

fourfold axis. The result can be deduced from the  $C_{4h}$  symmetry which then prevails. The observation of this polarization strongly supports the interpretation of the spectrum.

In  $\text{SrF}_2$ , the  $4f^5 5d$  levels fall at slightly higher energies, and a  $4f^8$  level,  ${}^5D_0(A_{1g})$ , gives much of the observed fluorescence spectrum. The lines due to high levels are weaker and more diffuse but we now identify the two levels observed earlier<sup>2</sup> as being  $A_{1u}$  and  $T_{1u}$  of  $4f^5 5d$ . This conclusion is based on the observation of an induced absorption line at  $6635.9 \text{ \AA}$ , polarized parallel to the field, which we interpret as  $A_{1g} - A_{1u}$ . The almost constant separation of these  $A_{1u}$  and  $T_{1u}$  levels of  $\text{Sm}^{2+}$  in  $\text{CaF}_2$  has been used<sup>2</sup> to suggest that a vibrational frequency is involved, but in the limit that the crystal field seen by the  $5d$  shell is large, the separation of these levels is due primarily to terms in the free-ion Hamiltonian and so is expected not to vary. In  $\text{BaF}_2$  no normal or induced lines due to  $4f^5 5d$  can be seen.

For both  $\text{CaF}_2$  and  $\text{SrF}_2$  the earlier work of

Wood and Kaiser<sup>2</sup> located levels where we now establish the occurrence of  $A_{1u}$ . That this was done successfully is gratifying, since in both cases this involved the interpretation of three separate transitions which did not correspond from  $\text{CaF}_2$  to  $\text{SrF}_2$ , and in each case one was observable only at  $77^\circ\text{K}$ , so that it is not possible to be confident without our result that vibrations or other sources of misinterpretation might not be involved. The  $T_{1u}$  level has already been identified<sup>1</sup> in  $\text{CaF}_2$ , and is now also identified in  $\text{SrF}_2$ . We plan to continue and apply high magnetic fields to other systems where a breakdown of selection rules may produce valuable results.

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<sup>2</sup>D. L. Wood and W. Kaiser, *Phys. Rev.* **126**, 2079 (1962).

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## LONG-RANGE CORRELATIONS BETWEEN POINT DEFECTS ON DISLOCATION LINES

Georg Alefeld

John Jay Hopkins Laboratory, General Atomic Division of General Dynamics Corporation, San Diego, California  
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This communication intends to show that pinning points on dislocation lines which are or have been mobile along the line are not equally distributed along the line as it is usually assumed. Pinning points tend to group together even without a force between them. The reason is that a solid with dislocation lines has the higher entropy, the longer the free segments of the present dislocation lines are. A dislocation string with a node in the middle cannot have as many different forms as with the node close to one of the ends or as without the node. The frequencies of the dislocation lines, which are part of the spectrum of the complete solid, depend on the positions and number of pinning points. Longer line segments have lower frequencies and correspondingly higher entropy per unit length. There will be an equilibrium between the entropy increase due to long dislocation segments and the entropy decrease due to the grouping of the pinning points.

We first consider three pinning points on a dislocation line, which interact with the dislocation so strongly as to create two line segments which oscillate independently of each other. The pinner

in the middle is supposed to be mobile, whereas neither of the others can move. We assume that the middle pinner does not move past the immobile pinners. The motion of a dislocation segment of the length  $l$  can, in terms of the string model,<sup>1</sup> be decomposed into a set of harmonic oscillators, with a Hamiltonian  $H(l)$ , which is a function of  $l$ , since the frequencies  $\omega_m = \omega_0(b/l)m$ ,  $m = 1, \dots, l/b$ , depend on the length  $l$ . [ $\omega_0 = (E_L/M)^{1/2}\pi$ ,  $E_L$  = line tension,  $M$  = mass per unit length,  $b$  = lattice constant.]

To this set of  $N$  harmonic oscillators the laws of statistical mechanics can be applied,<sup>2</sup> which yield for the partition function in the high-temperature approximation

$$Z = \prod_{m=1}^{l/b} \left( \frac{kT}{\hbar\omega_m} \right) = \left( \frac{kT}{\hbar\omega_0} \right)^{l/b} e^{l/b} \left( \frac{2\pi l}{b} \right)^{-1/2} \quad (1)$$

The probability  $f(q)dq$  for finding the mobile pinner in the interval between  $q$  and  $q+dq$  is given by

$$f(q) = CZ(l_1)Z(l_2) \quad (2)$$

$l_1$  and  $l_2$  are the line segments on both sides of the pinner, and depend on  $q$ . Using (1) and normalizing we get (see Fig. 1)

$$f(q) = (\pi L)^{-1} [1 - (q/L)^2]^{-1/2}. \quad (3)$$

The probability density has a minimum at  $q = 0$  and increases towards both the other pinning points. For  $q = \pm(L-b)$ ,  $f(q)$  reaches the value  $1/\pi(2bL)^{1/2}$  which is  $(2L/b)^{1/2}/\pi$  times larger than for equal distribution.

The probability  $W(d)$  for finding the pinner closer than  $d$  near the other pinners can be calculated from Eq. (3), as

$$W(d) = 2 \int_{L-d}^L f(q) dq \approx \frac{2}{\pi} \left( \frac{2d}{L} \right)^{1/2},$$

compared with  $d/L$  for equal distribution. If we require  $d = 10^{-3}L$ , we get a 30 times higher probability for a group of two, compared with equal distribution.

The difference in entropy due to the dislocation line between the states with the pinner at  $q = L$  and  $q = 0$  can be written as

$$\Delta S = k \ln(Z_0/Z_1 Z_2),$$

where  $Z_0$  = partition function of the pinner-free line. Using (1) we get  $\Delta S = (\frac{1}{2}k) \ln(\pi L/b)$ , which

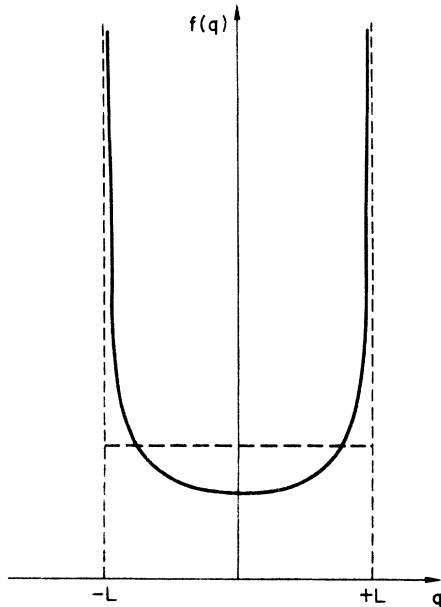


FIG. 1. Distribution density of a pinning point on a dislocation line of the length  $2L$ . The dashed line would be the distribution without taking into account the entropy of the dislocation line.

is  $4k$  for  $L = 10^3b$ .

The probability density for  $N$  mobile pinners on a line of the length  $(N+1)L$  is analogous to (2), given by

$$f(x_1, \dots, x_N) = C \prod_i Z_i(l_i) = C(x_i - x_{i-1})^{-1/2}, \quad (4)$$

where  $x_0 = 0$  and  $x_{N+1} = (N+1)L$ . By differentiating one shows that  $f(x_1, \dots, x_N)$  has a minimum for  $x_i = iL$ . Thus the configuration with all pinning points equally spaced along the line has the lowest possible probability. Any deviation from this equal distribution has higher probability. The probability density  $f(x_1, \dots, x_N)$  is the larger, the more pinners are close to each other ( $x_i = x_{i-1} + b$ ). The pinners thus group together, to create free line segments with correspondingly high entropy. The fact that  $f(x_1, \dots, x_N)$  is strongly peaked for the configurations for which many pinners are close to each other cannot lead to the conclusion that the pinners form only some large groups, and there are no small groups or single pinners. Large groups would give a large entropy increase due to the longer dislocation segments. Grouping of  $N$  equally spaced pinning points on a line with the length  $(N+1)L$  to one group means a line entropy increase

$$\begin{aligned} \Delta S &= k \ln Z_0 / \prod_i Z_i \\ &= \frac{1}{2} N k \ln \frac{2\pi L}{b} - \frac{1}{2} k \ln(N+1), \end{aligned}$$

which is  $30k$  for  $L = 10^2b$  and  $N = 10$ . On the other hand, many small groups have a larger probability because of their larger number of possible arrangements along the line. These two tendencies balance each other in the equilibrium distribution (4).

It should be pointed out that the radial distribution of point defects in the stress field of a dislocation<sup>3</sup> is also modified, if one takes into account the line entropy. The closer a pinner comes to the core of a free line segment, the more the entropy of the line decreases. It changes only slightly if the pinner moves radially towards an already existing pinner. Consequently, the grouping tendency for pinning points is not confined to the dislocation core. How far it extends into the lattice depends on the interaction energy between the pinning points and the dislocation lines. An upper limit is 3 to 4 atomic distances.

Thus, one finds density fluctuations in the dilute Cottrell atmosphere, which are larger and

of longer lifetime than they would be for uncorrelated pinners. The correlations between the pinners do not result from their mutual interaction, but from the entropy change due to their interaction with the dislocation lines. They extend over distances which are large compared with the range of interaction between pinning points (see Fig. 1).

The question of the entropy of dislocation lines has not received much attention in the past.<sup>3</sup> We think that it plays a significant role in the nucleation and the rate of clustering and precipitation on dislocation lines,<sup>4,5</sup> either of impurities<sup>6</sup> or of defects created by radiation damage.<sup>7</sup> It strongly increases the probability that a certain critical number of pinners come close to each other to form a nucleus and acts furthermore as a force on other pinners near or on the line to join existing clusters.

Internal friction experiments, especially the amplitude-dependent breakaway problem,<sup>1</sup> depend sensitively on the spatial distribution of the pinners on the line. Impurities already have the grouped or clustered distribution when the solid is cooled from higher temperature. Point defects on dislocation lines created by radiation damage at low temperatures will change from an uncorrelated distribution to the grouped distribution at that temperature for which pipe diffusion is possible.

Finally, it should also be mentioned that the formation entropy of vacancies near a free dislocation line is lowered by the amount of line entropy because of the pinning action of vacancies. It, thus, can even be negative. The formation

entropy is not lowered near any already existing pinner. The vacancies, therefore, group mainly near impurities or jogs<sup>8</sup> or other nodal points.

To summarize, one can say the following: The dislocations establish correlations between mobile point defects in or close to the dislocation core. These correlations extend over distances which are large compared with the range of forces between the point defects. Dislocation modes differ from regular crystal modes by being sensitive to the position of point defects.

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<sup>5</sup>J. W. Cahn, *Acta Met.* **5**, 163 (1957).

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<sup>8</sup>A jog forms a nodal point if it has some barrier against conservative motion. The statements about grouping apply then to jogs too. If the jog acts as a sink for vacancies, the entropy of the dislocation line acts as a driving force toward the sink.

## NOTTINGHAM EFFECT IN FIELD AND $T$ - $F$ EMISSION: HEATING AND COOLING DOMAINS, AND INVERSION TEMPERATURE

F. M. Charbonnier, R. W. Strayer, L. W. Swanson, and E. E. Martin

Field Emission Corporation, McMinnville, Oregon

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Electron emission is accompanied by energy exchanges between the conduction electrons and the cathode lattice, which become particularly important at the very high emission densities feasible with field and  $T$ - $F$  emission cathodes. Their study is of basic interest as it provides a complementary check, through a direct measurement of the average energy of the emitted electrons, of the theory of field and  $T$ - $F$  emission; it is also of practical importance because these

energy exchanges control the cathode tip temperature and set an upper limit on the feasible emission density. This paper presents recent data confirming the theoretically predicted temperature dependence of the exchange and its reversal (from cathode heating to cooling) at high temperatures. A more comprehensive theoretical and experimental study is approaching completion.<sup>1</sup>

There are two main emission-induced energy-exchange phenomena. The familiar resistive or