qquad |x|=a. \tag{2}$$

The concentrations inside and outside of the grain boundary are c' and c, respectively. The grain-boundary width is $2a$ and δ denotes Dirac's delta function.

The solutions of Eqs. (1) and (2) are found by using Fourier–Laplace transforms and the same retransformation techniques as applied in Whipple's[1] paper: The Fourier–Laplace transform

$$\bar{c}(x,\mu,\lambda)=\int_0^\infty\int_0^\infty c(x,y,t)\cos(\mu y)\exp(-\lambda t)dtdy$$

yields for the system of Eqs. (1)

$$(\partial^2\bar{c}/\partial x^2)=k^2\bar{c}-(\gamma/D) \qquad |x|>a$$

$$(\partial^2\bar{c}'/\partial x^2)=k'^2\bar{c}'-(\gamma/D') \qquad |x|<a$$

with $k^2=\mu^2+\lambda/D$, $k'^2=\mu^2+\lambda/D'$. Far away from the grain boundary the solutions will be independent of x, or

$$\partial c/\partial x=0 \qquad \text{for } x\rightarrow\infty,$$

$$\partial c'/\partial x=0 \qquad \text{for } x\rightarrow 0.$$

The solution of the transformed system will then be given by the following general form

$$\bar{c}(x,\mu,\lambda)=\gamma/Dk^2+A\exp(-kx) \qquad |x|>a$$

$$\bar{c}'(x,\mu,\lambda)=\gamma/D'k^2+A'\cosh(k'x) \qquad |x|<a$$

A and A' are defined by the boundary conditions (2) yielding the solution

$$\bar{c}(x,\mu,\lambda)=\frac{\gamma}{Dk^2}-\frac{\gamma(\Delta-1)\mu^2}{D'k'^2k^2}(1+N)^{-1}\exp[-k(x-a)] \qquad |x|>a$$

$$\bar{c}'(x,\mu,\lambda)=\frac{\gamma}{D'k'^2}+\frac{\gamma(\Delta-1)\mu^2}{D'k'^2k^2}\frac{N}{1+N}\frac{\cosh(k'x)}{\cosh(k'a)} \qquad |x|<a$$

$$N=[Dk\cosh(k'a)/D'k'\sinh(k'a)]$$
$$=(k'^2\Delta a)^{-1}[(k'a)\cosh(k'a)/\sinh(k'a)].$$

The retransformation is given by

$$c(x,y,t)=\tfrac{1}{2}\pi^2 i\int_{-\infty}^{+\infty}\int_{-i\infty}^{+i\infty}c(x,\mu,\lambda)\cos(\mu y)\exp(\lambda t)\,d\lambda d\mu.$$

The following techniques may be used for the integration:

$$\lambda\rightarrow\lambda/t \quad\text{and}\quad \mu\rightarrow\mu/(Dt)^{1/2}\ \text{yielding}$$

$$k\rightarrow\nu/(Dt)^{1/2} \quad\text{and}\quad k'\rightarrow\omega/(Dt)^{1/2}.$$

The denominator may be replaced by the integration

$$(1+N)^{-1}=\int_0^\infty\exp(-(1+N)\sigma)\,d\sigma$$

thus yielding

$$c(\xi,\eta,t)=\gamma(\pi Dt)^{-1/2}\exp(-\tfrac{1}{4}\eta^2)-\frac{\gamma}{\pi^2(Dt)^{1/2}}\int_1^\Delta\int_{\xi-\alpha}^{\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}f(\xi,\eta,\phi,\sigma,\mu,\nu)\,d\mu d\nu d\xi d\sigma, \tag{3}$$

$$c'(\xi,\eta,t)=\gamma(\pi D't)^{-1/2}\exp(-\eta^2/\Delta)+\frac{\gamma}{\Delta\pi^2(Dt)^{1/2}}\int_1^\Delta\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{\cosh(\omega\xi)}{\omega\sinh(\omega\alpha)}f(0,\eta,\phi,\sigma,\mu,\nu)\,d\mu d\nu d\sigma. \tag{4}$$

The abbreviations stand for

$$f(\xi,\eta,\phi,\sigma,\mu,\nu)=\mu^2\cos(\mu\eta)\exp\{-\mu^2\sigma-\nu^2(\Delta-\sigma)/(\Delta-1)-i\nu[\xi-\alpha+(\sigma-1)\phi/\beta]\}, \tag{5}$$

$$\phi=\alpha\omega\cosh(\alpha\omega)/\sinh(\alpha\omega), \tag{6}$$

$$\omega^2=[(\Delta-1)\mu^2-\nu^2]/\Delta, \tag{7}$$

$$\xi=x(Dt)^{-1/2},\qquad \eta=y(Dt)^{-1/2},\qquad \alpha=a(Dt)^{-1/2},\qquad \Delta=D'/D,\qquad \beta=(\Delta-1)\alpha. \tag{8}$$

THE OUTSIDE SOLUTION

The solution (3) outside the grain boundary is almost identical to Suzuoka's solution. The only difference is that the integrand of the general solution (3) is $f(\xi,\eta,\phi,\sigma,\mu,\nu)$ instead of $f(\xi,\eta,1,\sigma,\mu,\nu)$ as in Suzuoka's approximation. By expanding ϕ in Eq. (5) into a series,

$$\phi=1+2\sum_k\omega^2/[\omega^2+(k\pi/\alpha)^2]=1+2S_k, \tag{9}$$

the integrand of Eqs. (3) and (4) can be expressed in terms of the integrand of Suzuoka's solution

$$f(\xi,\eta,\phi,\sigma,\mu,\nu)=f(\xi,\eta,1,\sigma,\mu,\nu)\times\exp[-2i\nu(\sigma-1)\beta^{-1}S_k]. \quad (10)$$

The exponential function in Eq. (10) is expanded into a power series

$$\exp[-2i\nu(\sigma-1)\beta^{-1}S_k]=1-2i\nu(\sigma-1)\beta^{-1}\times\sum_k\omega^2/[\omega^2+(k\pi/\alpha)^2]+O[(\sigma-1)^2S_k^2]. \quad (11)$$

According to the operational calculus of Fourier–Laplace transforms[9] ω^2 terms in the numerator of Eq. (11) are replaced by repeated application of the operator

$$\omega^2=-[(\Delta-1)\partial^2/\partial\eta^2-\partial^2/\partial\xi^2]/\Delta. \quad (12)$$

Similarly, ω^2 terms in the denominator are replaced by an integration,

$$[\omega^2+(k\pi/\alpha)^2]^{-1}=\int_0^\infty\exp\{-[\omega^2+(k\pi/\alpha)^2]\rho\}d\rho. \quad (13)$$

Upon performing the replacements indicated in Eqs. (12) and (13) and retaining only the first two terms, the series expansion shown in Eq. (11) becomes

$$\exp[-2i\nu(\sigma-1)\beta^{-1}S_k]=1+2\frac{(\sigma-1)}{\Delta\beta}\sum_k\times\left((\Delta-1)\frac{\partial^2}{\partial\eta^2}-\frac{\partial^2}{\partial\xi^2}\right)\int_0^\infty\exp\left\{-\left[\omega^2+\left(\frac{k\pi}{\alpha}\right)^2\right]\rho\right\}d\rho. \quad (14)$$

By combining Eqs. (10) and (14) the integrand $f(\xi,\eta,\phi,\sigma,\mu,\nu)$ of Eq. (3) can now be written completely in terms of the integrand $f(\xi,\eta,1,\sigma,\mu,\nu)$ of Suzuoka's solution and additional integrations and differentiations with respect to ξ and η. Thus, the solution (3) can be integrated,

$$c(\xi,\eta,t)=c_0(\eta,t)-c_1(\xi,\eta,t)-c_2(\xi,\eta,t), \quad (15)$$

where the first two terms represent Suzuoka's solution and the additional term $c_2(\xi,\eta,t)$ is given by

$$c_2(\xi,\eta,t)=\frac{2\gamma}{\Delta\pi(Dt)^{1/2}}\int_1^\Delta\left[(\Delta-1)\frac{\partial^4}{\partial\eta^4}-\frac{\partial^4}{\partial\xi^2\partial\eta^2}\right]\frac{\sigma-1}{\beta}\times\sum_{k=1}^\infty\left(\frac{\Delta-1}{\Delta-\sigma}\right)^{1/2}\exp(-q_k)\frac{d\rho}{\rho^{1/2}}d\sigma, \quad (16)$$

with

$$q_k=\frac{1}{4}\frac{\eta^2}{\rho}+\frac{1}{4}\frac{(\Delta-1)[\xi-\alpha+(\sigma-1)/\beta]}{\Delta-\rho}+\left(\frac{k\pi}{\alpha}\right)^2\frac{\Delta(\rho-\alpha)}{\Delta-1}.$$

The first two terms of the solution (15) result from the zeroth approximation of the exponential function in Eq. (10). The third term represents the first approximation in the form of a twofold integral. The nth approximation would contain up to $(n+1)$ fold integrals. However, due to the factor $(\Delta-1)/(\Delta-\sigma)$ in the exponent of Eq. (16) the integrals contribute only for values of σ close to one. As the nth approximation contains the factor $(\sigma-1)^n$ all but the zeroth approximation may be neglected leaving only Suzuoka's solution

$$c(\xi,\eta,t)=c_0(\eta,t)-c_1(\xi,\eta,t), \quad (17)$$

where

$$c_0(\eta,t)=\gamma(\pi Dt)^{-1/2}\exp(-\tfrac{1}{4}\eta^2/\Delta)\Delta^{-1/2} \quad (18)$$

and

$$c_1(\xi,\eta,t)=\frac{\gamma}{(\pi Dt)^{1/2}}\int_1^\Delta\frac{\partial^2}{\partial\eta^2}\frac{\exp(-\frac{1}{4}\eta^2/\sigma)}{\sigma^{1/2}}\times\operatorname{erf}\left[\frac{1}{2}\left(\frac{\Delta-1}{\Delta-\sigma}\right)^{1/2}\left(\xi-\alpha+\frac{\sigma-1}{\beta}\right)\right]d\sigma. \quad (19)$$

The expressions for c_0 and c_1 in Eqs. (18) and (19) differ only formally from Suzuoka's solution, but mathematically they are equivalent. The different presentation has been chosen to facilitate a direct comparison to the inside solution to be derived below.

It is noted that Suzuoka's and likewise Whipple's solutions are close approximations of the rigorous outside solution independent of the width of the grain boundary. However, in the case of wide grain boundaries a large fraction of the diffused material will be located "inside" the boundary and hence sectioning experiments may no longer be analyzed on the basis of the outside solution only.

THE INSIDE SOLUTION

The solution (4) inside the grain boundary is even in ξ. The Taylor series of an even function $f(\xi)=g(\xi^2)$ is given by

$$f(\xi)=f(\alpha)+(2\alpha)^{-1}[\partial f(\xi)/\partial\xi]|_{\xi=\alpha}(\xi^2-\alpha^2)/1!+\sum_{n=2}^\infty[(2\xi)^{-1}(\partial/\partial\xi)]^nf(\xi)|_{\xi=\alpha}[(\xi^2-\alpha^2)^n/n!]. \quad (20)$$

Utilizing the boundary conditions (2) the inside solution can be written as

$$c'(\xi)=c(\alpha)+\frac{\xi^2-\alpha^2}{2\alpha\Delta}\frac{\partial c(\xi)}{\partial\xi}\bigg|_{\xi=\alpha}+\sum_{n=2}^\infty\left((2\xi)^{-1}\frac{\partial}{\partial\xi}\right)^nc'(\xi)\bigg|_{\xi=\alpha}\frac{(\xi^2-\alpha^2)^n}{n!}. \quad (21)$$

In Eq. (21) the first and second terms give Suzuoka's approximation for the inside solution. The higher approximations have to be calculated by expanding $\cosh(\omega\xi)$ into a series. According to Eq. (20) this leads to

$$\frac{\cosh(\omega\xi)}{\omega\sinh(\omega\alpha)}=\frac{\phi}{\alpha\omega^2}\,(1+\sum_{k=1}^{\infty}h_{2k}\omega^{2k})+\sum_{k=1}^{\infty}h_{2k-1}\omega^{2k-1},\quad(22)$$

where ϕ and ω are given by Eqs. (6) and (7), respectively, and the functions h_m are given by

$$h_m=\sum_{n=m}^{\infty}\frac{b_{mn}}{n!\alpha^{n-1}}\left(\frac{\xi^2-\alpha^2}{2\alpha}\right)^n,\qquad m>1.\qquad(23)$$

The first few coefficients b_{mn} are

$$\begin{array}{llll} b_{11}=1 & b_{12}=1 & b_{13}=3 & b_{14}=15\\ & b_{22}=1 & b_{23}=3 & b_{24}=15\\ & & b_{33}=1 & b_{34}=6.\end{array}\qquad(24)$$

Upon inserting the series expansion of the hyperbolic function given by Eq. (22) into Eq. (4) the inside solution can be expressed as

$$c'(\xi,\eta,t)=\gamma(\pi Dt)^{-1/2}\exp(-\tfrac{1}{4}\eta^2/\Delta)\Delta^{-1/2}+\gamma[\Delta\pi^2(Dt)^{1/2}]^{-1}\int_1^{\Delta}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}f(0,\eta,\phi,\sigma,\mu,\nu)\phi\alpha^{-1}\omega^{-2}$$

$$\times(1+\sum_k h_{2k}\omega^{2k})\,d\mu d\nu d\sigma+\gamma[\Delta\pi^2(Dt)^{1/2}]^{-1}\int_1^{\Delta}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}f(0,\eta,\phi,\sigma,\mu,\nu)\sum_k h_{2k-1}\omega^{2k-1}d\mu d\nu d\sigma.\quad(25)$$

According to the boundary condition (2) the first term in each integral of Eq. (25) can be calculated from the outside solution evaluated at $\xi=\alpha$:

$$\int_1^{\Delta}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\alpha^{-1}\omega^{-2}\phi f(0,\eta,\phi,\sigma,\mu,\nu)\,d\mu d\nu d\sigma=\int_1^{\Delta}\int_0^{\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}f(\xi,\eta,\phi,\sigma,\mu,\nu)\,d\mu d\nu d\xi d\sigma,$$

$$\int_1^{\Delta}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Delta f(0,\eta,\phi,\sigma,\mu,\nu)\,d\mu d\nu d\sigma=\left(\frac{\partial}{\partial\xi}\right)\int_1^{\Delta}\int_0^{\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}f(\xi,\eta,\phi,\sigma,\mu,\nu)\,d\mu d\nu d\xi d\sigma.\quad(26)$$

As all powers of ω^2 may again be replaced by the operator (12), the integrals in Eq. (25) can be expressed completely in terms of the outside solution. If Eq. (17) is used for the outside solution the first three approximations of the inside solution read

$$c'(\xi,\eta,t)=c_0(\eta,t)-\left[1-\frac{h_1}{\Delta}\frac{\partial}{\partial\xi}-\frac{h_2}{\Delta}\left((\Delta-1)\frac{\partial^2}{\partial\eta^2}-\frac{\partial^2}{\partial\xi^2}\right)-\frac{h_3}{\Delta}\left((\Delta-1)\frac{\partial^3}{\partial\xi\partial\eta^2}-\frac{\partial^3}{\partial\xi^3}\right)\right]c_1(\alpha,\eta,t).\quad(27)$$

As Suzuoka's outside solution has been found to be a close approximation to the rigorous solution the inside solution given by Eq. (27) is a close approximation to the rigorous solution as well. In contrast to the situation outside of the grain boundary, however, Eq. (27) differs considerably from Suzuoka's ξ^2 approximation. This approximation considers only the first term of the polynomial h_1 and therefore represents an incomplete first approximation of the inside solution.

Equation (27) together with Eq. (17) can be applied to an analysis of complete two dimensional grain-boundary diffusion profiles or suitably integrated, they may serve as a basis for the analysis of sectioning experiments. An example for the former is given in the following section.

DIFFUSION PROFILES IN WIDE GRAIN BOUNDARIES

Diffusion profiles may be calculated from Suzuoka's solution given by Eq. (17) as long as the width of the grain boundary is small and the amount of diffused material inside the grain boundary may be neglected. For wide grain boundaries this simplification does not apply, however. In this case, the material inside the grain boundary has to be taken into account and its concentration profile calculated from Eq. (27).

The concentration profile resulting from the diffusion of Ni^{2+} into MgO bicrystals at 1200°C reported by Wuensch and Vasilos and reproduced in Fig. 1 strongly suggests a wide grain boundary. As the source configuration of the above experiment is in agreement with an instantaneous source the approximations for the concentration profile developed in the preceding paragraphs may be applied to these data. Consequently, the total concentration profile is given by Eqs. (17) and (27). As only the first four terms of the polynomial h_1 contribute substantially in Eq. (27) the latter may be approximated by

$$c'(\xi,\eta,t)=\gamma(\pi Dt)^{-1/2}\exp(-\tfrac{1}{4}\eta^2/\Delta)\Delta^{-1/2}-\frac{\gamma}{(\pi Dt)^{1/2}}$$

$$\int_1^{\Delta}\left(\frac{\eta^2}{4\sigma}-\frac{1}{2}\right)\exp\left(-\frac{\eta^2}{4\sigma}\right)\text{erf}\left[\left(\frac{\Delta-1}{\Delta-\sigma}\right)^{1/2}\frac{\sigma-1}{2\beta}\right]\frac{d\sigma}{\sigma^{3/2}}$$

$$-\frac{\gamma h_1'}{\Delta\pi(Dt)^{1/2}}\int_1^{\Delta}\left(\frac{\eta^2}{4\sigma}-\frac{1}{2}\right)$$

$$\times\exp\left[-\frac{\eta^2}{4\sigma}-\left(\frac{\Delta-1}{\Delta-\sigma}\right)\left(\frac{\sigma-1}{2\beta}\right)^2\right]\left(\frac{\Delta-1}{\Delta-\sigma}\right)^{1/2}\frac{d\sigma}{\sigma^{3/2}},\quad(28)$$

where h_1' represents the first four terms of the polynomial h_1 given by Eq. (23):

$$h_1' = \left(\frac{\xi^2-\alpha^2}{2\alpha}\right) - \alpha^{-1}(2!)^{-1}\left(\frac{\xi^2-\alpha^2}{2\alpha}\right)^2 + \frac{3}{\alpha^2}(3!)^{-1}\left(\frac{\xi^2-\alpha^2}{2\alpha}\right)^3 - \frac{15}{\alpha^3}(4!)^{-1}\left(\frac{\xi^2-\alpha^2}{2\alpha}\right)^4.$$

The results of numerical calculations based on Eqs. (17) and (28) are shown in Fig. 1. The data points in this figure have been taken from Fig. 6 of Ref. 7 representing diffusion profiles of Ni^{2+} diffusing into a MgO bicrystal. The solid lines correspond to the best fit obtained by varying the parameters D, Δ and a. The values of D, Δ and a corresponding to the best fit are

$$D_b = (2.9\pm0.1)\times10^{-12}\ \text{cm}^2\ \text{sec}^{-1}$$

$$\Delta_b = 1.5\pm0.1$$

$$a_b = (75\pm5)\mu.$$

The stated error limits represent the ranges of the deviations in which a visual comparison of the numerical and experimental data was equally satisfactory.

The dashed lines in Fig. 1 give the numerical results of Suzuoka's ξ^2 approximation. It can be seen that this approximation is satisfactory in the bulk but fails to reproduce the experimental data inside the grain boundary. This result is in agreement with the observations made concerning the structure of the outside solution as given by Eq. (16).

The values of the diffusion parameters obtained are in reasonable agreement with other bulk diffusion data[10] and with the probable extent of the region in which precipitates form around the grain boundary.[11] It is realized that the particular magnitude of Δ_b and a_b reflects the assumption of two distinct diffusivities inside and outside of the grain boundary respectively. As the mathematical difficulties arising from any other spatial dependence of the diffusivities are considerable,[12] however, Δ_b and a_b are offered as substitutes for the height and width of the maximum describing the true spatial variation of the diffusivity.

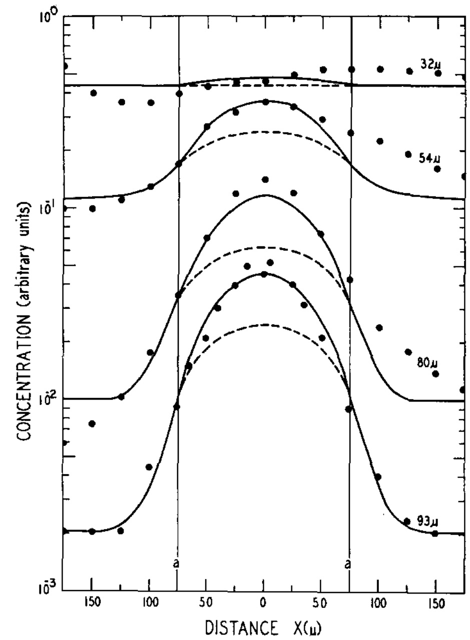

FIG. 1. Calculated and experimental relative concentration profiles of Ni^{2+} diffused into MgO bicrystals at 1200°C. ··· data points taken from Ref. 7, Fig. 6, — best fit of Eqs. (17) and (28) to data points, - - - Suzuoka's ξ^2 approximation.

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