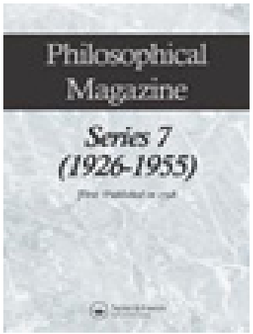

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XLVI. *Anomaly in the Rigidity Modulus of Copper Alloys for Small Concentrations*

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Summary

In his recent theory of work hardening, Mott assumes that face-centred cubic crystals usually contain, prior to deformation, a network of dislocations, as suggested first by Frank; and he computes the decrease in the modulus of rigidity due to the existence of such a network. His computation may be extended to solid solutions, if one assumes the dislocations to be 'pinned down' by the solute atoms. Thus the addition of solute atoms will always at first *increase* the shear modulus, though larger concentrations may lead to a decrease. An anomaly of the type predicted has actually been observed by Bradfield and Pursey (1953) for small concentrations in copper alloys. One deduces from Bradfield's recent measurements an average length of about 10^{-5} cm for the dislocations of the network; and the small value of the anomaly for pure copper perhaps indicates that a large fraction of the dislocations are sessile. The anomaly has also been observed for silver alloys. It disappears after long annealing at 650°C, probably by formation of loose Cottrell clouds.

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§ 1. Review of Mott's Theory of the Anomaly for Pure Metals

In a recent paper on work-hardening (1952 a), Mott assumes that face-centred cubic crystals usually contain, before deformation, a network of dislocations. That they contain dislocations seems necessary to explain their low critical shear stresses σ_c. This is of order $10^{-4}G$ (G is the rigidity modulus), while, as shown by Frank, the stress necessary to induce plastic flow in a perfect crystal is at least $10^{-1}G$, even at high temperature. It seems also reasonable energetically that these dislocations should form a network, and this allows the operation of Frank–Read sources (1950) to create the large number of dislocations necessary for plastic flow.

The presence of such a network decreases the rigidity modulus G of the metal. For, under a *small* shear stress σ in its glide plane, a dislocation line AB locked at A and B (fig. 1) will assume a curvature $1/\rho$, which disappears elastically with σ. Balancing σ by the line tension W of the dislocation, one has:

$$\sigma \mathbf{b} = W/\rho \,, \qquad \ldots\ldots\ldots \quad (1)$$

with

$$W \simeq \frac{G\mathbf{b}^2}{4\pi k} \ln\left(\frac{l}{\mathbf{b}}\right),$$

* Communicated by the Author.

where l is the size of the network and $\mathbf{b}$ the Burgers vector of AB ; k is unity for a screw and $1-\nu$ for an edge dislocation (ν is the Poisson ratio).

Following Mott, the area swept out by AB is

$$A=\tfrac{1}{2}\rho^2(\theta-\sin\theta)\simeq\rho^2\theta^3/12\simeq l^3/12\rho, \quad \text{for} \quad \theta\simeq l/\rho.$$

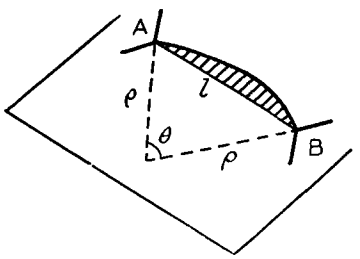
If there are N dislocation lines such as AB per unit volume, the additional shear is

$$\Delta\epsilon\simeq NA\mathbf{b}\simeq Nl^3\sigma/6G\alpha,$$

where $\alpha(l)=(2k\pi)^{-1}\ln(l/\mathbf{b})$ is a slowly varying function of l, near to unity for $l\simeq 10^{-5}$. The decrease in G is thus*

$$\Delta G/G\simeq -Nl^3/6\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Fig. 1



Elastic displacement of a Frank–Read source.

Nl^3 is near to unity if the crystal is filled by a three dimensional network and all the dislocations are mobile. But if a proportion $1-x$ of them are *sessile*, we have $Nl^3\simeq x$. Thus, for a *pure* metal,

$$(\Delta G/G)_0\simeq -x/6\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

A direct check of this formula is difficult, for the network of dislocations can only be locked by introducing impurity atoms which alter G themselves. It is therefore of interest to extend the theory to solid solutions.

§ 2. Extension of the Theory to Solid Solutions

For a large enough concentration c of the solute elements, a dislocation line AB meets solute atoms on the average at distances say l_0 which decrease when the concentration c of impurity increases (fig. 2). If σ is *small*, as is usual in ultrasonic experiments, we may assume that the dislocation line is ' pinned down ' at the solute atoms, and can only bend between them.

Formula (2) must therefore be replaced by

$$\Delta G/G\simeq -Nl_0^3/6\alpha,$$

where one easily sees that $N\simeq x/l_0l^2$. Hence :

$$\Delta G/G\simeq(\Delta G/G)_0(l_0/l)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* For $\alpha=1$, Mott's paper gives 24 instead of 6, owing to a numerical error.

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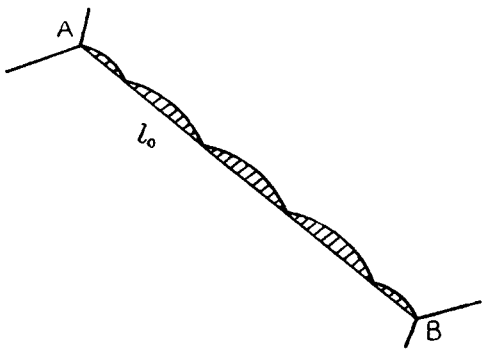
At small concentrations, the rigidity modulus should thus deviate from its quasi linear variation with c and present a negative anomaly ΔG. $|\Delta G|$ should be almost constant for very small concentrations ($l_0 \gg l$), but should decrease as l_0^2 for larger concentrations ($l_0 \ll l$) and become rapidly

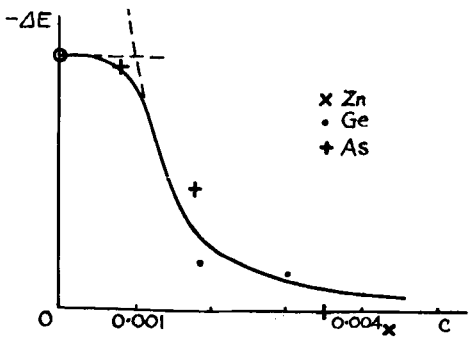
Fig. 2



Elastic displacement of a dislocation in a solid solution.

negligible (fig. 3 gives the anomaly $-\Delta E$ of Young's modulus, where the same theory applies and the experimental points are somewhat less scattered).

Fig. 3



$\Delta E(c)$ for copper alloys. Experimental points after Bradfield.

If the dislocation line AB was perfectly straight, one would have $l_0 \simeq \mathbf{b}/c$. One should however expect the dislocation line to deviate slightly from this path so as to pass through neighbouring solute atoms (Mott 1952 b). This will reduce l_0 somewhat.

Mott shows that

$$l_0 = \mathbf{b}\beta/c,$$

where

$$\beta \simeq (4T\mathbf{b}c/V)^{1/3},$$

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varies slowly with concentration. T is the energy of the dislocation line per unit length and V the energy of interaction of a solute atom with the dislocation line. One has

$$T \simeq 2\pi G\mathbf{b}^2,$$

$$V = \gamma G\mathbf{b}^3\epsilon,$$

where ϵ is the ' misfit ' of the solute atom, deduced from the variation of the lattice parameter with composition : $\epsilon = (1/\mathbf{b})(d\mathbf{b}/dc)$. Thus

$$\beta \simeq (8\pi c/\gamma\epsilon)^{1/3}.$$

For carbon in iron, $V \simeq 0{\cdot}5$ to 1 ev (Mott 1952 b) and $\epsilon \simeq 0{\cdot}4$, so that $\gamma \simeq 2$. In the case considered in this paper, $0{\cdot}01 < c < 0{\cdot}001$ and $0{\cdot}05 < \epsilon < 0{\cdot}15$ (Owen 1947). Thus V is of the order of 0·1 ev and β has a value between 0·3 and 1 : the dislocation line does not deviate much from a straight line.

In conclusion, when the concentration c is increased, $|\Delta G|$ should be almost constant and then decrease as c^{-2}. The transition between the two types of curve occurs for $l \simeq l_0$, or $c = c_0 \simeq \mathbf{b}\beta/l$.

§ 3. Comparison with Experiment

A deviation of the type pictured (fig. 3), is well known in copper alloys (Köster and Rauscher 1948). Recent ultrasonic measurements by Bradfield and Pursey (1953) show in CuZn, CuGa, CuGe and CuAs and for large concentrations a quasi-linear variation of G and E. These straight lines converge by extrapolation to pure copper on a value G_1 somewhat larger than the actual value G_0 :

$$(\Delta G/G)_0 = (G_0 - G_1)/G_0 = -0{\cdot}015.$$

The anomalies ΔG and ΔE seem only function of the atomic concentration of impurities, not of their nature. The experimental points fit reasonably well with the theoretical curve (fig. 3), with $c_0 \simeq 0{\cdot}001$ hence $l \simeq 10^{-5}$ cm.

This value of l is somewhat smaller than those deduced by Mott (1952) from the critical shear stress σ_c . σ_c corresponds to $\rho = l/2$ in eqn. (1), thus $\sigma_c \simeq G\mathbf{b}\alpha/l$. Measurements on silver (Andrade and Henderson 1951) and aluminium (Rosi and Mathewson 1950) monocrystals give $l \simeq 10^{-3}$ to 10^{-4} cm. On the other hand crystals with one dimension smaller than l probably have no such network, and should exhibit high critical shear stresses, of the order of $G/10$. Possible examples are Herring and Galt's ' whiskers ' of Sn, Al . . . (1952) with a diameter of about 10^{-4} cm ; also thin plates of silver (Beams, Walker and Morton 1952) with thickness smaller than 5×10^{-5} cm. Finally $l \simeq 10^{-4}$ to 10^{-5} cm corresponds to the usual size of the ' mosaic bloc ' as deduced from x-rays diffraction.

Some other points may be noted. The value of $(\Delta G/G)_0$ gives here $x \simeq 0{\cdot}1$. This seems to indicate that the network is made in major part of sessile dislocations, in agreement with Mott's interpretation of the barriers for the piled up groups (1952 a).

For silver alloys, Smith's measurements (1952) give a similar anomaly with $(\Delta G/G)_0 \simeq (\Delta E/E)_0 \simeq -0{\cdot}025$ and $c_0 < 0{\cdot}01$.

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§ 4. Disappearance of the Anomaly by Long Annealing

Finally it is interesting to note that the anomaly disappears completely even for 'pure' copper (e.g. 99·99%) after long annealing at 650°c (Bradfield and Pursey *loc. cit.*).

This we interpret as due to the crowding by diffusion of impurity atoms on the dislocations. The concentration of solute atoms along the dislocation lines after annealing at temperature T will be (Cottrell 1948):

$$c' \simeq c \exp (V/kT).$$

For 'pure' copper, i.e. with probably about $c = 10^{-4}$ iron atoms, $\epsilon \simeq 0{\cdot}2$ (Köster 1948), hence $V \simeq 0{\cdot}4$ ev. At 650°c, this gives $c' \simeq 0{\cdot}015 \gg c_0$. The concentration of iron atoms along the dislocation line is thus large enough to suppress the anomaly completely. For the alloys, the locking is also mainly by iron atoms, but perhaps partly by arsenic atoms in Cu As.

As c' is much smaller than 1, the dislocation lines are far from saturated and no yield point is to be expected. This seems to agree with experiment (Ardley and Cottrell 1953).

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