

FIG. 4. Chemical etching pattern near the same boundary as shown in Fig. 3 ( $\times 320$ ).

Fig. 3. It may be concluded that the edge dislocations in the (110) grain have not contributed to the formation of silver particles.

The density of dislocations in well annealed AgCl has been found to be  $10^6$  or  $10^7$  per  $\text{cm}^2$  in our experiments.

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<sup>1</sup> J. R. Haynes and W. Shockley, Phys. Rev. **82**, 935 (1951); F. C. Brown, Phys. Rev. **97**, 355 (1955).

<sup>2</sup> F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

<sup>3</sup> J. M. Hedges and J. W. Mitchell, Phil. Mag. **44**, 223, 357 (1953).

<sup>4</sup> The surface of the crystals grown from the melt was usually parallel to (100) or (110). The crystals with (111) surface were prepared under special conditions of crystal growth.

<sup>5</sup> Etching was carried out for a few minutes by the FF-H photographic fixer (Fuji Photo Film Company, Ltd., Kanagawa, Japan).

## Thermoelectric Power of Indium Antimonide

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THE thermoelectric power of single crystals of InSb has been measured on two samples between 60 and 400°K. The four-probe method used for the determination of this quantity has been described in recent years by several authors.<sup>1-3</sup> The Hall coefficient and resistivity of the specimen were also determined. One sample appeared to be *p*-type and had an effective impurity concentration of  $6.7 \times 10^{15}$  per cc; the hole mobility at 80°K was 3300  $\text{cm}^2/\text{volt-sec}$ . The other sample showed electron conduction; its carrier concentration at low temperature (80°K) was  $7 \times 10^{15}$  per cc, and the electron mobility  $10^5$   $\text{cm}^2/\text{volt-sec}$ .

Figure 1 shows the thermoelectric power  $Q$  as a function of temperature. In the intrinsic range this quantity

can be described by the following formula<sup>4</sup>:

$$Q = -\frac{k}{e} \left[ \frac{b-1}{b+1} \left( \frac{E_G}{2kT} + 2 \right) + \frac{3}{4} \ln \frac{m_1^*}{m_2^*} \right], \quad (1)$$

where  $k$  = Boltzmann constant,  $b$  = mobility ratio,  $E_G$  = energy gap at  $T^\circ\text{K}$ , and  $m_1^*$ ,  $m_2^*$  = effective masses of electrons and holes respectively. Taking  $b = 35$  and  $E_G$  (at 300°K) = 0.16 eV,<sup>5</sup> we find  $m_1^*/m_2^* = 0.11$ .

Calculations of the thermoelectric power in the impurity range, when lattice scattering is predominant, yields the following result<sup>4</sup>:

$$Q = \pm \frac{k}{e} \left[ 2 - \ln \frac{n_{1,2} h^3}{2(2\pi m_{1,2}^* kT)^{3/2}} \right], \quad (2)$$

where  $n_{1,2}$  = number of free carriers (electrons or holes); the plus or minus sign refers to *p*- or *n*-type respectively. At low temperatures one has to consider the increased influence of impurity scattering which will change the expression (2) slightly. For reasons explained below, only the results for the *n*-type sample between 100 and 200°K can be compared with theoretical predictions. Calculation of the effective mass of the electron at temperatures between 160 and 200°K yields consistently the value  $m_1^* = 0.014 m_e$ . Combining this value with the above-mentioned result for the ratio  $m_1^*/m_2^*$ , one obtains an effective hole mass  $m_2^* = 0.13 m_e$ . These values are in reasonable agreement with results from microwave measurements.<sup>6</sup>

An interesting feature of the thermoelectric power of InSb is the fact that the "phonon-drag" effect<sup>3,7</sup> is observed in *p*-type but not in *n*-type samples. The steep rise of the thermoelectric power of the *p*-type sample below 150°K illustrates this point. (The rather high degeneracy temperature for the *n*-type sample—about 90°K—is a complicating factor.) The contribu-

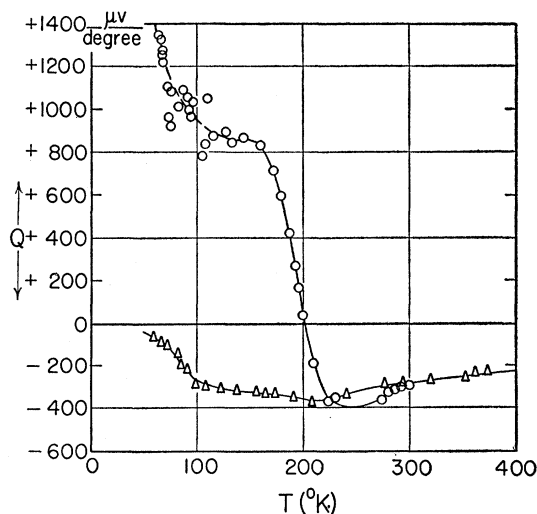


FIG. 1. Thermoelectric power of InSb.  $\circ$  *p*-type;  $\triangle$  *n*-type.

tion to the thermoelectric power due to electron-phonon interaction is proportional to  $l_{\phi}'/l_{e\phi}$ ;<sup>3</sup> the numerator  $l_{\phi}'$  represents the mean free path of those phonons which interact with electrons, while  $l_{e\phi}$  is the free carrier mean free path determined by collisions with phonons. From the mobilities one calculates that  $l_{e\phi}$  at 150°K is  $5 \times 10^{-6}$  cm for holes and  $6 \times 10^{-5}$  cm for electrons. The average mean free path of all the phonons can be evaluated from thermal conductivity data<sup>8</sup>; assuming that the mean free path for long wavelength phonons is about 10 times larger, one finds for  $l_{\phi}'$  a value of  $10^{-5}$  to  $10^{-4}$  cm. Calculation then shows that the phonon-hole interaction yields already a measurable contribution to the thermoelectric power at 150°K, while that due to the phonon-electron interaction is quite negligible.

*Note added in proof.*—The values for the effective masses have been calculated taking the proper correction for impurity scattering into account.

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## Electron Spin Resonance of $V_1$ -Centers\*

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THE electron spin resonance of the  $F$ -center (electron bound to a negative ion vacancy) has been investigated extensively in the past.<sup>1</sup> The hyperfine splitting has not been resolved. This suggests that the electron interacts with the magnetic moments of many nuclei and consequently that its wave function is distributed over many ions near the vacancy. The present work indicates that the electronic structure of the supposed antimorph of the  $F$ -center, the  $V_1$ -center (hole bound to a positive ion vacancy<sup>2</sup>), is entirely different. A large resolvable hyperfine splitting has been observed in the  $V_1$ -center resonance. The pattern per-

TABLE I.  $g$ -factors of the different families in the KCl spectra. Limit of error  $\pm 0.001$ . The calculated  $g$ -factors are based on  $g_{\perp} = 2.042$  and  $g_{\parallel} = 2.0023$ .

Field direction	$\theta = 45^\circ, 35^\circ$ and $60^\circ$			$\theta = 90^\circ$ Exp.	$\theta = 0^\circ$ Exp.
	Exp.	Calc.	$\theta$		
(100)	2.024	2.022	$45^\circ$	2.042	...
(111)	2.015	2.015	$35^\circ$	2.042	...
(110)	2.032	2.032	$60^\circ$	2.042	2.002 $g_{\parallel}$

TABLE II. Average spacing in gauss between the groups in the different families of the KCl spectra. Limit of error  $\pm 0.5$  gauss.

Field direction	$\theta = 45^\circ, 35^\circ$ , and $60^\circ$			$\theta = 90^\circ$	$\theta = 0^\circ$
	$\theta$				
(100)	69.6	$45^\circ$	10.5	...	
(111)	83.0	$35^\circ$	10.0	...	
(110)	54.2	$60^\circ$	10.0	102.0	

mits a detailed analysis of the electronic structure of this center and we have concluded that the hole is localized on but two negative ions.

KCl, NaCl, KBr, and LiF single crystals were placed in a resonant cavity and irradiated with x-rays at  $-180^\circ\text{C}$ . Then, without warming the crystal, we investigated the magnetic resonance spectrum with a high sensitivity resonance spectrometer operating at about 9300 Mc/sec. A modulation of the dc magnetic field of 0.1 to 1.0 gauss was used. The crystals were then warmed to a selected temperature and cooled again to  $-180^\circ\text{C}$ . Upon remeasurement of the spectrum it was found that all lines had faded in the same proportion. This indicates that every spectrum is essentially due to a single kind of trap. The temperature region in which fast fading occurs coincides in the case of KCl and KBr with the temperature region in which the  $V_1$ -band bleaches.<sup>3</sup> In NaCl, fast fading occurs between  $-140^\circ\text{C}$  and  $-120^\circ\text{C}$ , in LiF between  $-160^\circ\text{C}$  and  $-140^\circ\text{C}$ . No optical data are available for these two substances.

The resonance spectra depend very sensitively upon the orientation of the crystals in the magnetic field. The cases  $H \parallel (100)$ ,  $H \parallel (111)$  and  $H \parallel (110)$  have been investigated. In the case of KCl the spectra can be decomposed into families of lines, each family consisting of seven almost equally spaced groups. The integrated intensity ratio of the groups is 1:2:3:4:3:2:1. The number of families is 2 for  $H \parallel (100)$  and  $H \parallel (111)$ , and 3 for  $H \parallel (110)$ . The  $g$ -factors corresponding to the center lines of the families are larger than the free-electron value except in the case of one of the families in the  $H \parallel (110)$  pattern, for which  $g$  is equal to the free-electron value within experimental error. As the nuclear spin of Cl is  $\frac{3}{2}$ , the number of the groups (7) and their intensity ratio indicates that the hole spends its time near two halogens only, i.e., the  $V_1$ -center is essentially a  $\text{Cl}_2^-$  molecule-ion which is presumably near a positive-ion vacancy. The observed splitting agrees satisfactorily with the theoretical splitting calculated under the assumption of dipolar interaction by using Sternheimer's<sup>4</sup>  $\langle 1/r^3 \rangle$  values of the halogen  $p$ -functions. The  $g$ -shifts as well as the splittings can be explained quantitatively if we assume axially symmetric  $\text{Cl}_2^-$  molecule-ions oriented in the (110) directions. The distribution over the six different (110) directions is statistical. Tables I and II show as an example the main resonance data for KCl.