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Author
Rosenblatt, G.M.

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Berkeley, CA 94720

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Preface

The following paper is part of the written proceedings of the Symposium on High Temperature and Materials Chemistry held in Berkeley, California, October 24-25, 1989. It was omitted inadvertently from the primary proceedings volume, LBL-27905.

Gerd M. Rosenblatt
Berkeley, California
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HOW TEMPERATURE GRADIENTS CAN INFLUENCE MELTING POINTS

Alan W. Searcy, Dario Beruto and Rodolfo Botter

If a crystalline solid at a fixed temperature is brought to equilibrium with respect to exchange of atoms and vacancies at a surface the chemical potential μ_g of the gas phase is related to the chemical potential of the atoms μ_a and vacancies μ_v in the solid by[1-3]

$$\mu_g = \mu_a - \mu_v \tag{1}$$

But because the free volumes of liquids are insensitive to temperature, we can expect that small changes in free volumes do not significantly effect chemical potentials of a liquid phase. Consequently, $\mu_l = \mu_g$, where μ_l is the chemical potential of the liquid phase. Therefore,

$$\mu_l = \mu_a - \mu_v \tag{2}$$

Equation 2 implies that if a nonequilibrium concentration of vacancies can be established at a liquid-solid interface held at the normal melting point, the activity of the solid will be raised and its melting point will be depressed.

One means of changing the vacancy concentration in a solid at its liquid interface is to establish a steady state temperature gradient through the solid so placed in an inert container that its interface with its liquid becomes, on annealing, the only significant vacancy source.

Most evaluations of mass transport in temperature gradients have assumed that creation and anihilation of vacancies at grain boundaries or dislocations will always maintain the vacancy concentrations at the values characteristic of the local temperature despite the imposition of a temperature gradient. But Stark[4] and Kossak and Hohenkamp[5] have independently concluded from thermal diffusion studies that vacancies move towards the cold end of the gradient, and Kossak and Hohenkamp have concluded that in metal bars steady state vacancy concentrations are readily achieved in which those concentrations are raised toward the cold end of the gradient. A reduced vacancy concentration at a liquid interface and a lowered melting temperature is predicted from Eq. (2).

A steady state vacancy distribution consistent with the observations of Kossak and Hohenkamp is predicted from a model for vacancy distribution between two sites of different bonding environments[2,3] if the restriction of constant temperature is removed and if the effective temperature for exchange is assumed to be the average of the temperatures of the sites between which the exchange occurs. This latter assumption differs from that usually used in irreversible thermodynamic theory,[6] but is consistent with the suggestion of Allnatt and Rice,[7] that the transition temperature may be an average of the temperatures of atoms surrounding both the source and sink sites of an atom that exchanges with a vacancy. The steady state rates in vacancy concentrations at two temperatures, X_{v1}/X_{v2} is predicted to be related to the ratio of equilibrium concentrations $X^{\circ}_{v1}/X^{\circ}_{v2}$ by

$$\frac{X_{V1}}{X_{V2}} = \frac{X^{\circ}_{V1}}{X^{\circ}_{V2}} \exp\frac{H(T_2-T_1)}{RT_1T_2} \tag{3}$$

where H is the enthalpy content of the solid. The total vacancy concentration has been evaluated in terms of two alternate assumptions, a) that the total number of vacancies is the sum of the number for isothermal equilibrium at each T, and b) that the total is the number that minimizes$(\mu_{v1}/T_1) = (\mu v_2/T_2)\ldots = k$.[8] Either assumption yields a predicted lowering in the vacancy concentration at the interface, and Eq. (2) then predicts a melting point depression. A question to be resolved by experiment is whether a gradient-insensitive crystal growth mechanism at the surface will override the predicted interface vacancy depletion.

Beruto, Botter, and Searcy[8] have measured the effect of temperature gradients on the melting point of tin confined in a graphite cell (Figure 1). Not shown is a 10 cm layer of glass wool which effectively eliminates heat loss through the side walls. Seven thermocouples at carefully measured heights within the sample yield the temperature gradient. They were calibrated before and after a series of temperature gradient runs by measurement of the normal melting point of tin when the graphite cell was heated by tapes. Positions of the interface in gradient runs were measured to within 0.05 mm by means of a quartz "dip stick". Interface temperatures were calculated from linear extrapolation of thermocouple temperatures in the solid or liquid phase to the interface height. Interface temperatures are shown in Figure 2 to decrease with temperature gradients to 3.8 ± 1.7 K below the normal melting point for a 2 K/mm gradient. It is expected that further decreases in the melting point will be limited by the gradient which is high enough to overcome the kinetic barrier to nucleation of crystal layers.

References

1. C. Herring in The Physics of Powder Metallurgy, Ed. by W.E. Kingston (McGraw-Hill Book, New York, 1951), p. 150.
2. A.W. Searcy, J. Chem. Phys. 81, 2489 (1984).
3. A.W. Searcy, J. Chem. Phys. 83, 3095 (1985).
4. J.P. Stark, Phys. Rev. B 18, 711 (1978).
5. R. Kossak and Th. Hehenkamp, Materials Science Forum 15-18, 211 (1987).
6. R.M. Young, R. McPherson, J. Am. Ceram. Soc. 72, 1080 (1989).
7. A.R. Allnatt and S.A. Rice, J. Chem. Phys. 33, 573 (1960).
8. A.W. Searcy, unpublished work.
9. D. Beruto, R. Botter, and A.W. Searcy, submitted for publication.

Figures

1. Cross sectional drawing of apparatus. Glass wool insulation not shown.
2. Variation of the melting point of tin with temperature difference through the solid. Diamonds are from extrapolations in the solid, crosses are extrapolations in the liquid, and squares are from both.

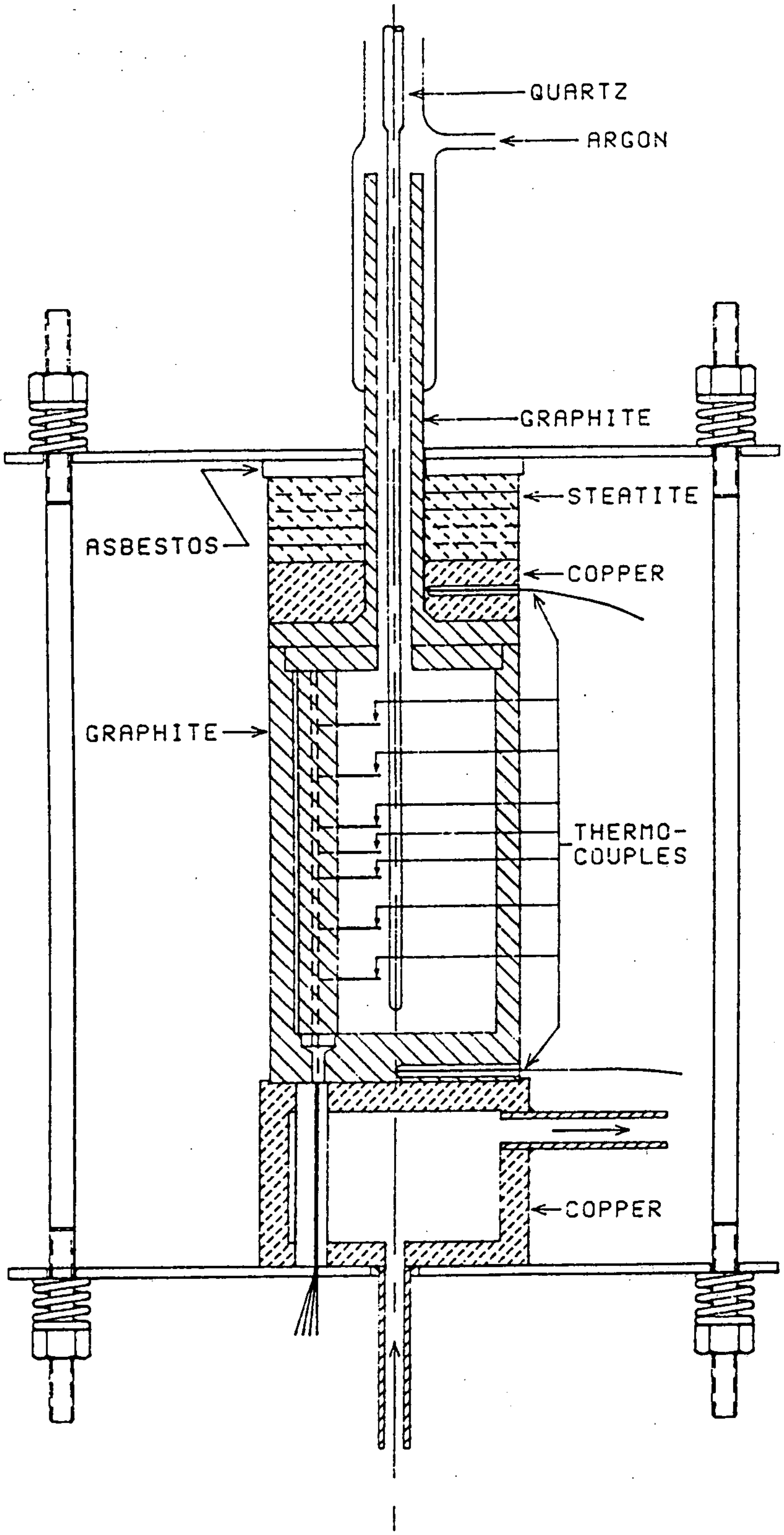

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Fig. 1

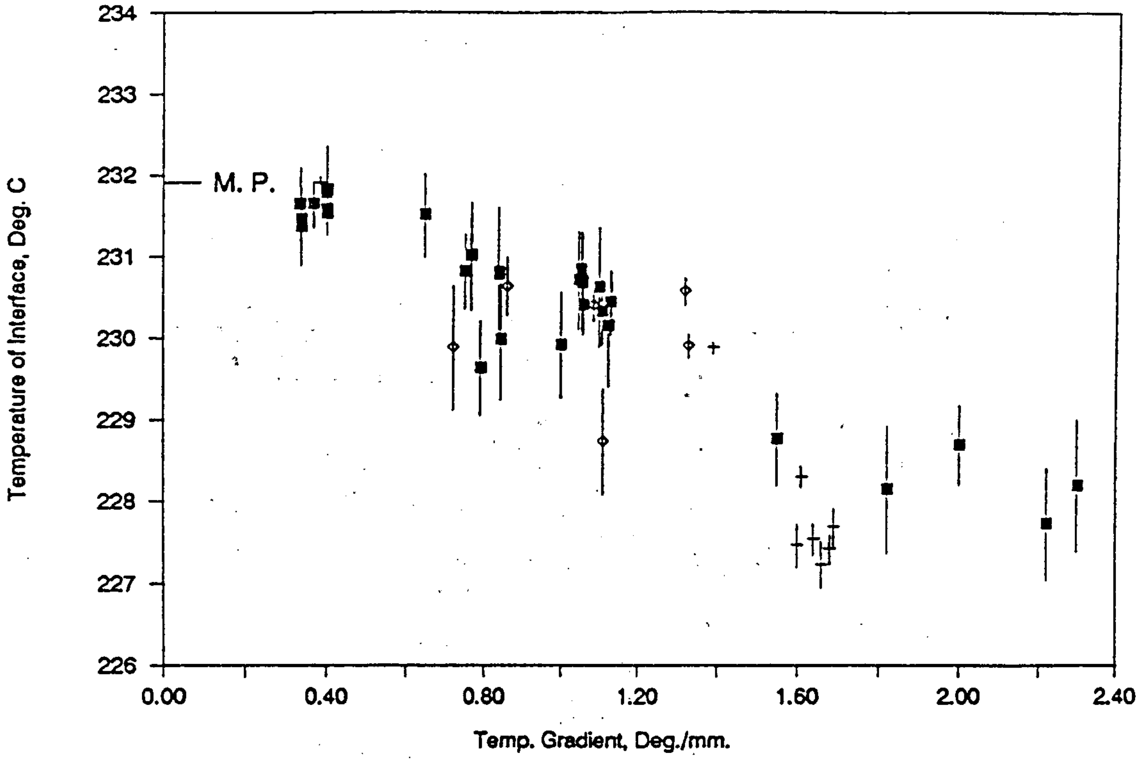

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Fig. 2

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720