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Stationary Dislocations in Sodium Chloride as Possible Vehicles for the Electrical Conductivity Mechanism

Wendell Gayle Bradley
Upper Iowa University

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Abstract. Pairs of crystals were grown simultaneously from melts of sodium chloride containing various amounts of divalent cation impurity. One of the crystals of each pair was grown from a distorted seed in an attempt to introduce extra dislocations into this crystal. The electrical conductivities of samples cleaved from each of the crystals were measured in a temperature range from 100°C to 300°C. A comparison of the results of these measurements indicated that there was a slight extra conductivity in the crystals grown from the bent seeds.

From X-ray diffraction of crystals, it is readily observed that certain imperfections exist in the lattice structure. The exact nature of these imperfections is difficult to ascertain from this type of experiment. What is important is that these experiments conclusively demonstrate that a real crystal is not a perfectly ordered array of atoms. Indeed, the experimental facts are best explained in terms of certain types of lattice imperfections. This research is

concerned with a particular type of imperfection called the dislocation and its effect on the ionic conductivity.

DISLOCATIONS

There are two fundamental dislocation models. The first model was proposed independently in 1934 by G. I. Taylor and E. Orowan (1) to explain plastic behavior in solids and is called the edge dislocation. Consider the atomic arrangement of Fig. 1A. The upper right section of the crystal has been arranged one atomic spacing to the left with respect to the lower right
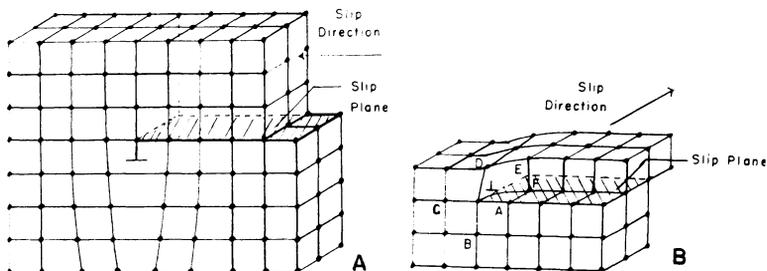

Figure 1. A. Edge dislocation. B. Screw dislocation.

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section. No rearrangement has occurred in the left half. The symbol ⊥ represents the "dislocation line".

The second dislocation model was proposed in 1939 by J. M. Burgers (2) and is known as a screw dislocation. In Fig. 1B the upper right portion of the crystal has been pushed one atomic spacing backward. The dislocation line ⊥, in this case, is parallel to the slip direction. Paths such as ABCDEF proceed around the dislocation line advancing one actomic spacing per turn hence the name screw dislocation.

Dislocations and Crystal Growth

Nearly all theories of crystal growth depend upon the individual molecular process of nucleation. If we imagine the molecules to be tiny cubes, a growing crystal might appear as in Fig. 2. When a unit alights on the crystal surface it will most
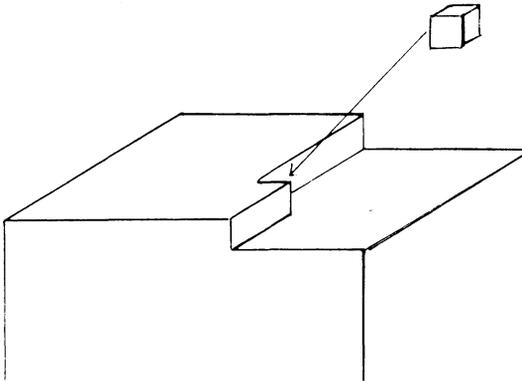

Figure 2.   Monolayer nucleation.

likely stick only where three of its six faces may be bonded to units already fixed in the crystal. As the growth proceeds, however, all the niches suitable for nucleation will eventually become filled and further growth becomes improbable. Frank (3) suggested that if a screw dislocation is present, there are always suitable steps for nucleation. Since one end of the step is fixed, the random nucleation causes the outer end of the step to fall behind, and the crystal is built up in spiral fashion. Experimental evidence confirms this theory. Such patterns are observed in natural crystals, as well as crystals grown synthetically from vapor, the solution, and the melt (4). It seems to be a safe conclusion that nearly all crystals contain dislocations and that these dislocations play an important role in their growth.

Dislocations as Sources and Sinks for Vacancies, Interstitials, and Impurities

Because of stress fields due to the distortion of the lattice, edge

dislocations tend to attract the foreign atoms in a crystal. Impurity atoms that are "larger" than the atoms of the host lattice have a tendency to move to the tension side of the dislocation where there is more room between regular lattice neighbors. Similarily "smaller" impurity atoms will tend to be deposited on the compression side of the dislocation. Screw dislocations, and combinations of edge and screw dislocations, might also be expected to act as sinks for impurity atoms for analogous reasons.

If in an edge dislocation, or in any dislocation containing some edge character, there is a jog to another slip plane, part of the
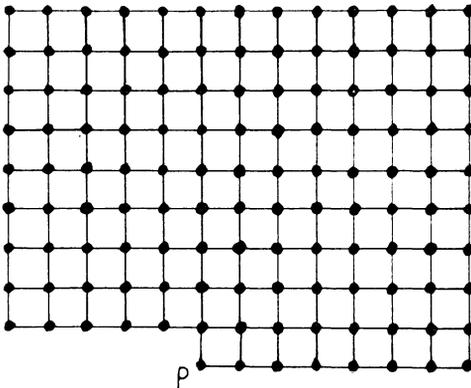

Figure 3.   Extra plane of atoms.

extra plane of atoms may appear as in Fig. 3. The atom P might diffuse into an interstitial position or annihilate a vacancy in the normal lattice at the expense of the extra plane. Similarly if a diffusing atom from the normal lattice assumes a position directly to the left of P, the extra half plane will grow and either an interstitial will be annihilated or a vacancy will be created in the normal lattice. Here as with the case of impurities, the lattice distortion makes such diffusion feasible. Thus we have dislocations acting as sources and sinks for both vacancies and interstitials.

During plastic flow, sodium chloride exhibits a large increase in conductivity (5). It is presumed that the moving dislocations generate the appropriate number of vacancies to account for the conductivity increase. Although the mechanism of generation is not entirely clear, the observation does show that dislocations and vacancies are intimately connected.

IONIC CONDUCTIVITY IN THE ALKALI HALIDES

It is shown from statistical thermodynamics (6) that a certain amount of lattice defect occurs for $T > 0°$ K. By lattice defects, we mean only that disorder implicit from thermodynamic prin-

ciples. Accidental faults in the crystal such as those resulting from nonideal growing conditions are thereby excluded.

Lattice Defects

In equilibrium, lattice defects requiring the smallest energy of formation will predominate. There are several types of defects that could be imagined. Two simple types of lattice defects are Schottky defects (7) and Frenkel defects (8). Schottky defects are vacancies (missing atoms) in the crystal lattice (Fig. 4a). The missing atoms have presumably migrated to a

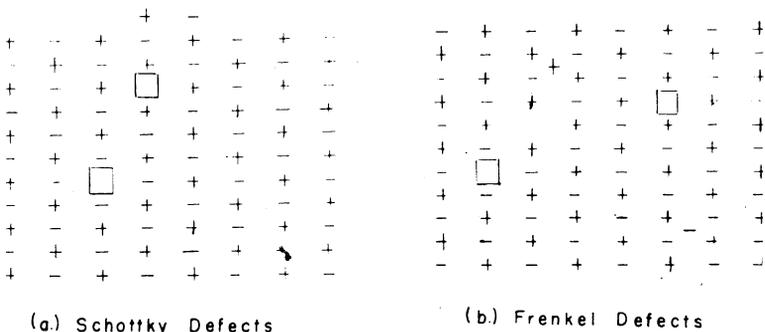(a.) Schottky Defects   (b.) Frenkel Defects

Figure 4.   Lattice defects.

crystal sink. Cracks, dislocations, and the crystal surface all can act as such sinks. Frenkel defects consist of interstitial and vacancy pairs. They are created when atoms leave their position in the perfect lattice to assume positions in the interstitial regions as in Fig. 4b. For the alkali halides, there is general agreement that defects of the Schottky type are the most likely to occur (9). The following discussion will be limited only to the alkali halides and defects of the Schottky type.

In order to maintain electrical neutrality within the crystal, it is assumed that equal numbers of positive and negative vacancies are formed. Let the total energy associated with the creation of a positive-negative vacancy be θ. Starting with a perfect lattice of N positive and N negative ions, the production of n vacant lattice sites requires an amount of energy equal to nθ. For n<<N, it is assumed that θ is independent of n.

The equilibrium number of vacancies at a temperature T is shown (10) to depend upon a Boltzman factor,

$$n = N e^{\frac{-\theta}{2kT}} \ .$$

The Electrical Conductivity

The application of a potential difference across a section of an

alkali halide crystal produces an electrical current. The experimental validity of Faraday's law indicates that the conductivity is ionic in nature (11), and that the positive ions are much more mobile than the negative ions. Conductivity in a perfect lattice is impossible (unless the conductivity is by interstitials) since the ions have no place to go. As indicated above, the mechanism responsible for the conductivity is the migration of positive ions by means of vacancies.

As a positive ion jumps into a vacancy it must overcome a potential barrier. If the barrier is of height ε, and the number of attempts to cross the barrier per second is Y, the probability p, per unit time of the ion jumping into the vacancy is (12),

$$p = Ye^{\dfrac{-\varepsilon}{kT}}$$

The quantity p is called the jump frequency. The electrical field, E, increases the probability of a positive ion jumping toward the cathode. The superposition of the applied and lattice potentials is shown in Fig. 5, where λ is an inter-ionic distance, and e is
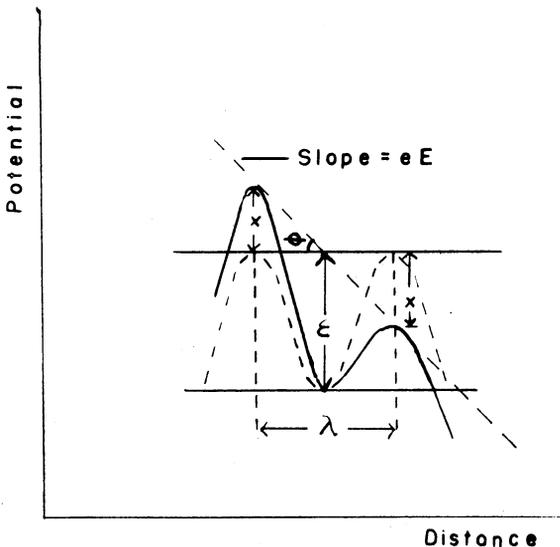

Figure 5.   The superposition of the applied and lattice potentials.

the charge. To a first order approximation the conductivity σ obeys Ohm's law (13) and can be written

$$\sigma = \text{const}\ \frac{n}{T}\ \frac{n}{N}\ e^{\dfrac{-\varepsilon}{kT}}$$

The constant depends upon the lattice structure. Substituting the exponential $e^{-\frac{\theta}{2kT}}$ for $\dfrac{n}{N}$, the conductivity may be written,

$$\sigma = \frac{const}{T}\, e^{-\left[\frac{\frac{\theta + \varepsilon}{2}}{kT}\right]}\quad.$$

Impurities

When alkali halide crystals are "doped" with varying concentrations of divalent impurities, such Cd^{++}, Sr^{++}, and Ca^{++}, a plot of log σ T vs. $\dfrac{1}{T}$ would appear as in Fig. 6 (14). The numbers 1 through 5 indicate increasing amounts of divalent impurity. A concentration of one part per million is significant. The doping range may extend to concentrations of several hundred parts per million. Density measurements in connection with this type of doping indicate that the divalent ions enter the lattice structure substitutionally (15). For instance, consider
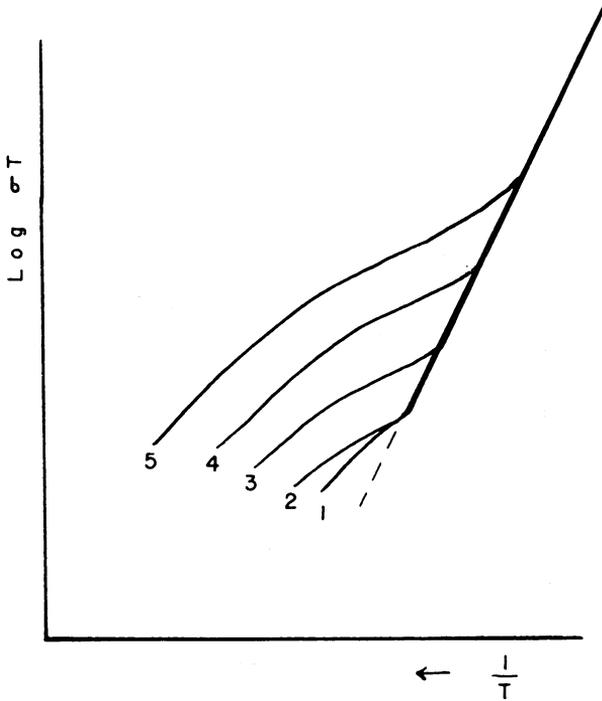

Figure 6. Log σ T vs. $\dfrac{1}{T}$.

a NaCl crystal which is doped with $CaCl_2$. Ca^{++} ions are incorporated in the crystal by replacing Na^+ ions. If we require the resultant internal structure to be electrically neutral, there must be formed a single positive ion vacancy for each incorporated Ca^{++} ion. At low temperatures, the vacancies created in this way might be sufficient in number to dominate the thermally generated vacancies. If this is the case, the conductivity should be independent of the thermally generated vacancies below a critical temperature (which depends upon the divalent ion concentration) and the number of vacancies should remain essentially constant. Above this critical temperature, in the so-called intrinsic region, the conductivity should be essentially determined by the number of thermally generated vacancies. Such an interpretation leads to an explanation of the observed curves in Fig. 6. Referring to the expression

$$\sigma = const_1 \frac{n}{N} e^{\frac{-\varepsilon}{kT}} ,$$

since n becomes temperature independent in the impurity region,
$\overline{N}$

$$\sigma = const_2 e^{\frac{-\varepsilon}{kT}} .$$

In the intrinsic region as before,

$$\sigma = \frac{const}{T} e^{-\left[\frac{\frac{\theta}{2} + \varepsilon}{kT}\right]} .$$

Since ε is determined by the slope in the impurity region and $\frac{\theta}{2} + \varepsilon$ is determined by the slope in the intrinsic region, both values can be obtained experimentally. Experimental investigations of this type (16) also show that at a given temperature the impurity conductivity is nearly proportional to the concentration of the divalent ion. This means that the divalent impurity ions and their corresponding vacancies are essentially completely dissociated.

We have already seen how impurity atoms tend to deposit along dislocations. When the impurity atoms are divalent, the condition of electrical neutrality demands that a corresponding number of vacancies be formed. This leads one to expect that in the impurity region the equilibrium number of vacancies and
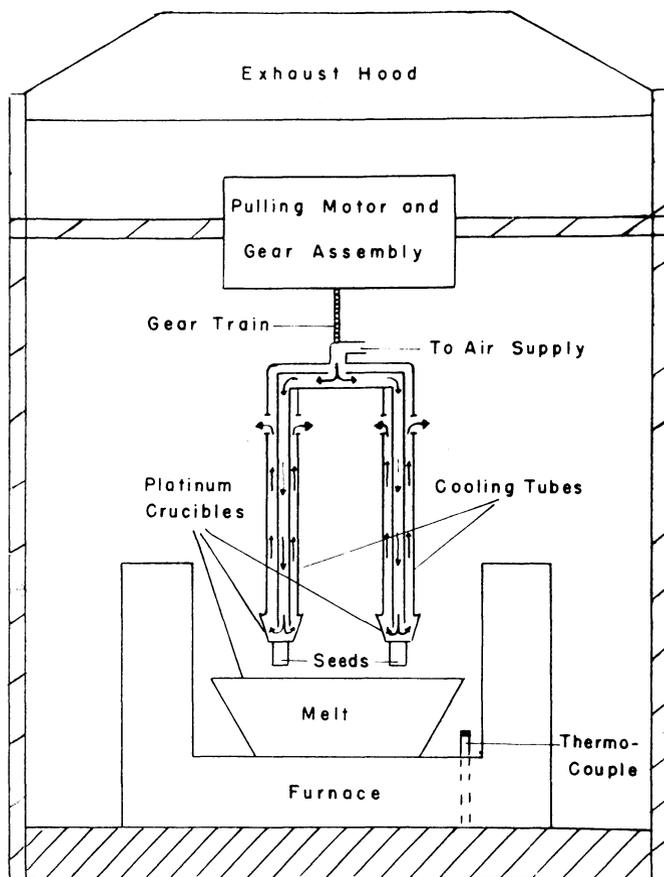
Figure 7. Schematic diagram of the crystal growing apparatus.

hence the ionic conductivity is affected by the dislocation density. Since dislocations play an important role in the growth of crystals, it may be possible to introduce extra dislocations into a crystal by growing it from a distorted seed. Assuming that this is possible, samples cleaved from each of two simultaneously grown crystals (one from a distorted and one from a non-distorted seed) might exhibit different conductivities. It was the purpose of this investigation to detect such possible differences in the ionic conductivity of NaCl doped with different amounts of $CaCl_2$, $CdCl_2$, and $SrCl_2$.

EXPERIMENTAL METHODS AND TECHNIQUES

Crystal Growth

The Kyropoulos method of crystal growth was used. A seed, which is mounted on a cooling tube, is immersed part way into

a vessel containing the melt. The temperature of the melt is maintained slightly above the freezing point. When the crystal begins to form, the seed is pulled slowly upward.[3] In this way the crystal is permitted to grown downward as well as outward from the seed. A schematic diagram of the crystal growing apparatus used in this research is given in Fig. 7.

The melt was formed from reagent grade NaCl to which small amounts of divalent chlorides were intentionally added as impurities. The mole ratio of the divalent chloride to sodium chloride was determined with an analytical balance. The largest mole ratio used was 500×10^{-6}. It is estimated that the ratio of the divalent ions in the melt to those in the crystal is of the order of 10. This ratio depends upon the pulling rate (17). The average pulling rate used in this work was .3 mm per minute.

The seeds were cleaved from single crystal blanks purchased from Harshaw Chemical Company. The approximate dimensions of the seeds were 1 cm x 2cm x .05 cm. All seeds were annealed in air at 700°C for one hour. Then one seed of each pair was bent. A small vise, one jaw of 1.5 in. diameter brass stock and the other of Silastic—room temperature vulcanizing silicon rubber, manufactured by Dow Corning Corporation—was used (Fig. 8). The Silastic and seed readily conformed to the radius of curvature of the brass stock. The bent and non-bent seeds were then mounted on the growth apparatus in the manner of Fig. 7. As a test for asymmetry, the bent seed was mounted alternately on the left and right cooling tubes for the different growings. No asymmetry was detected. Two crystals were grown simultaneously, one from each seed.
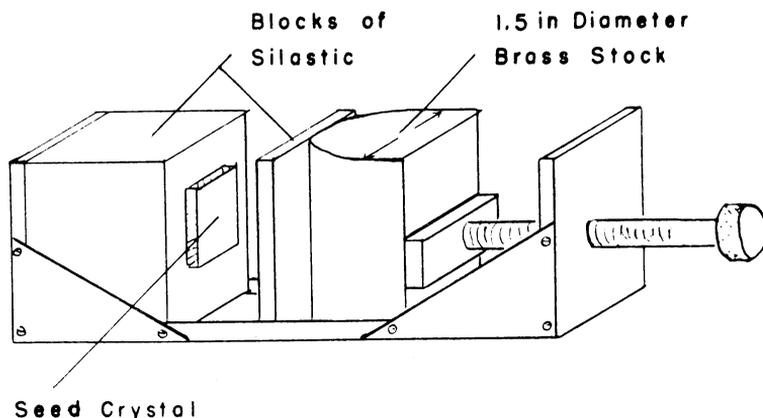

Figure 8.   Vise for bending the seeds.

[3] The original method of Kyropoulos was to induce the seed to grow by carefully cooling the furnace. With this technique no pull-appartus was required.

Measurement of the Conductivity

From each of the simultaneously grown crystals, several samples (from different positions) of approximately 1 mm thickness were cleaved. These samples were dipped into a colloidal suspension of graphite in alcohol (Dag No. 154) and allowed to dry. The edges were then cleaved off, leaving two square graphite electrodes about .25 cm^2 in area. Two corresponding samples, one from each crystal, were then placed in the conductivity measuring appartus and their conductivity measured as a function of temperature, in helium atmosphere. The conductivity measuring circuit is shown schematically in Fig. 9. The
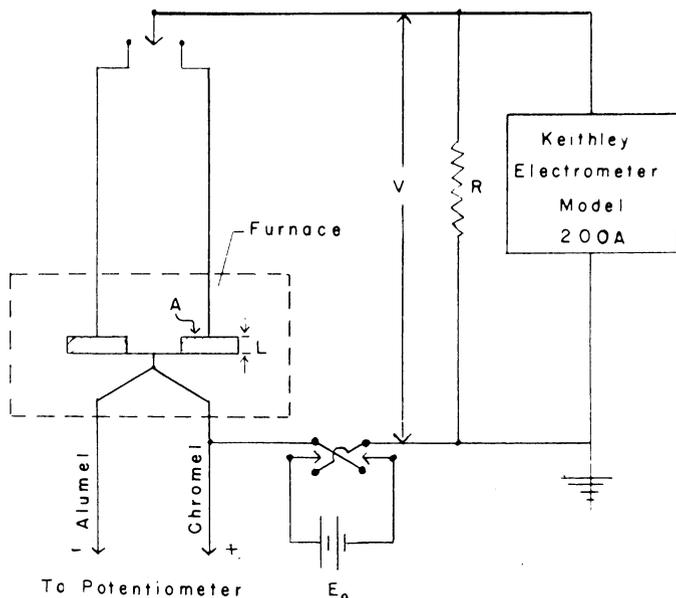

Figure 9.   Circuit for measuring the conductivity.

furnace is designed so that both samples are measured under the same conditions. No difference was observed in the conductivity of a sample whether it was measured on the right or left electrode.

The function of the reversing switch in Fig. 9 was to avoid possible polarization effects in the sample. The conductivity, σ, as calculated from the geometry of the circuit in Fig. 9 is:

$$\sigma = \left[\cfrac{1}{R \left(\cfrac{E_o}{V} - 1 \right)} \right] \frac{L}{A} \quad .$$

In this equation, R is the electrometer shunt resistance. R may be

varied in steps of successive powers of ten from $10°$ ohms to 10^{11} ohms. V is the voltage appearing across R. L and A are rspectively the thickness and area of the sample. Ohm's law was verified by establishing the independence of σ on the terminal potential of the cell E_0 (between 10 to 110 volts) at a given temperature. E_0 was then maintained at 50 volts for all measurements.

Data were taken for both increasing and decreasing temperatures of the samples with no detectable differences.

Results

The effect of the condition of the seed on the conductivity can most readily be discussed with the aid of Fig. 10. The notation
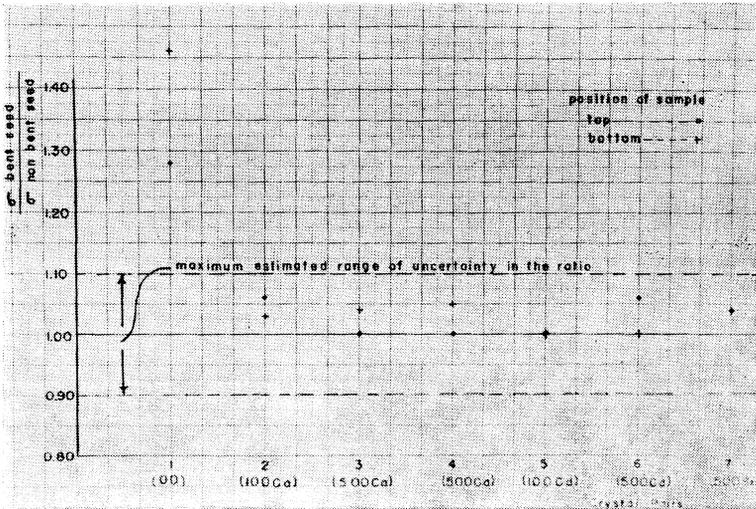

Figure 10.   The effect of bending the seed crystal on the conductivity.

"σ bent seed" is used to indicate the conductivity of a sample cleaved from a crystal grown from a bent seed. It was determined that the per cent deviation of σ is about 7%. For the ratio σ bent seed/σ non-bent seed, the per cent deviation,

$$\sqrt{(7\%)^2 + (7\%)^2} \approx 10\% ,$$

is indicated in the figure.

As a first impression one might assume that since the ratio in Fig. 10 is greater than unity for all crystal pairs, some conductivity mechanism has definitely been introduced by bending the seed. Before such an assumption can be justified, however, there are two fundamental considerations. First of all, in only one

crystal pair was the effect suffciently pronounced for the ratio to exceed the limits of the estimated uncertainty. Secondly, it is possible that the effect is not a unique result of bending the seed.

Great care was taken to exclude all instances where non-parallel treatment of the crystals within a pair might cause a systematic effect in the conductivity. All seeds were annealed simultaneously. Each crystal pair was grown simultaneously. The two corresponding samples from each pair of crystals were put into the furnace together and measured under the same conditions. The crystal associated with the bent seed was alternated from left to right on both the cooling tubes and the measuring electrodes for successive pairs.

If there is a conductivity mechanism introduced by bending the the crystal seed, it is interesting to know whether the mechanism has a positional dependence within the crystal. On the average, the conductivity was found to be independent of position within the crystal for both bent and non-bent seeds. This is probably a conclusion peculiar to the particular apparatus used in this research. It is believed that no positional dependence in the conductivity of the sample is observed when the crystal is much smaller than the melt.

It seems to be a reasonable conclusion that the slight increase in conductivity is a result of the bent seed introducing extra dislocations into the crystal. Since for each divalent ion which tends to deposit along these extra dislocations a vacancy is created, the crystal grown from the bent seed has slightly more vacancies than the one grown from the non-bent seed and it exhibits a slight increase in conductivity. The samples of "0" concentration, i.e., the pairs with the least impurity concentration, appear to be very structurally sensitive.

To be sure, the conductivity increase is small. For the doped samples, it is probably less than 7%. In order to demonstrate the effect conclusively one would need highly refined experimental techniques.

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