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Diffusion, Solubility, and Electrical Properties of Copper in Indium Antimonide

HANS JUERG STOCKER*
Texas Instruments Incorporated, Dallas, Texas
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Radiotracer and sheet resistivity measurements show four distinct mechanisms of the diffusion of Cu in InSb: (A) Rapid diffusion as an interstitial atom with a diffusion coefficient of approximately 10^{-5} cm^2/sec. No electrical activity of interstitial Cu is observed. (B) Dissociative diffusion due to reaction of interstitial Cu with vacancies diffusing in from the surface. This process has an activation energy of 1.08 ± 0.08 eV and a D_0 between 10^{-4} and 10^{-3} cm^2/sec. (C) Diffusion due to reaction of interstitial Cu with vacancies inherited in dislocation-free crystals during growth. It is possible to free low-dislocation density crystals from such vacancies by a low-temperature heat treatment. The reaction of vacancy aggregates with diffusing interstitial Cu is analyzed as an example of a mechanism which explains the observed behavior. (D) The diffusion due to interstitial Cu reacting with vacancies supplied through dislocations. Diffusion in crystals containing 10^5 dislocations cm^{-2} is 5 orders of magnitude faster than in dislocation-free and annealed InSb crystals. The solubility of substitutional Cu in InSb is expressed by the relation $C_s(T)=1.5\times10^{22}\exp(-0.76/kT)$. The solubility of interstitial Cu is approximately 50 times lower. From the Cu-labeling technique suggested by mechanism (C), the equilibrium In-vacancy concentration at the melting point is estimated to be 1.0×10^{16} cm^{-3}, corresponding to an activation energy of 1.0 eV. The activation energy for the self-diffusion of indium in InSb is calculated to be 1.84 ± 0.14 eV, in excellent agreement with Eisen and Birchenall's measured value of 1.81 ± 0.25 eV. However, the diffusion coefficients calculated are one order of magnitude lower than their measured values, presumably because they were measured in high-dislocation density material.

I. INTRODUCTION

THE diffusion of Cu into Ge and Si has been studied rather extensively by several authors.[1–6] The diffusion and electrical behavior of Cu in single crystals of GaAs have also been reported.[7,8] These investigations have shown that Cu has substitutional as well as interstitial properties and is capable of existing in various ionic states. Cu enters at a rapid interstitial rate into these crystals and reacts readily with vacancies. The diffusion was found to be very sensitive to structural defects in these crystals.

This paper describes the diffusion of Cu into single crystals of InSb and the electrical properties of Cu in the InSb lattice. There is a marked similarity in behavior between elemental semiconductors and InSb. In addition, there are some new features which have to be attributed to the compound nature of InSb. Our results enable us to make some estimates of the vacancy concentration and the diffusion coefficient of vacancies in InSb. We also compare Eisen and Birchenall's work on self-diffusion in InSb[9] with values calculated from our data.

* Present address: Syracuse University, Syracuse, New York.
[1] C. S. Fuller, J. D. Struthers, J. A. Ditzenberger, and K. B. Wolfstirn, Phys. Rev. **93**, 1182 (1954).
[2] C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **28**, 40 (1957).
[3] A. G. Tweet and C. J. Gallagher, Phys. Rev. **103**, 828 (1956).
[4] C. J. Gallagher, J. Phys. Chem. Solids **3**, 76 (1957).
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[7] C. S. Fuller and J. M. Whelan, J. Phys. Chem. Solids **6**, 173 (1958).
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[9] F. H. Eisen and C. F. Birchenall, Acta Met. **5**, 265 (1957).

II. EXPERIMENTAL

For our investigations we used pulled InSb single crystals grown in this laboratory. The crystals were n type with electron concentrations of 3×10^{14} through 1×10^{15} cm^{-3} at liquid-nitrogen temperature. For two measurements with radioactive Cu^{64} we used p-type InSb of 1×10^{15} cm^{-3} hole concentration. The diffusion behavior in these p-type crystals was identical to that in n-type material.

The dislocation density was determined by counting the etch pits in the (111) plane obtained by etching in a 3 HNO_3:2HF:10 acetic acid:10 H_2O solution. Only the larger pits, which probably correspond to edge dislocations, were counted.[10] The slices were usually cut normal to the [111] direction. In some cases we also used (113) slices with no apparent influence on the diffusion behavior.

Cu was plated on the optically polished surfaces by electrochemical deposition from a 1:10 HF solution, containing 20 or more parts per million (ppm) of Cu^{++} ions. Larrabee[11] has shown that approximately 1×10^{16} or more Cu atoms cm^{-2} are deposited on the InSb surface from such a solution.

Our diffusion, therefore, occurred from a practically unlimited planar source. If the diffusion of Cu in InSb follows Fick's Law, the concentration of Cu, $C(x)$, found at distance x at time t from the surface will be given by the complementary error function

$$C(x)=C_S^0[1-\operatorname{erf}(x/2(Dt)^{1/2})]. \quad (1)$$

This is the solution of the diffusion equation with the boundary condition of an infinite source. C_S^0 in Eq. (1) is the surface concentration and D, the diffusion co-

[10] H. C. Gatos and M. C. Lavine, J. Appl. Phys. **31**, 743 (1960).
[11] G. Larrabee (private communication).

efficient. Standard measurement techniques were used, namely, (A) incremental lapping and measurement of the sheet resistance with a four-point probe (at liquid-nitrogen temperature)[12]; (B) incremental lapping and counting the amount of radioactive Cu^{64} in the lapped-off portion of the crystal. We used our own Hall measurements of Cu-doped InSb for the conversion of sheet resistivity to acceptor concentration (see part VII). Through a combination of both the sheet resistance and radioactive tracer technique on the same sample, it was possible to determine what portion of the diffused Cu was electrically active. The samples were placed in quartz ampoules sealed under less than 10^{-3} mm residual gas pressure. Heating was carried out in a furnace controlled to $\pm 3°C$ and extended over the range 200 to 500°C. Quenching by immersing the quartz ampoule in water required 5–10 sec.

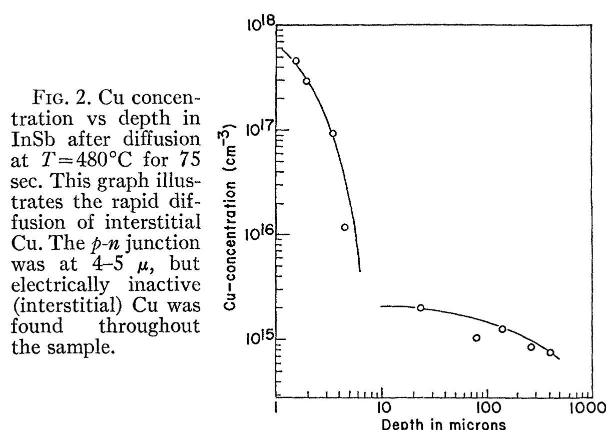

FIG. 2. Cu concentration vs depth in InSb after diffusion at $T=480°C$ for 75 sec. This graph illustrates the rapid diffusion of interstitial Cu. The *p-n* junction was at 4–5 μ, but electrically inactive (interstitial) Cu was found throughout the sample.

III. RESULTS

A. Structure Sensitivity

Our first experiments established the strong influence of dislocations on the diffusion of Cu. Figure 1 illustrates the diffusion coefficient variation by five orders of magnitude at fixed temperature. Samples of various dislocation densities were diffused at $350 \pm 3°C$ for 20 min, and sheet resistance measurements were taken until the *p*-type layer was completely lapped off. Examination of the Cu concentration vs depth profile showed that the diffusion did not obey Fick's Law, but that it has similar structure to that described in detail below:

The diffusion coefficients plotted in Fig. 1 were calculated by taking the best fit of a complementary error function to the concentration vs depth profile. Therefore, they are only "apparent diffusion coefficients," but they clearly indicate the general trend. For unannealed samples, the diffusion coefficient is 2×10^{-10} cm^2/sec and is not affected by dislocations up to a density of 10^3 dislocations cm^{-2}. For higher dislocation densities the diffusion coefficient increases steeply, reaching a maximum of approximately 10^{-7} cm^2/sec at dislocation densities higher than 10^5 cm^{-2}. A sample with less than 20 dislocations cm^{-2} was annealed at 175°C for three days. The diffusivity was two orders of magnitude lower than the previous value in unannealed samples, namely 2×10^{-12} cm^2/sec. Annealed high-dislocation density material did not show a significant decrease in diffusivity.

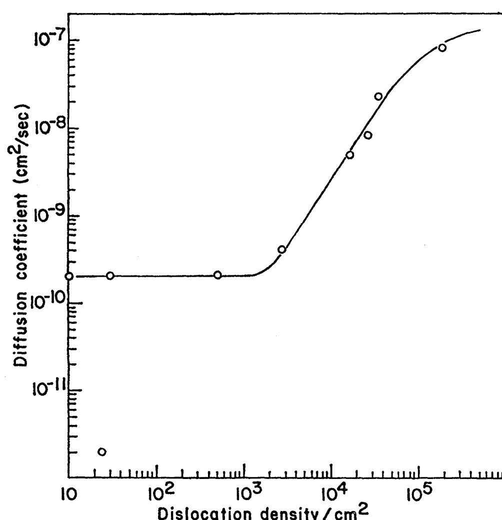

FIG. 1. Dependence of the diffusion coefficient of Cu in InSb on dislocation density. The low point at $D=2\times 10^{-12}$ cm^2/sec was obtained when the sample was subjected to a heat treatment prior to diffusion.

The importance of crystal imperfections is further substantiated by the following observations:

(A) In samples with local regions of high-dislocation density, we observed penetration depths ten or more times larger than in the more perfect regions,

(B) We observed that regions around scratches and edges were converted to *p* type, while the rest of the sample was still *n* type,

(C) In one experiment with annealed material of dislocation density lower than 100 cm^{-2}, we optically polished one side of the slice while the other side was only lapped roughly with 1800 carborundum. After Cu-diffusion at 350°C for 20 min, the *p-n* junction at the optically polished side was at a depth of 1–2 μ from the surface, while at 8–10 μ depth on the rougher side.

B. Diffusion of Cu in Low Dislocation Density InSb

As can be seen from Fig. 1, dislocation densities of less than about 10^3 cm^{-2} did not seem to enhance the diffusion of Cu. The experiments described below were all made with samples containing etch pit densities of less than 25 cm^{-2}, so one can safely assume that no macroscopically observable effect was due to dislocations.

[12] See, for instance, H. Reiss and C. S. Fuller, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 230.

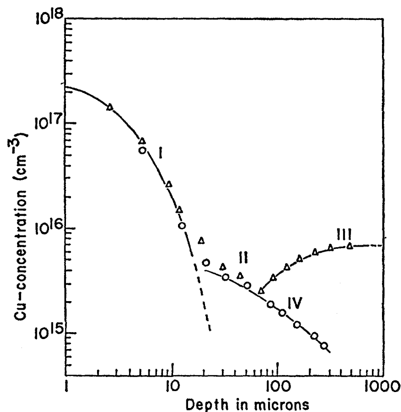

FIG. 3. Cu concentration vs depth in InSb after diffusion at $T=480°C$ for 30 min. The data points indicated by triangles were measured by the radiotracer technique, those indicated by circles by the sheet resistance technique. Branch I is due to the dissociative diffusion, Branches II and IV are due to the reaction of interstitial Cu with vacancies in the bulk of the crystal, Branch III is due to electrically inactive (interstitial) Cu.

Figure 2 shows the rapid diffusion rate of interstitial Cu on a log-log plot. The p-n junction was at 4–5 μ depth, but electrically inactive Cu was found throughout the sample after 75 sec of heating at $T=480°C$. The first four data points at depths of 1–4 μ can be fitted fairly well to a complementary error function corresponding to a surface concentration of $C_S^0 \cong 7\times10^{17}$ cm^{-3} and a diffusion coefficient of $D\cong 3\times10^{-10}$ cm^2/sec. These values, however, have to be taken with caution, since they are measured close to the surface so that scratches, etc., could easily enhance diffusion and concentration. The second group of data points, extending out to 400 μ depth, demonstrates the rapid diffusion of electrically inactive Cu, which we shall call interstitial Cu from now on. The experimental error in this experiment was, due to the low density of interstitial Cu, too great to make an accurate determination of the diffusion coefficient. From this and other experiments, however, we conclude that the interstitial diffusion proceeds at a rate of about $D_i=10^{-5}$ cm^2/sec.

Figure 3 shows the concentration vs depth of an unannealed sample diffused at $T=480°C$ for 30 min. The triangles in Fig. 3 represent data obtained from radioactive tracer measurements, the circles from simultaneous sheet resistance measurements. From 1 to 12 μ, the Cu concentration fits a complementary error function corresponding to a diffusion coefficient of 8×10^{-11} cm^2 sec^{-1}. Between 15 and 70 μ, the Cu concentration deviates from the complementary error function of the first branch. Electrical and radiotracer measurements roughly agree in this region. At depths greater than 70 μ the concentration of acceptor Cu, as determined by the sheet resistance measurements (circles in Fig. 3), continue to decrease. Figure 3 shows that branch III is a continuation of branch II. The total Cu concentration as measured by the radioactivity of Cu, however, increases at depths greater than 70 μ.

In Fig. 4, a semilog plot of Cu concentration vs penetration depth is shown for two samples with dislocation density approximately 25 cm^{-2}, which were diffused at 480°C for 30 min. One of these samples was annealed at $T=175°C$ for 72 h prior to the diffusion with Cu. Parallel radiotracers and sheet resistance measurements were made on both samples. Three definite branches have to be distinguished. The first branch shows essential agreement between electrical and radiotracer measurement and follows within experimental error, a complementary error function with a diffusion coefficient of 8×10^{-11} cm^2/sec and a surface concentration of $(2\text{–}2.5)\times10^{17}$ cm^{-3}. The sheet resistance measurements on the unannealed sample then reveals a second branch which approximately follows Fick's Law with $D=1.4\times10^{-8}$ cm^2/sec and $C_0\approx4\times10^{15}$ cm^3 (open squares in Fig. 4). The radioactive measurements revealed a third branch: The Cu concentration actually increases slightly at depths greater than 40 μ until it reaches 7×10^{15} cm^3, which was the average Cu concentration in the crystal after it was completely n type. The junction depth was at approximately 200 μ.

We attribute the first branch to the dissociative process, limited by the diffusion of vacancies in from the surface; the second branch to reaction of interstitial Cu with vacancies present in the bulk of the crystal; and the third branch to electrically inactive, interstitially diffused Cu.

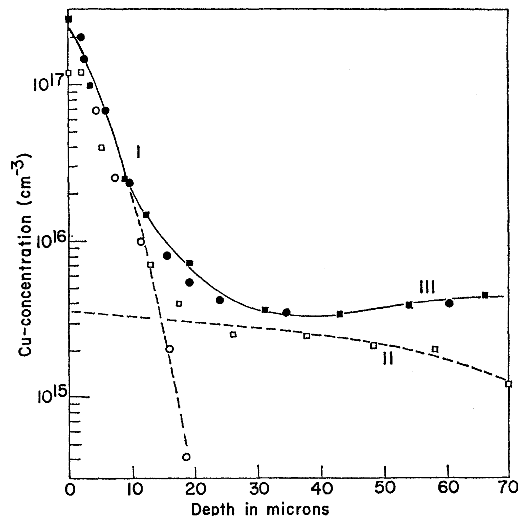

FIG. 4. Cu concentration vs depth for two InSb samples which were diffused at $T=480°C$ for 30 min. Both samples were identical except that the one indicated by circles was annealed prior to Cu plating. Branch I is due to dissociative diffusion; Branch II, attributed to reaction of interstitial Cu with bulk vacancies disappeared in the annealed sample; Branch III is due to electrically inactive (interstitial) Cu. Full circles and squares represent data measured by the radiotracer technique. Open circles and squares represent data determined simultaneously by the sheet resistance technique.

The increase in Cu concentration with greater depths beyond some interior point has been observed in all radioactive measurements of the Cu penetration. It is most likely due to the diffusion of interstitial Cu to the surface during the cooling cycle. Such an out-diffusion might seem impossible because the Cu concentration closer to the surface, due to the dissociative diffusion, is higher. Therefore, Cu would have to diffuse against the gradient of its own electrochemical potential. However, one has to remember that the higher Cu concentration is due to substitutional rather than interstitial Cu. Apparently, the processes maintaining equilibrium between the two are not fast enough, and interstitial Cu can, therefore, diffuse through a field of higher substitutional Cu concentration. In addition, there is some possibility that the thin film of Cu deposited on the surface might act as an external phase and help to attract Cu from the inside of the crystal.

The second branch attributed to bulk vacancies disappeared when an identical sample was first annealed and then diffused for the same time and temperature (circles in Fig. 4).

Figure 5 shows three penetration profiles for three samples diffused at $T=480°C$ for 1200, 1800, and 8200 sec, respectively. They have the same characteristics as the profiles in Figs. 3 and 4. The first branch corresponds to a slow diffusion with $D=8-11\times10^{-11}$ cm^2/sec. The second branch varies markedly in both slope and concentration for the three samples. We shall discuss below whether this is due to the time dependence of the process or a different initial content of bulk vacancies.

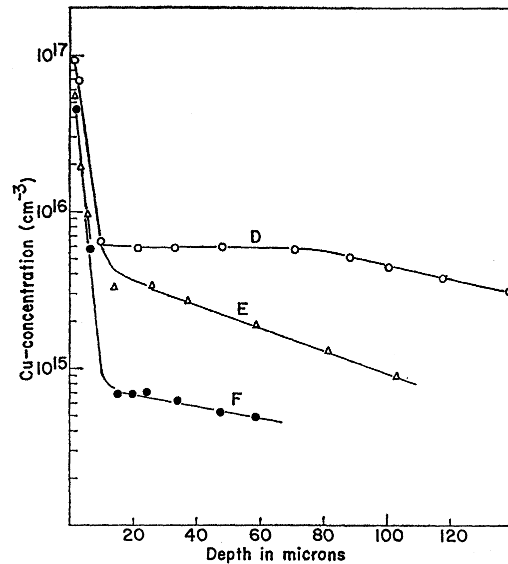

FIG. 6. Cu concentration vs depth for three InSb samples diffused at $T=420°C$. D was diffused for 3600 sec, E for 600 sec and F for 1800 sec. F was preannealed at $T=175°C$ for 26 h. The second branch in F is reduced markedly due to the heat treatment. All measurements here were made by the sheet resistance technique.

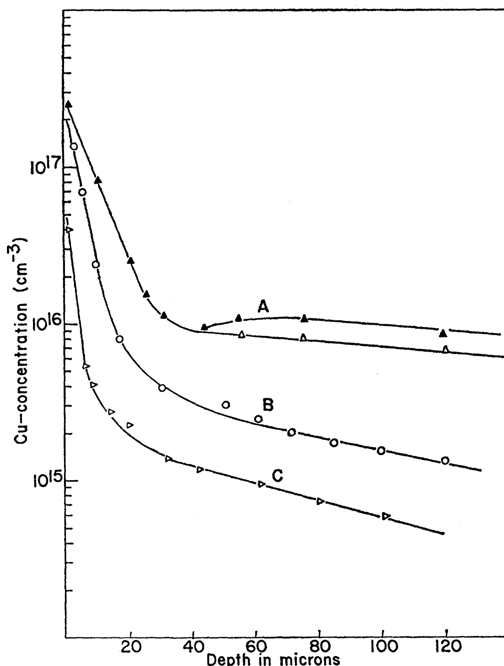

FIG. 5. Cu concentration vs depth for three low dislocation density InSb samples at $T=480°C$. A was diffused for 8200 sec, B for 1800 sec and C for 1200 sec. The first branch of each curve is due to dissociative diffusion. The second branch is due to the reaction of interstitial Cu with bulk vacancies. A was measured by both radiotracer and sheet resistance technique (full and open triangles, respectively). B and C were measured by the sheet resistance technique only.

Figure 6 shows similar penetration profiles for three samples diffused at $T=420°C$. One sample (full circles in Fig. 6) was pre-annealed at $T=175°C$ for 26 h. This resulted in a marked reduction of the second branch although it did not disappear completely, as it did in other samples which were annealed longer.

Figure 7 shows three penetration curves in which the second branch, tentatively attributed to bulk vacancies, has disappeared completely. The concentration vs depth closely follows a complementary error function down to the *p-n* junction. These samples were annealed at $T=190°C$ for at least 6 days.

The dependence of the diffusion coefficient on temperature for the dissociative mechanism (first branch) is shown in Fig. 8. The process has an activation energy of 1.08 ± 0.08 eV. The full circles represent radioactive measurements; the open circles electrical measurements. The points at lower temperatures are relatively inaccurate because of the rather shallow junctions obtained and the inhomogeneities in the starting material resistivity. All these samples had dislocation densities from 10–25 cm^{-2} and were annealed at 150–190°C for 3 to 6 days. An attempt to anneal at 100°C was only partially successful, as the second branch still appeared but with lower surface concentration and slower effec-

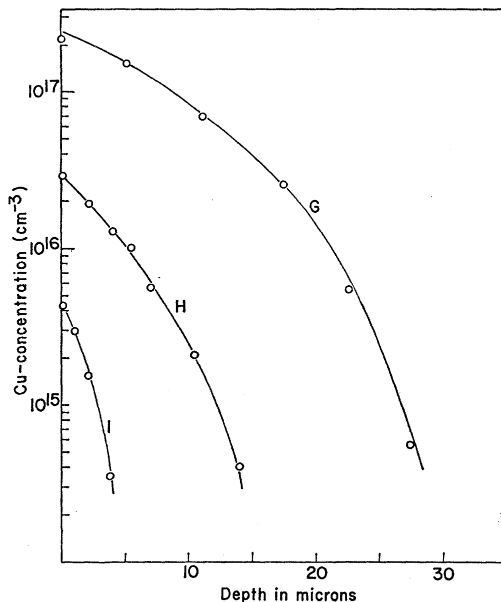

FIG. 7. Cu concentration vs depth for three InSb samples as determined by the sheet resistance technique. All samples were annealed at $T=190°C$ for 6 days. G was diffused at $T=480°C$ for 8200 sec, H at $T=357°C$ for 6.1×10^4 sec, and I at $T=287°C$ for 5.8×10^4 sec. The diffusion here is due to the dissociative mechanism only. All measurements here were made by the sheet resistance technique.

tive diffusion coefficient. Apparently, the concentration of vacancies in the bulk of the crystal was reduced, but not below the donor concentration.

IV. DIFFUSION MECHANISM OF Cu IN InSb

Our data have to be interpreted in terms of four different diffusion mechanisms: (A) the interstitial diffusion; (B) the dissociative mechanism, limited by vacancies diffusing in from the surface; (C) the reaction of interstitial Cu with vacancies generated in the bulk in dislocation-free InSb; and (D) the reaction of interstitial copper with vacancies supplied through dislocations. We neglect the genuine diffusivity of substitutional Cu, which is likely to be of similar order of magnitude to the self-diffusion on In in InSb, $D_{\mathrm{self}}\cong10^{-14}$ cm²/sec at 480°C.[8]

A. Interstitial Diffusion

The interstitial diffusivity of Cu is very high, as we might expect from Ge and Si studies. From Fig. 2, we can conclude $D_i\sim1\times10^{-5}$ cm²/sec at 480°C. Although the Cu concentration was five times larger than the initial donor concentration, the resistivity of the n-type bulk did not change. It seems, therefore, that interstitial Cu is electrically inactive in the InSb lattice. However, we cannot exclude the possibility that the interstitial Cu is precipitated during the cooling cycle (5–10 sec). Interstitial Cu is believed to be a donor in Ge.[4,13]

B. Dissociative Diffusion

Frank and Turnbull[14] first proposed a dissociative diffusion process in which both interstitial and substitutional Cu take part. Conversion from the interstitial to the substitutional state requires the presence of a vacancy, which is annihilated.

$$\mathrm{Cu}_s\rightleftharpoons\mathrm{Cu}_i+V. \tag{2}$$

The concentrations C_s, C_i, C_v are related by a mass-action law

$$C_s/C_iC_v=K=C_s^0/C_i^0C_v^0. \tag{3}$$

In low-dislocation density and annealed material the diffusion will be limited by the vacancies diffusing in from the surface. The diffusion coefficient is given by that of the slower moving species times the fraction of time the vacancies are free from combination with Cu:

$$D_d=D_v\frac{C_v}{C_v+C_s}. \tag{4}$$

If the high-interstitial diffusivity maintains C_i at equilibrium, and if the equilibrium concentration of vacancies C_v^0 is much lower than that of substitutional CuC_s^0 we can rewrite Eq. (4) as

$$D_d\cong D_v\frac{C_v^0}{C_s^0}=\frac{D_{\mathrm{self}}}{C_s^0}. \tag{5}$$

This assumption is rather trivial in the case of Ge or Si for self-diffusion by the vacancy mechanism, but not necessarily in a compound material such as InSb. As a working hypothesis we shall assume that $D_vC_v^0$ is equal

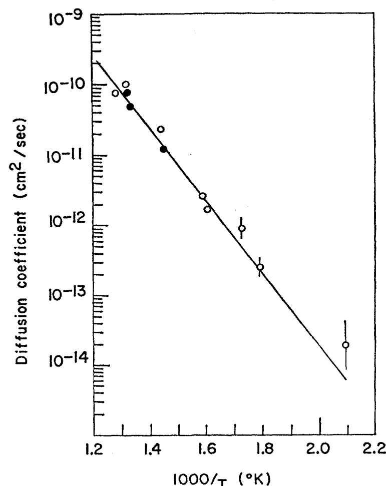

FIG. 8. Diffusion coefficient of Cu in InSb vs reciprocal temperature for the dissociative mechanism. This diffusion coefficient shows exponential temperature dependence with an activation energy of 1.08±0.08 eV.

[13] C. S. Fuller and J. C. Severins, Phys. Rev. **96**, 21 (1954).
[14] F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

to the self-diffusion coefficient of In in InSb, and we shall compare our calculated value of $D_{\rm self}$ to Eisen and Birchenall's measurements.[9] Their value for the activation energy 1.81±0.25 eV is in excellent agreement with our estimated value of 1.84±0.14 eV. It is composed of the activation energy of the dissociative process 1.08±0.08 eV plus the activation energy for the formation of substitutional Cu (Fig. 11) 0.76±0.06 eV. However, our calculated diffusion coefficients are approximately one order of magnitude lower (Fig. 12) than the ones of Eisen and Birchenall. Two possibilities have to be considered to explain this discrepancy. First, Eq. (5) might not be correct, i.e., self-diffusion of In and the dissociative diffusion of Cu proceed by a different vacancy interchange mechanism. Second, Eisen and Birchenall have probably worked with unannealed high dislocation density material which might have increased the supply of vacancies to a degree which accelerated the self-diffusion of In. The discrepancy suggests a remeasurement of the self-diffusion coefficient in dislocation-free and annealed material. In Ge, the enhancement of self-diffusion due to dislocations has been observed.[15]

C. Diffusion Due to Vacancies in the Bulk of the Crystal

The number of vacancies in a crystal at the time the diffusion process is started is a function of the history of the crystal as well as its physical perfection. During the growth, the equilibrium concentration of vacancies at the melting point is present in the crystal. If the crystal is cooled very slowly, the vacancies will have time to diffuse out to the surface unless they are trapped at dislocations. If sufficient time is not allowed for the vacancies to diffuse out and to reach equilibrium, they will either be frozen in as a supersaturated vacancy solution, or, more likely, they will form stable groups of vacancies (so called vacancy clusters). Tweet[16] has studied such vacancy clusters in dislocation-free Ge crystals. He actually attributed some etch configurations directly to such vacancy aggregates. If the crystal is again heated to the diffusion temperature, the vacancy complexes will dissolve and quickly attain and maintain the equilibrium concentration of vacancies at the diffusion temperature. Our experiments with annealed InSb prove that it is possible to dissolve these vacancy clusters in dislocation-free material and, since the single vacancies diffuse out to the surface, to free the crystal from vacancies in excess of the annealing temperature equilibrium concentration.

Our experimental data indicate that diffusion of Cu into dislocation-free, but unannealed InSb proceeds with an apparent diffusivity two to three orders of magnitude larger than the dissociative process limited by indiffusion of vacancies from the surface (Fig. 11). This "apparent diffusivity" was obtained by the best fit of a complementary error function to the second branch in the Cu-penetration curves. Since this portion is partially masked by the dissociative diffusion, and in the case of radiotracer measurements, by interstitial Cu, this fit is somewhat ambiguous. In most cases, as can be seen from Figs. 4–6, one can obtain a better fit

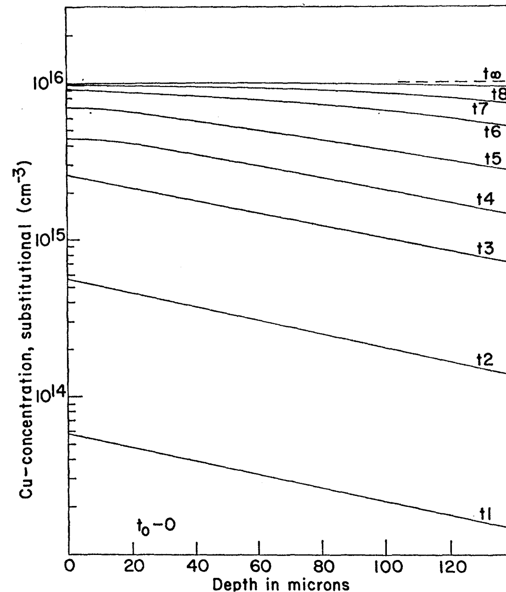

FIG. 10. Theoretical dependence of substitutional Cu concentration on distance from the surface and on time due to the reaction of interstitial Cu with bulk vacancies. The same parameters as in Fig. 9 were used.

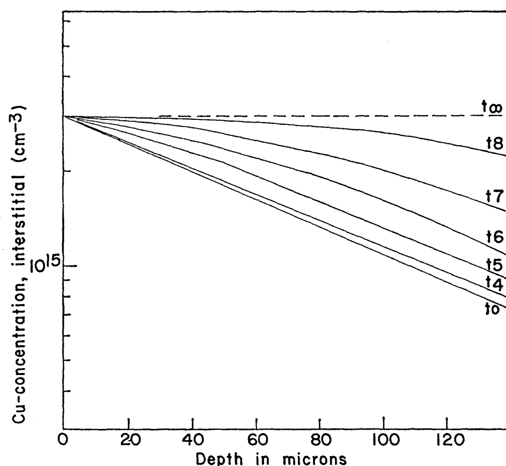

FIG. 9. Theoretical dependence of interstitial Cu concentration on distance from the surface and on time due to the reaction of interstitial Cu with bulk vacancies. These curves were obtained by numerical integration of Eqs. (10)–(12). The parameters used here were: $C_v^0=1\times10^{16}$ cm^{-3}, $C_i^0=3\times10^{15}$ cm^{-3}, $K_1=2\times10^{-19}$ cm^3/sec, $t_0=0$ sec, $t_1=10$ sec, $t_2=10^2$ sec, $t_3=5\times10^2$ sec, $t_4=10^3$ sec, $t_5=2\times10^3$ sec, $t_6=4\times10^3$ sec, $t_7=6\times10^3$ sec, $t_8=10^4$ sec.

[15] H. Widmer, Phys. Rev. **125**, 30 (1962).

[16] A. G. Tweet, J. Appl. Phys. **30**, 2002 (1959).

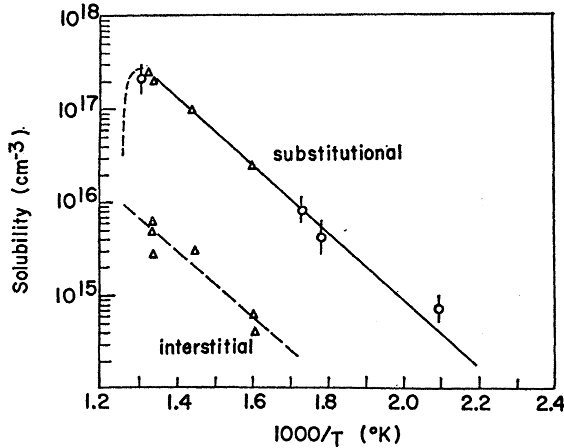

FIG. 11. Solubility of substitutional and interstitial Cu in InSb vs reciprocal temperature. Data were obtained by the radiotracer technique (triangles) as well as the sheet resistance technique and were confirmed by Hall measurements. The activation energy is 0.76±0.06 eV.

by an exponential dependence

$$C(x)=C_s \exp(-x/L). \tag{6}$$

This point is further discussed below.

Consider now the model of interstitial Cu interacting with vacancies as described by Eq. (2). For the present, we are not concerned with the detailed nature of the vacancy complexes. We simply assume that there is a density $C_v{}^0$ in the bulk of the crystal, ready to interact with interstitial Cu. The equations for the rate of change for the three components are

$$\frac{\partial C_i}{\partial t}=D_i\frac{\partial^2 C_i}{\partial x^2}-K_1C_iC_v+K_2C_s, \tag{7}$$

$$\frac{\partial C_s}{\partial t}=D_s\frac{\partial^2 C_s}{\partial x^2}+K_1C_iC_v-K_2C_s, \tag{8}$$

$$\frac{\partial C_v}{\partial t}=D_v\frac{\partial^2 C_v}{\partial x^2}-K_1C_iC_v+K_2C_s, \tag{9}$$

where C_i is the concentration of interstitial Cu; C_s is the concentration of substitutional Cu; C_v is the concentration of vacancies; D_i, D_s, D_v are respective diffusion coefficients; and $K_1C_iC_v$ is the number of interstitial copper atoms reacting with vacancies per sec, on which K_1 is the second-order rate constant. K_2C_s is the number of reverse processes with generation of one interstitial Cu-atom and a vacancy.

We now make the following simplifying assumptions:

(1) $D_s=0$, substitutional diffusion negligible. As pointed out earlier, D_s is likely to be of the same order as the self-diffusion coefficient in InSb.

(2) $D_v=0$, diffusion of vacancies negligible. From the dissociative mechanism we estimate the diffusion coefficient of vacancies to be 1 to 2 orders of magnitude lower than the one in question.

(3) $K_2=0$, the number of reverse processes is assumed to be relatively small. Under these conditions, Eqs. (7)–(9) can be written as

$$\frac{\partial C_i}{\partial t}=D_i\frac{\partial^2 C_i}{\partial x^2}-K_1C_iC_v, \tag{10}$$

$$\partial C_s/\partial t=K_1C_iC_v, \tag{11}$$

$$\partial C_v/\partial t=-K_1C_iC_v. \tag{12}$$

Experiment indicates that the time rate of change of interstitial Cu is small. Under this further assumption an approximate integral of Eqs. (10)–(12) can be obtained:

$$\begin{aligned} C_i(x,t)&\cong C_i{}^0 \exp(-x/L),\\ L&=\left(\frac{D_i}{K_1\cdot C_v(x,t)}\right)^{1/2},\\ C_s(x,t)&=C_v{}^0\{1-\exp[-(K_1\cdot C_i(x,t)\cdot t)]\},\\ C_v(x,t)&=C_v{}^0 \exp[-(K_1\cdot C_i(x,t)\cdot t)]. \end{aligned} \tag{13}$$

L in Eq. (13) has the dimensions of a diffusion length and is proportional to $C_v{}^{-1/2}$. This is certainly a reasonable result and is in agreement with the variety of exponential slopes obtained for substitutional Cu. Equations (10)–(12) can be integrated numerically, if appropriate boundary conditions are provided. Results for the x dependence with time as a parameter are shown in Figs. 9 and 10 for the concentration of interstitial and substitutional Cu, respectively. An exponential dependence of the form (6) was chosen as the boundary condition at $t=0$. The variation of the concentration of substitutional Cu with time and distance is markedly different from what one is used to expect from a "well-behaved" diffusion process. Comparison of Fig. 10 with Figs. 5 and 6 shows that the agreement of our model with experiment is quite good, even quantitatively. The only discrepancy seems to be the concentration of interstitial Cu found to be practically constant throughout the sample, actually increasing slightly with greater depths. As pointed out above, this might be due to an out-diffusion during the cooling cycle. It was also found that, for a numerical fit, the value of D_i had to be chosen lower than the one indicated by Fig. 2.

In deriving Eqs. (7) to (13), we assumed the vacancies to be single chemical quantities. It is more likely, however, that they occur in vacancy aggregates, e.g., divacancies. The hypothesis of divacancies is necessary to explain the fact that the crystal can be freed from vacancies by a low-temperature heat treatment (see below). A more sophisticated model of the process should take into account the detailed mechanism of interaction of interstitial Cu with vacancy aggregates.

The mathematics of such a model involving both macroscopic and microscopic diffusion (diffusion-limited reaction) becomes more formidable. Considering all the approximations made in the model described by Eqs. (10)–(12), the agreement with experiment is rather surprising. Our interpretation of the experiments with annealed and unannealed crystals implies that it is possible to free the crystal from vacancies by a low-temperature heat treatment. The diffusion coefficient of single In-vacancies calculated in the next paragraph is several orders of magnitude too low to explain the out-diffusion of such vacancies. We, therefore, postulate the existence of divacancies, consisting of a negatively charged vacant In-site and a neighboring positively charged vacant Sb site. Such a divacancy is likely to behave similarly to an electrically neutral impurity in the lattice. The diffusion of a neutral divacancy is expected to be faster than that of charged single vacancies.

Theoretical considerations[17,18] of the probability of vacancy-vacancy pairing on the basis of lattice strain energy predict repulsion rather than attraction of vacancies in covalent crystals. The binding in the III–V compounds, though, also has a considerable portion of ionic binding, which would make the existence of divacancies more plausible.

D. Diffusion Due to Reaction of Interstitial Copper with Vacancies Supplied through Dislocations

Dislocations may act in two ways as supply media for vacancies: (A) as vacancy sinks, trapping the vacancies produced during growth of the crystal; (B) as transport medium for fast diffusion of vacancies from the surface along dislocations ("vacancy pipes"). We neglect possible precipitation of Cu along dislocations, since such precipitated Cu would be electrically inactive.

Both properties of dislocations (we are considering edge dislocations only) substantiate the assumption that the vacancy supply is proportional to the number of dislocations N_D. Figure 1 indicates that the effective diffusion coefficient increases even more steeply with increasing dislocation density than a proportional relation.

If the dislocation density is high enough to supply enough vacancies to react with interstitial Cu, a further increase in dislocation density will not accelerate the diffusion.

From Fig. 1 it seems that this point is reached at a dislocation density of 10^6 cm^{-2}. The corresponding diffusion coefficient is approximately 10^{-7} cm^2/sec. Both mechanisms proposed for the action of the dislocations allow estimates for this upper limit of the diffusion coefficient. If the dislocations act solely as vacancy sinks, and if we suppose that the interstitial C_i and substitutional C_s concentrations maintain equilibrium in the ratio of their solubilities C_i^0/C_s^0, the diffusion coefficient will be given by the interstitial diffusivity times the fraction of time C_i^0/C_s^0 the copper atoms stay in their state of high diffusivity.[14]

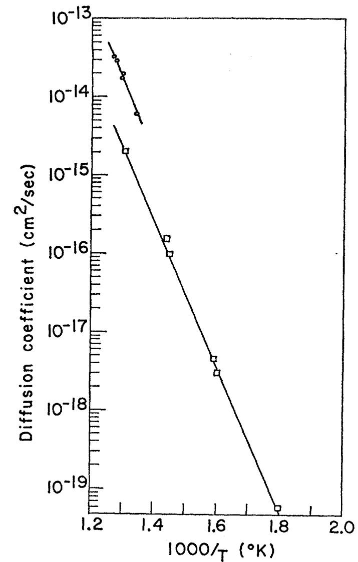

FIG. 12 Self-diffusion coefficient of In in InSb vs reciprocal temperature. Circles represent measurements by Eisen and Birchenall (reference 9). Squares represent points calculated from our measurements of the dissociative diffusion coefficient of Cu in InSb according to Eq. (5).

$$D_{\text{eff}}=D_i\frac{C_i^0}{C_s^0+C_i^0}\cong D_i\frac{C_i^0}{C_s^0}.$$

The interstitial diffusivity has been measured at approximately 10^{-5} cm^2/sec; the ratio of solubilities is 50–100 as determined in Fig. 11.

If the dislocations act as "vacancy pipes" only, the limiting factor will be the diffusion coefficient of vacancies D_v^d along dislocations. We shall estimate the diffusion coefficient D_v in dislocation-free crystal, to be approximately 1×10^{-10} cm^2/sec at 350°C. To explain our results, the transportation of vacancies along dislocations would have to be much faster.

As previously mentioned, it has not been possible to alter substantially the diffusion of Cu into dislocation-containing crystals by heat treatment prior to diffusion. This is an argument for the second mechanism without excluding the action of the dislocations as vacancy sinks. However, it is also possible that the binding energy of vacancies to dislocations is relatively high, and that low-temperature annealing (100–200°C) does not dissolve vacancy aggregates bound to dislocations.

V. SOLUBILITY OF Cu IN InSb

The solubility of substitutional Cu was determined from the surface concentration of the dissociative diffusion from both radiotracer and sheet resistance techniques. It follows the relation (Fig. 11)

$$C_s^0(T)=C_s^0(\infty)\exp(-\Delta E/kT), \quad (15)$$

[17] A. Uhlir, Bell System Tech. J. **34**, 105 (1955).
[18] R. L. Longini and R. F. Greene, Phys. Rev. **102**, 992 (1956).

with $C_s^0(\infty)=(1.5\pm1)\times10^{22}$ cm^{-3} and $\Delta E=0.76\pm0.06$ [eV].

The solubilities for interstitial Cu in Fig. 11 are the average concentrations of electrically inactive Cu found throughout the crystals in radiotracer experiments. The possibility that part of this concentration was actually precipitated (or some other form of electrically inactive Cu) rather than interstitial Cu cannot be excluded and might explain the wider scatter in these data. In any event, the solubility of interstitial Cu is at least 50 times lower than that of substitutional Cu.

VI. AN ESTIMATE OF THE VACANCY CONCENTRATION AND THE DIFFUSION COEFFICIENT OF VACANCIES

Cu diffusion into almost dislocation-free InSb crystals with a diffusion coefficient larger than the dissociative mechanism is interpreted, in this paper, to be due to vacancies trapped in the crystal during growth. Accordingly, the acceptor concentration in Cu diffused, dislocation-free InSb is equal to the number of vacancies incorporated during growth.

Tweet[16] has successfully used such a Cu labeling technique for the determination of the vacancy content of dislocation-free Ge with very reasonable results. As Tweet observed in Ge, we noted that slices cut from the top of the InSb crystal have a lower vacancy content than those cut from the bottom of the crystals. The slices cut from the top of the crystal usually show a slower diffusion coefficient than those from the bottom. This can be explained as due to the heat treatment the upper part of the crystal gets during growth, while the bottom is usually pulled out rapidly from the melt and quenched.

The concentration corresponding to the diffusion due to generation of vacancies in the bulk (second branch in Figs. 4–6) varied between 2×10^{15} and 1×10^{16} cm^{-3}. Hall measurements also showed carrier concentrations in this range. These samples were diffused long enough to allow all vacancies in the bulk of the crystal to react with the interstitial Cu. A surface layer thicker than the one corresponding to the penetration of Cu due to vacancies in diffusing from the surface was lapped off, and resistivity and Hall coefficient measured at liquid-nitrogen temperature. The acceptor concentration was independent of the diffusion temperature in the range 400–500°C and lies well below the substitutional solubility. If our interpretation is correct, the equilibrium vacancy concentration at the melting point is approximately equal to the maximum acceptor Cu concentration measured 1.0×10^{16} cm^{-3}. This corresponds to an activation energy of $\Delta E=1.02$ eV. The equilibrium vacancy concentration at any temperature is, therefore, estimated to be:

$$C_v^0=1.5\times10^{22}\exp(-1.02/kT). \tag{16}$$

We have considered only In vacancies here, assuming that the concentration of In vacancies at infinite temperature is equal to the total In concentration. We also can make an estimate of the diffusion coefficient of vacancies from Eq. (5):

$$D_v(T)=D_d(T)\frac{C_s^0(T)}{C_v^0(T)}. \tag{17}$$

Thus,

$$D_v=5\times10^{-4}\exp(-0.82/kT). \tag{18}$$

At 500°C, D_v is calculated from our data to be $D_v=3.7\times10^{-9}$ cm^2/sec; at 400°C, $D_v=4.7\times10^{-10}$ cm^2/sec. Based on Eisen and Birchenall's[9] values, the diffusion coefficients would be approximately one order of magnitude larger. The activation energy of the self-diffusion 1.84 ± 0.14 eV is divided into the energy required for the jump of an In atom into a vacant neighbor in the In sublattice, $E\cong0.82\pm24$ eV, plus the activation energy for formation of a vacancy, 1.02 eV.

VII. ELECTRICAL PROPERTIES OF Cu IN InSb

Cu behaves as an acceptor in InSb similar to its behavior in Ge and Si. According to Carlson and Collins,[19] copper shows a donor level in Si which is attributed to the interstitial state. As previously brought out, samples containing four times more Cu than initial donors showed no change in resistivity. We are not able to decide whether interstitial copper is electrically inactive or if this copper has precipitated during the cooling cycle. Hall measurements vs temperature of Cu-doped InSb vs temperature revealed an acceptor level at 0.023 eV in agreement with the results of Engeler.[20] Engeler also determined a second acceptor level at 0.056 eV. This second acceptor level was not seen in our measurements because the first acceptor level was not compensated by donor impurities in our samples. From an analysis of the Fermi-Dirac statistics it can be shown that indeed one cannot observe a temperature dependence corresponding to the second acceptor level unless the first acceptor level is compensated by donors.

It remains to be shown how the actual Cu concentration was deduced from resistivity measurements. From Fermi-Dirac statistics, applied to the problem of N acceptor levels at 0.023 and 0.056 eV and a negligible amount of donors, it turns out that the concentration of free holes is within a few percent equal to N in the range $N=10^{14}$ to 3×10^{15} cm^{-3} (at liquid-nitrogen temperature). In this range, in which most measurements were made, the free hole concentration determined from Hall measurements was simply equated to the total acceptor Cu concentration. The resistivity was determined simultaneously with the Hall coefficient. It was found experimentally that there was a well-defined re-

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lationship with very little spread between them and, therefore, the total Cu concentration could be directly deduced from resistivity measurements. At Cu concentrations higher than 3×10^{15} cm^{-3}, the free hole concentration is lower than the Cu concentration, and corrections based on Fermi-Dirac statistics had to be made. This admittedly introduces a higher experimental error for higher Cu concentrations, but there is no better method to deduce acceptor concentration from electrical measurements in this case.

VIII. CONCLUSION

We have demonstrated that Cu has interstitial as well as substitutional properties in InSb. If the crystal is originally free from vacancies, the in-diffusion of vacancies from the surface is the rate-limiting factor ("dissociative diffusion"). Good agreement with measurements of the self-diffusion is obtained from the dissociative process. If vacancies are already present in the bulk of the crystal, the reaction of interstitial Cu with vacancies (probably vacancy aggregates, e.g., divacancies) is the rate limiting factor. It is possible to free InSb crystals from vacancies inherited during growth by a low temperature heat treatment. The concept of fast diffusing divacancies has been introduced to explain the latter effect.

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Low-Temperature Coloration in KCl and KBr near the Fundamental Edge

CLIFFORD C. KLICK AND DAVID A. PATTERSON
U. S. Naval Research Laboratory, Washington, D. C.
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Crystals of KCl and KBr have been cooled with liquid helium, x rayed, and investigated for coloration near their fundamental absorption edge. Three bands are seen in both materials with the largest band closest to the fundamental edge. In KBr the first band is broad and peaks at 2300 Å, the second is the α band at 2020 Å, and the third, called the γ band, is at 1895 Å. The areas of the three bands with respect to the F band are, respectively, 1:8:20. In KCl similar bands are found at 1940 Å, 1790 Å, and 1640 Å. The areas are, respectively, 1:6:16 as large as the F band. The α and γ bands are also found in KBr:H on bleaching in the U band, and the α and γ bands have similar bleaching rates on warming. It is concluded that the γ band arises when an exciton is created at a slightly larger distance from the negative-ion vacancy than is the case for the α band. It is proposed that the centers responsible for the first band, the α and γ bands, and the F and H bands all are formed from the creation of Frenkel defects but differ in the distance of separation of the interstitial and vacancy and in the resulting ability to trap electrons and holes. With this assumption the x-ray energy dissipated in producing a Frenkel defect is 240 eV for KBr and 450 eV for KCl using 50-kV x rays.

I. INTRODUCTION

TWO absorption bands near the fundamental absorption edge in alkali halides were first observed by Delbecq, Pringsheim, and Yuster[1] in KI. The longer wavelength band was called the α band and was associated with negative-ion vacancies; the shorter wavelength band was called the β band and was associated with F centers. It was proposed that the absorptions correspond to fundamental absorption transitions perturbed by the presence of the defects. Similar results have also been found for KBr, NaBr, NaF, NaCl, and KCl.[2–9]

Calculations have been made to test these proposed models of the α and β bands. In all cases, it has been assumed that the fundamental absorption band arises from the creation of excitons. The problem then is to calculate the properties of excitons perturbed by nearby negative-ion vacancies or F centers. Oscillator strengths for the transitions have been computed by Dexter[10] and by Fuchs.[11] The shift of the α and β bands from the first exciton band has been computed by Bassani and

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