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Thermoelectric Power of the Non-Polar Semiconductor, That of Tellurium Crystals as an Example*

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Synopsis

In order to explicate the experimental results on the thermoelectric power of the crystals of pure tellurium and those alloyed with antimony less than 5 per cent, the thermoelectric power of the non-polar composite semiconductor in general has been derived as follows,

$$\frac{d\Theta}{dT}=\frac{k}{|e|}\left\{\left(2+\frac{\varDelta E(0)}{2kT}\right)\cdot\tanh\left(\frac{\varDelta E(T)-2\phi}{2kT}-\frac{3}{4}\log\frac{m_e}{m_h}-\frac{1}{2}\log b\right)\right.$$
$$\left.-\frac{\varDelta E(T)-2\phi}{2kT}+\frac{\beta}{2k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right\},$$

where ϕ is the height of the electrochemical potential above the valence band, $\varDelta E(T)=\varDelta E(0)+\beta T$ is the width of forbidden band, m_e and m_h are effective masses of electrons and holes, b is the ratio of electron and hole mobilities and χ is the energy required to extract the electron at the top of the valence band to rest outside of the crystal. Numerical calculations carried out for tellurium crystals have shown that the measured characteristics can well be accounted for throughout the temperature range being studied. The quantitative discordance observed at higher temperatures has been explained by a more or less elaborated theory in which a dual band structure which consists of two overlapped energy bands is assumed for the conduction band, the same band scheme being compatible with other electric properties of tellurium.

I. Introduction

By virtue of the recent progress of the experimental and theoretical investigations on the electrical properties of silicon, germanium, selenium, tellurium and so forth, the systematic knowledge on the non-polar substances has been greatly developed. However, the generally recognized energy band scheme for these semiconductors is not fully justified by all of the electrical properties, nay more, certain experimental facts that are likely to suggest the roughness of this energy band model have been found. The thermoelectric power, in spite of its important nature, is one of the properties with which systematic investigations have not been fully performed. Such an investigation may be of very interest in order to check the appropriateness of the electronic energy band model now generally accepted for a semiconductor. The explanation of the measured characteristics of thermoelectric effect of tellurium crystals is carried out on the basis of the conduction mechanism worked out from the analysis of the experimental data of the resistivity and the Hall effect.

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II. General expression of the Seebeck effect of the non-polar semiconductor

The polarization wave inherent in the lattice vibration interferes essentially with the behaviour of conduction electrons in the ionic crystal, while in the case of a non-polar crystal it possesses no such a significant meaning, hence the interaction between the electrons and the lattice vibration is relatively small in comparison with the case of an ionic semiconductor. Therefore, the mean free path which is defined for conduction carriers by the usual way may have the physical significance and then we can carry out the calculation by solving the Boltzmann's equation written in terms of the mean free path integrals in the presence of the electric field and the temperature gradient in the crystal. Moreover, being the number of conducting carriers very scant as an essential feature of the semiconductor, the calculation is usually simplified by adopting the classical statistics to the carriers assemblage.

When an *isotropic* and *homogeneous* conductor having a single energy band which contains conduction particles of effective mass m carrying an electric current J under the coexistence of an electric field F and a temperature gradient $\partial T/\partial x$ in the x direction, the Boltzmann's equation becomes as follows,(1)

$$F=\frac{J}{|e|^2K_1}-\frac{kT}{|e|}\frac{\partial}{\partial x}\left(\frac{\zeta}{kT}\right)-\frac{K_2}{K_1|e|T}\frac{\partial T}{\partial x}, \tag{1}$$

where ζ is the electrochemical potential measured from the bottom of this energy band, η is the energy of conduction particles and K's are the following integrals involving the mean free path l.

$$K_s=-\frac{16\pi m}{3h^3}\int_0^{\infty}l(\eta)\eta^s\frac{\partial f_0}{\partial\eta}d\eta, \tag{2}$$

and

$$f_0=\frac{1}{1+\exp\left(\frac{\eta-\zeta}{kT}\right)}. \tag{3}$$

This equation devoid of generality is only applicable to the case of a single band conductor, that is, as for semiconductors, it is available for an extreme extrinsic semiconductor in which either the conduction band or the valence band alone participates in the conduction in consequence of a fairly wide forbidden band as well as a large density of either donors or acceptors. Generally the non-polar semiconductor has a relatively small forbidden band width as compared with an ionic semiconductor, its conduction should be considered to be due to both electrons and holes, at least a part of which are generated in pairs by excitations of electrons in the valence band to the conduction band over the forbidden band. In the present calculation, we consider a non-polar crystal having a secondary structure in both bands, namely either band consists of an overlapping of several bands, apexes of which are situated with small energy differences with each other.

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(1) R. H. Fowler, *Statistical Mechanics*, Cambridge, (1936), 411.

In such a crystal, each of all bands in concern should be treated individually and let us denote the energy of the extremity of ith band (the top for a valence band or the bottom for a conduction band) by E_i. It is measured with reference to the vacuum just outside the crystal* as the zero of energy. Let the Fermi level of the crystal similarly measured be ζ, the charge of a current carrier moving in the ith band be e_i, the effective mass be m_i, the mean free path be l_i and the current responsible for ith band be J_i, then Eq. (1) is extended as follows,

$$F=\sum_i \left\{ \frac{J_i}{|e_i|^2 K_{1i}} - \frac{kT}{|e_i|} \frac{\partial}{\partial x}\left(\frac{\zeta_i}{kT}\right) - \frac{K_{2i}}{K_{1i}|e_i|T} \frac{\partial T}{\partial x} \right\}, \tag{4}$$

where K_{si} is the mean free path integral represented by Eq. (2) in which m, l, ζ are replaced by m_i, l_i, ζ_i respectively. And ζ_i and ζ are related by

$$\zeta_i = \frac{e_i}{|e_i|}(E_i - \zeta). \tag{5}$$

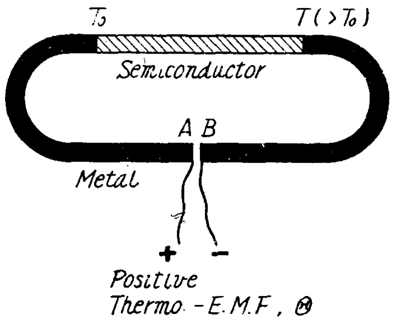

Fig. 1. Sign convention for the thermoelectric effect. The thermoelectromotive force Θ under the temperature difference, $T-T_0$, is defined as positive when the thermoelectric current flows from the hot to the cold junction in a semiconductor as shown in the figure.

When this semiconductor is connected with an ordinary metal to make a closed circuit, keeping the two junction points at different temperatures T_0 and $T\,(>T_0)$ a thermoelectric current is set up in this circuit. If one point of the circuit is cut off as in Fig. 1, a thermoelectric force Θ gives rise to between the open ends A and B which are kept at the same temperature, then the magnitude of Θ is found by integrating F along the circuit from A to B allowing no total current J to flow. I. e.,

$$\Theta = -\oint F(T)_{J=0}\,dx,$$

where x is the direction lying along the circuit, and the sign of Θ is taken positive when the thermoelectric current, if the circuit is closed, flows from the metal to the semiconductor at the hot junction. If the medium is isotropic, the component currents J_i's have no cancelling component in any direction, hence it follows that $J_i=0$ from $J=0$. Then from Eq. (4)

$$\begin{aligned}\Theta &= -\oint F_{J_i=0}\,dx \\ &= -\oint \frac{1}{\sum\limits_i e_i^2 K_{1i}} \sum_i \left(-\frac{e_i K_{1i}\zeta_i}{T}\frac{\partial T}{\partial x} + \frac{e_i K_{2i}}{T}\frac{\partial T}{\partial x} + \frac{e_i^2 K_{1i}}{|e_i|}\frac{\partial E_i}{\partial x} \right) dx - \left[\frac{1}{|e_i|}\zeta \right]_A^B \end{aligned} \tag{6}$$

ζ being a single valued function of T, the second term is zero. Therefore,

$$\begin{aligned}\Theta = &\left[\int_{T_0}^{T} \frac{1}{\sum\limits_i e_i^2 K_{1i}} \sum_i \left(-\frac{e_i K_{1i}\zeta_i}{T} + \frac{e_i K_{2i}}{T} + \frac{e_i^2 K_{1i}}{|e_i|}\frac{\partial E_i}{\partial T} \right) dT \right]_{\text{in semiconductor}} \\ &- \left[\qquad\qquad ” \qquad\qquad \right]_{\text{in metal}}. \end{aligned}$$

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* A position whose distance from the crystal surface must be remote far enough for justifying the defiance of the image force but be near compared with a macroscopic length.

Since the first term is usually very large in comparison with the second term, the latter can be ignored, i. e., the thermoelectric power of this circuit is approximately given by the absolute thermoelectric power of the semiconductor,* thus the following general expression is obtained.

$$\frac{d\Theta}{dT}=\frac{1}{\sum\limits_i e_i^2K_{1i}}\sum_i\left(-\frac{e_iK_{1i}\zeta_i}{T}+\frac{e_iK_{2i}}{T}+\frac{e_i^2K_{1i}}{|e_i|}\frac{\partial E_i}{\partial T}\right)_{\text{in semiconductor}}. \tag{7}$$

In order to proceed with the calculation, let us make the following assumptions that in each energy band (i) the assemblage of charge carriers obeys the classical statistics, and (ii) the mean free path does not depend on the energy of carriers.** The mean free path l_i and the mean free path integral K_{si} are obtained as follows, when the carrier density in the ith band is denoted by n_i per unit volume and the carrier mobility by μ_i,(3)

$$\left.\begin{aligned} l_i &=\frac{3}{4|e_i|}(2\pi m_ikT)^{1/2}\mu_i\,,\\ K_{si}&=\frac{4}{3}\,\frac{l_in_i}{(2\pi m_i)^{1/2}}(kT)^{s-3/2}S\,!=\frac{1}{|e_i|}(kT)^{s-1}S\,!\,n_i\mu_i\,,\end{aligned}\right\} \tag{8}$$

namely,

$$\left.\begin{aligned} K_{1i}&=\frac{1}{|e_i|}n_i\mu_i\,,\\ K_{2i}&=\frac{2}{|e_i|}n_i\mu_ikT\,.\end{aligned}\right\} \tag{9}$$

The carrier density follows from the assumption (i),

$$n_i=\frac{2(2\pi mk)^{3/2}}{h^3}\left(\frac{m_i}{m}\right)^{3/2}T^{3/2}\exp\left(\frac{\zeta_i}{kT}\right), \tag{10}$$

or

$$\frac{\zeta_i}{kT}=\log n_i-\log\frac{2(2\pi mk)^{3/2}}{h^3}-\frac{3}{2}\log T-\frac{3}{2}\log\frac{m_i}{m}\,, \tag{11}$$

where m is the free electron mass. From Eqs. (7), (9) and (11), we obtain the next formulae.

$$\frac{d\Theta}{dT}=\frac{k}{\sum\limits_i|e_i|n_i\mu_i}\sum_i\left(\frac{-e_i}{|e_i|}\frac{\zeta_i}{kT}+\frac{2e_i}{|e_i|}+\frac{1}{k}\frac{\partial E_i}{\partial T}\right)n_i\mu_i\,, \tag{12}$$

or

$$\begin{aligned}\frac{d\Theta}{dT}=\frac{k}{\sum\limits_i|e_i|n_i\mu_i}\sum_i\Bigg\{&\frac{e_i}{|e_i|}\left(2+\log\frac{2(2\pi mk)^{3/2}}{h^3}+\frac{3}{2}\log T\right.\\ &\left.-\log n_i+\frac{3}{2}\log\frac{m_i}{m}\right)+\frac{1}{k}\frac{\partial E_i}{\partial T}\Bigg\}n_i\mu_i\,.\end{aligned} \tag{13}$$

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* For instance, if copper is used as the metal, the absolute thermoelectric power of copper is 2.8 μV/degree at ice point, while the magnitude of thermoelectric power of a circuit coupled with a semiconductor is usually observed to amount to several tens or hundreds μV/degree.

** This assumption is valid for the case of the mean free path l_L determined from the lattice scattering when the most part of carriers distribute in a small energy range of the band,(2) but is incorrect for l_I due to the impurity scattering. For instance, as for the impurity ion scattering, l_I is proportional to the second power of the carrier energy.

(2) H. Fröhlich, *Elektronen Theorie der Metalle*, Berlin, (1936), 232.

(3) R. H. Fowler, *Statistical Mechanics*, Cambridge, (1936), 408.

III. Thermoelectric power of the normal two bands semiconductor

We apply the general expression above obtained to the more common semiconductor model which consists simply of two bands separated with a forbidden band as shown in Fig. 2,* and rewrite it in a more concrete form convenient for the comparison with the experimental results. By denoting the electron charge by e, the width of forbidden band by ΔE and the energy height from the top of valence band to the Fermi level by ϕ, we have

$$\left.\begin{aligned} &E_2=E_1+\Delta E, \\ &e_1=|e|, \quad e_2=-|e|, \\ &\zeta_1=E_1-\zeta=-\phi, \\ &\zeta_2=-(E_2-\zeta)=\phi-\Delta E. \end{aligned}\right\} \qquad (14)$$

Further let us take into account the temperature shift of the band structure, and assume approximately the linear dependence of ΔE on temperature,

$$\Delta E=\Delta E(0)+\beta T. \qquad (15)$$

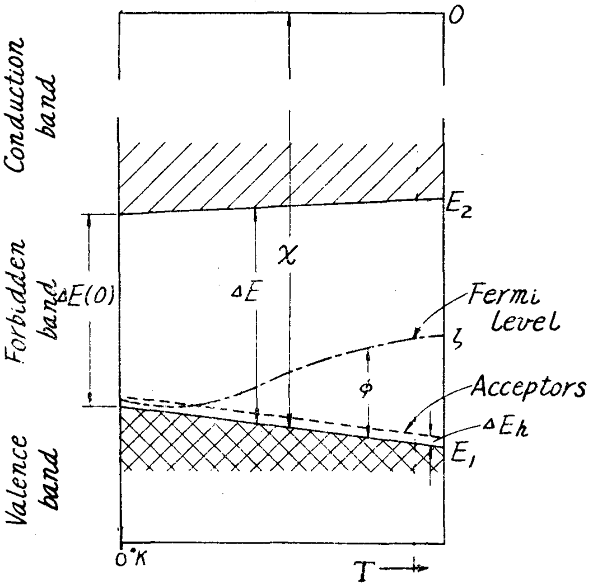

Fig. 2. The energy band model of a p-type composite semiconductor assuming approximate linear temperature variation of the width of forbidden band.

By putting Eqs. (14) and (15) into Eq. (13), the thermoelectric power of a composite semiconductor is given by the following expression.

$$\begin{aligned} \frac{d\Theta}{dT}&=\frac{k}{|e|}\ \frac{1}{n_h+n_eb}\left\{(n_h-n_eb)\left(2+\log\frac{2(2\pi mk)^{3/2}}{h^3}+\frac{3}{2}\log T\right)\right. \\ &\quad -n_h\left(\log n_h-\frac{3}{2}\log\frac{m_h}{m}\right)+n_eb\left(\log n_e-\frac{3}{2}\log\frac{m_e}{m}\right)+\Delta \\ &=1.970\times10^2\frac{1}{n_h+n_eb}\left\{(n_h+n_eb)\left(38.12+\frac{3}{2}\log T\right)\right. \\ &\quad -n_h\left(\log n_h-\frac{3}{2}\log\frac{m_h}{m}\right)+n_eb\left(\log n_e-\frac{3}{2}\log\frac{m_e}{m}\right)+\Delta, \ \mu\text{V/deg} \end{aligned} \qquad (16)$$

$$\begin{aligned} \Delta&=\frac{k}{|e|}\left(\frac{n_eb}{n_h+n_eb}\ \frac{\beta}{k}-\frac{1}{k}\ \frac{\partial\chi}{\partial T}\right) \\ &=1.970\times10^2\left(\frac{n_eb}{n_h+n_eb}\ \frac{\beta}{k}-\frac{1}{k}\ \frac{\partial\chi}{\partial T}\right)\ \mu\text{V/deg}, \end{aligned} \qquad (17)$$

where

$$n_h=n_1,\ n_e=n_2,\ \mu_h=\mu_1,\ \mu_e=\mu_2,\ b\equiv\mu_e/\mu_h \text{ and } \chi=-E_1.$$

If the densities, the effective masses, the ratio of mobilities of electrons and holes and the correction term Δ accrued from the temperature effect on the band

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* Fig. 2 shows the case that acceptor impurity levels exist above the valence band, but the ensuing results are equally applicable to either case where the donor levels or both levels are present.

structure are known, we can calculate the thermoelectric power of the semiconductor at any temperature from the above equation. $\partial\chi/\partial T$ in Δ is deduced experimentally as the temperature coefficient of the photon energy corresponding to the longer threshold wave-length in the outer photoelectric effect, which is observed under necessary cares paid to the surface condition.(4)

In order to derive another expression of the same quantity, we set Eqs. (14) and (15) into Eq. (12),

$$\frac{d\Theta}{dT}=\frac{k}{|e|}\left\{\frac{n_h-n_e b}{n_h+n_e b}\left(2+\frac{\Delta E(T)}{2kT}\right)-\frac{\Delta E(T)-2\phi}{2kT}\right\}+\frac{k}{|e|}\left(\frac{n_e b}{n_h+n_e b}\frac{\beta}{k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right),$$

where

$$\frac{n_h-n_e b}{n_h+n_e b}=\frac{1-\exp\left(-\frac{\Delta E-2\phi}{kT}+\frac{3}{2}\log\frac{m_e}{m_h}+\log b\right)}{1+\exp\left(-\frac{\Delta E-2\phi}{kT}+\frac{3}{2}\log\frac{m_e}{m_h}+\log b\right)}$$

$$=\tanh\left(\frac{\Delta E-2\phi}{2kT}-\frac{3}{4}\log\frac{m_e}{m_h}-\frac{1}{2}\log b\right),$$

$$\frac{n_e b}{n_h+n_e b}=\frac{1}{2}\left\{1-\tanh\left(\frac{\Delta E-2\phi}{2kT}-\frac{3}{4}\log\frac{m_e}{m_h}-\frac{1}{2}\log b\right)\right\}.$$

Therefore,

$$\frac{d\Theta}{dT}=\frac{k}{|e|}\left\{\left(2+\frac{\Delta E(0)}{2kT}\right)\cdot\tanh\left(\frac{\Delta E(T)-2\phi}{2kT}-\frac{3}{4}\log\frac{m_e}{m_h}-\frac{1}{2}\log b\right)\right.$$
$$\left.-\frac{\Delta E(T)-2\phi}{2kT}+\frac{\beta}{2k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right\}^{*}. \qquad (18)$$

This equation is equivalent to Eq. (16) and is used in the case where the densities of electrons and holes are unknown. Thus we have arrived at the expression for a composite semiconductor in which electrons and holes both participate in the conduction. Next, let us simplify these formulae by applying them for some particular cases.

Extrinsic semiconductors: We consider the case of the conduction due to either electrons or holes alone, that is, the case of a crystal which contains predominantly either donors or acceptors and is kept at such low temperatures that the intrinsic excitation is hardly possible. For instance, taking a case where acceptors are predominant, $n_e=0$, therefore, by referring to Eq. (11), we may write,

$$\frac{d\Theta}{dT}=\frac{k}{|e|}\left(2+\frac{\phi}{kT}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right). \qquad (19)$$

The thermoelectric power for this case is more exactly derived directly from Eq. (7) by taking solely the valence band into account,

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(4) R. H. Fowler, E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge, (1934), 484.

* In the case where the mobilities of electrons and holes have to do with the lattice vibration alone, their ratio becomes $b=\frac{\mu_e}{\mu_h}=\left(\frac{m_e}{m_h}\right)^{-5/2}$ (5), then we can write simply in Eq. (18), $-\frac{3}{4}\log\frac{m_e}{m_h}-\frac{1}{2}\log b=\frac{1}{2}\log\frac{m_e}{m_h}$.

(5) F. Seitz, Phys. Rev. **73** (1948), 549.

$$\frac{d\Theta}{dT}=\frac{k}{|e|}\left(\frac{1}{kT}\frac{K_2}{K_1}+\frac{\phi}{kT}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right). \tag{20}$$

For the limiting case that the assumption (ii) holds, namely, the mean free path does not depend upon the kinetic energy of holes, $\frac{1}{kT}\cdot\frac{K_2}{K_1}$ becomes 2, then Eq. (20) is reduced to Eq. (19). Although the mean free path in a crystal envisaged here is generally subjected to both the lattice scattering and the impurity scattering and the latter factor becomes more and more important as the temperature decreases, thus the assumption (ii) in consequence is rather inadequate for this case, and exactly speaking, Eq. (20) should be used.*

Intrinsic semiconductors: In a crystal which contains no impurities, there are no carriers other than the same number of electrons and holes which have been generated through the direct excitation from the valence to the conduction band. Actually, this condition applies to a very pure crystal at relatively high temperatures. In this case n_h and n_e far surpass the impurity level density N; for instance, a crystal which has shown more or less p-type extrinsic conduction at low temperatures becomes intrinsic with temperature rise, namely, $n_e=n_h-N\fallingdotseq n_h$, in which case the electrochemical potential becomes**

$$\phi=\frac{\Delta E}{2}-\frac{3}{4}kT\log\frac{m_e}{m_h}. \tag{21}$$

Thereby Eq. (18) becomes,

$$\frac{d\Theta}{dT}=\frac{k}{|e|}\left\{\frac{1-b}{1+b}\left(2+\frac{\Delta E(0)}{2kT}\right)-\frac{3}{4}\log\frac{m_e}{m_h}+\frac{\beta}{2k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right\}. \tag{22}$$

IV. Numerical calculations on the tellurium crystals

In the preceding paper,(7) experiments were described in which the electric properties of tellurium crystals showed various degrees of p-type semiconduction by alloying different amounts of antimony as acceptor impurities, but the theoretical interpretation of the observed thermoelectric behaviours has been postponed. Now, we embark on the solution of this pending problem. Previously we determined the width of forbidden band under the influences of the thermal dilation and vibration of the lattice as follows,(8)

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* In this connection, the low temperature thermoelectric power of silicon specimens containing known impurities was calculated by Z. Yamashita and M. Watanabe.(6) According to this report, for instance, K_2/kTK_1 of the silicon specimen containing 0.002% boron takes a value of about 2 at room temperature, but increases as the temperature falls, reaching about 3 at 100°K. In tellurium specimens, the calculation on the basis of the approximation $K_2/kTK_1=2$ is unlikely to give such a large difference as above, as touched later.

** Cf., for instance, Fröhlich, l. c. p. 81, Eq. (24); we can also get Eq. (21) by putting $n_e=n_h$ in Eq. (26) referred to below.

(6) Z. Yamashita, M. Watanabe, Busseiron Kenkyû (in Japanese), No. 35 (1951), 40.

(7) T. Fukuroi, S. Tanuma, S. Tobisawa, Sci. Rep. RITU (A), 4 (1952), 283.

(8) T. Fukuroi, S. Tanuma, S. Tobisawa, Sci. Rep. RITU (A), 1 (1949), 373;
T. Fukuroi, Sci. Rep. RITU (A), 3 (1951), 175.

$$\Delta E(T)=0.34+1.7\times10^{-4}T\ \text{eV},^{*} \tag{23}$$

that is, in Eq. (15), $\Delta E(0)=0.34$ eV, $\beta=1.7\times10^{-4}$ eV/deg. Furthermore we estimated the effective masses of electrons and holes from the estimated value of the mobilities by means of the following relations deduced by Seitz(5) in the case where the mobility is tubject to the lattice scattering only.

$$\mu_h T^{3/2}=\left(\frac{m_h}{\alpha_h}\right)^{-5/2}, \qquad \mu_e T^{3/2}=\left(\frac{m_e}{\alpha_e}\right)^{-5/2}, \tag{24}$$

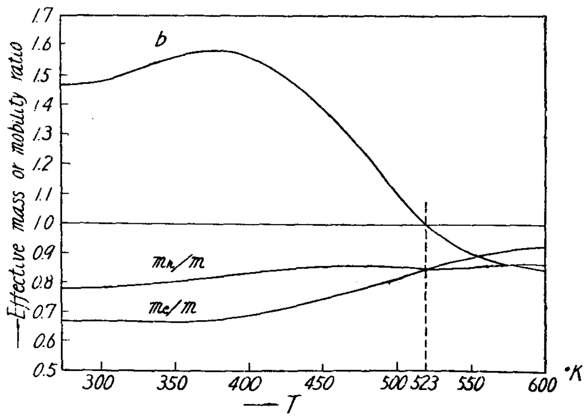

Fig. 3. The mean effective masses and the ratio of mobilities of electrons and holes, $\frac{m_e}{m_h}$, $\frac{m_h}{m}$ and $b\left(=\frac{\mu_e}{\mu_h}\right)$, in the intrinsic range.

where α_h or α_e is the quantities concerning the interaction between the phonons of lattice vibration and an electron in the conduction band or a hole in the valence band and these two factors would not be strictly equal, but, as they are difficult to be determined, are put equal throughout the course of calculation. Effective masses of electrons and holes obtained by this procedure are plotted in Fig. 3. These quantities m_e and m_h, m_e in particular, are apparently not constant over the temperature range under investigation, and even reverse their magnitude each other at 523°K. As for the origin of this variation of effective masses, we shall put forward a possible explanation in the last section, in which the conduction band of tellurium is not a single band but consists of two overlapping bands whose bottoms are located with a slightly different height from each other. As for the assumption $\alpha_h=\alpha_m$ used above, we cannot assign any theoretical basis for it. However, the theory of the variation of electronic energy bands due to the deformation of the crystal lattice developed by Bardeen and Shockley(10) gives a result that the energy shifts of the bottom of conduction band, $|E_{1c}|$, and the top of valence band, $|E_{1v}|$, due to the unit dilation of the lattice are equal if $\alpha_h=\alpha_e$ because of the relation $|E_{1c}|^2/|E_{1v}|^2=\alpha_h/\alpha_e$ derived from Eq. (3.8) in the literature (10) and Eq. (24) of this paper. In the case of silicon, if the mobilities of electrons and holes obtained by Pearson and Bardeen(11) and the values of effective masses $m_e/m=\frac{1}{1.5}$, $m_h/m=1$, assumed by them to make the most consistent analysis of the experiment, are used, we can evaluate that $|E_{1c}|/|E_{1v}|=1.07/11.3=0.95$ and $\alpha_h/\alpha_e=0.90$, so that α_h and α_e in silicon

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* S. Moss obtained from the experiment of photoconductivity the value of $\beta=2.0\times10^{-4}$ eV/deg(9) which accords well with our estimation that $\beta=\beta_1$ (lattice dilation) $+\beta_2$(lattice scattering) in which $\beta_1=+2.2\times10^{-4}$ and $\beta_2=-0.5\times10^{-4}$ eV/deg.

(9) S. Moss, Phys. Rev. **79** (1950), 1011.

(10) J. Bardeen, W. Shockley, Phys. Rev. **80** (1950), 72.

(11) G. L. Pearson, J. Bardeen, Phys. Rev. **75** (1949), 865.

are nearly equal. If this result is allowed to be extended to our case, the assumption $\alpha_h = \alpha_e$ would give rise to no serious error and it leads to $\frac{\partial E_1}{\partial T} \fallingdotseq -\frac{\partial E_2}{\partial T}$ from $|E_{1v}| \fallingdotseq |E_{1c}|$. Therefore, considering that $\frac{\partial E_2}{\partial T} = \frac{\partial E_1}{\partial T} + \beta$, Eq. (17), the correction term of the thermoelectric power, becomes

$$\Delta = -\frac{1}{2|e|}\frac{n_h - n_e b}{n_h + n_e b}\beta . \tag{25}$$

In this case, the quantity $\partial\chi/\partial T$ which is difficult to be evaluated has been eliminated.

The carrier densities are obtained from Eq. (10),

$$\left.\begin{aligned} n_h &= \frac{2(2\pi m_e kT)^{3/2}}{h^3}\exp\left(\frac{-\phi}{kT}\right), \\ n_e &= \frac{2(2\pi m_h kT)^{3/2}}{h^3}\exp\left(\frac{\phi - \Delta E}{kT}\right). \end{aligned}\right\} \tag{26}$$

The electron density excited to the acceptor levels which must be equal to $n_h - n_e$ is given as follows,

$$n_h - n_e = \frac{N}{1 + \exp\left(\frac{\Delta E_h - \phi}{kT}\right)}, \tag{27}$$

where N is the effective density of acceptor levels and ΔE_h is the excitation energy from the top of the valence band. Therefore the electrochemical potential ϕ is determined from the next equation, by specifying ΔE_h and N for a semiconductor provided the energy band structure is definitely known.

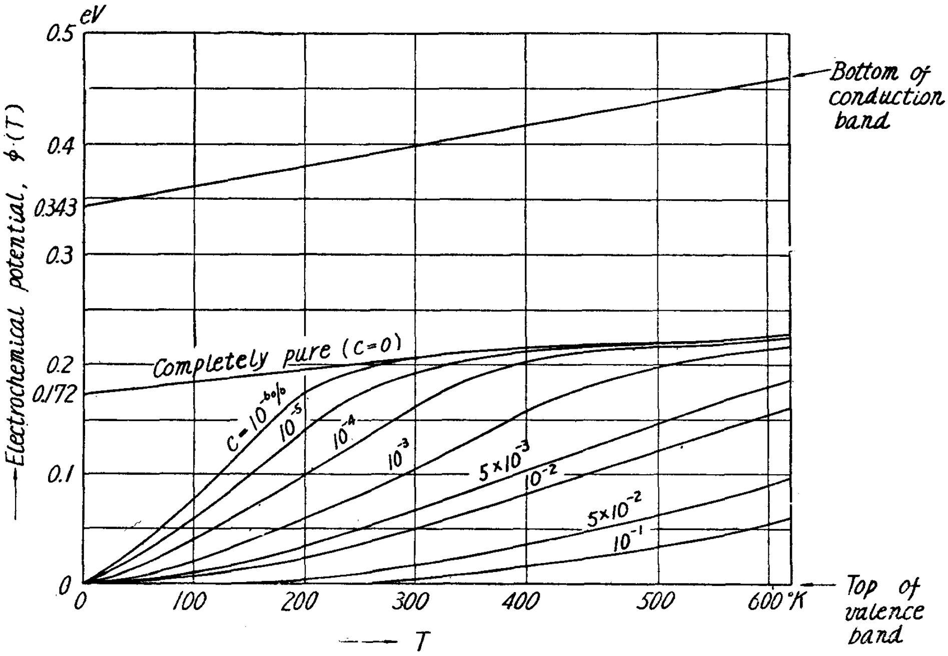

Fig. 4. The calculated values of the electrochemical potential, $\phi(T)$, of tellurium crystals containing various concentrations, atomic per cent C, of acceptor levels having approximately null excitation energy, i. e. $\Delta E_h = 0$. The width of forbidden band is taken as $\Delta E(T) = 0.34 + 1.9 \times 10^{-4} T$ eV and the magnitudes of effective masses are taken as shown in Fig. 3.

$$\left(\frac{m_e}{m}\right)^{3/2} e^{\frac{-\Delta E}{kT}} y^3 + \left\{\left(\frac{m_e}{m}\right)^{3/2} e^{\frac{-\Delta E+\Delta E_h}{kT}} + \frac{Nh^3}{2}(2\pi mkT)^{-3/2}\right\} y^2 - \left(\frac{m_h}{m}\right)^{3/2} y$$
$$-\left(\frac{m_h}{m}\right)^{3/2} e^{\frac{\Delta E_h}{kT}} = 0, \qquad (28)$$

where

$$y = e^{\frac{\phi}{kT}}.$$

In the case of antimony-doped tellurium, we found in the previous paper(7) that ΔE_h is too small to evaluate from the observed temperature dependence of the Hall coefficient above liquid air temperature, so it is allowed to accept it as zero in the present calculation unless one is concerned well below the liquid air temperature. And N is set equal to $2.97 \times 10^{22} \times 10^{-2} C$ where 2.97×10^{22} is the number of tellurium atoms in a unit volume of the crystal and C is the atomic per cent of the effective acceptor concentration. Thus, in Eq. (28), further by making use of the value ΔE in Eq.(23), and of m_e, m_h values in Fig. 3 for the range above room temperature and of those values at room temperature for the lower temperature range as they seem to be almost constant at low temperatures, we can evaluate numerically ϕ as a function of temperatures taking the impurity concentration C as a parameter and the results are plotted in Fig. 4. Furthermore, n_e and n_h are calculated by Eq. (26) using the ϕ values of Fig. 4 and shown in Fig. 5 in terms of the same parameter C. The chain line in Fig. 5 denotes the degeneracy temperature T_d of tellurium crystal pertaining to holes calculated from the next equation using the foregoing value of m_h/m.

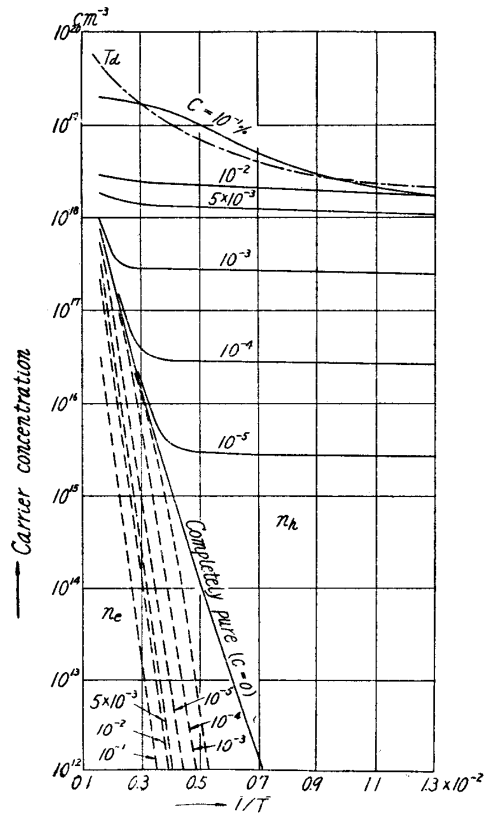

Fig. 5. The calculated carrier concentrations as a function of temperature with respect to various acceptor concentrations. The parameter C means the acceptor concentration in atomic per cent. The full and the dashed lines represent the concentrations of electrons and holes, n_e and n_h, respectively. As to an absolutely pure crystal viz. $C=0$, curves of n_e and n_h coalesce to a line. The chain line borders the degeneracy temperature, below this line the approximation of classical statistics is applicable.

$$T_d = \frac{h^2}{8m_h k}\left(\frac{3}{\pi}\right)^{2/3} n_h^{2/3} = 4.2 \times 10^{-11}\left(\frac{m_h}{m}\right)^{-1} n_h^{2/3}. \qquad (29)$$

Fig. 5 indicates that the classical statistics holds true for the carriers assemblage, provided the impurity concentration $C \leqq 0.05\%$. As for $b(=\mu_e/\mu_h)$, the values of μ_h and μ_e are obtained by analysing the data in intrinsic range or those above room temperature, so it is justifiable only when the effect of lattice scattering is preponderant to that of impurity scattering, and it is not legitimate to use this value of b towards the tellurium crystals containing an appreciable amount of antimony. On the other hand, provided that the impurity scattering overpowers the lattice scattering, the extrinsic conduction prevails and the general expression for the thermoelectric power, Eq. (16), is superseded by Eq. (19) which does not involve b. Then the value of b is less important for the nearly extrinsic condition, so that the value referred to above may be used without appreciable error irrespective of the impurity concentration C. Thus having been known all characterizing quantities, n_h, n_e, m_h, m_e, β and b, it is possible to calculate the thermoelectric power as a function of temperatures corresponding to various acceptor concentrations by means of Eqs. (16) and (25). The result of numerical calculations is shown in Fig. 6. The dashed low temperature parts of the curves designate the uncertain portions resulted from the approximate treatment $\Delta E_h=0$, and if any finite value is assigned to ΔE_h the thermoelectric power at the lowest temperature range should indicate an increasing tendency with decreasing temperature as expected from Eq. (19). For instance, in an extrinsic case of $\Delta E_h=0.001$ eV, $\frac{\partial\chi}{dT}=\frac{\beta}{2}$ and $\phi=\frac{\Delta E_h}{2}+\frac{kT}{2}\log\frac{\nu_h}{N}$ where $\nu_h=\frac{2(2\pi m_h kT)^{3/2}}{h^3}$ and N is the acceptor density, Eq. (19) gives the dotted curve A and every dashed

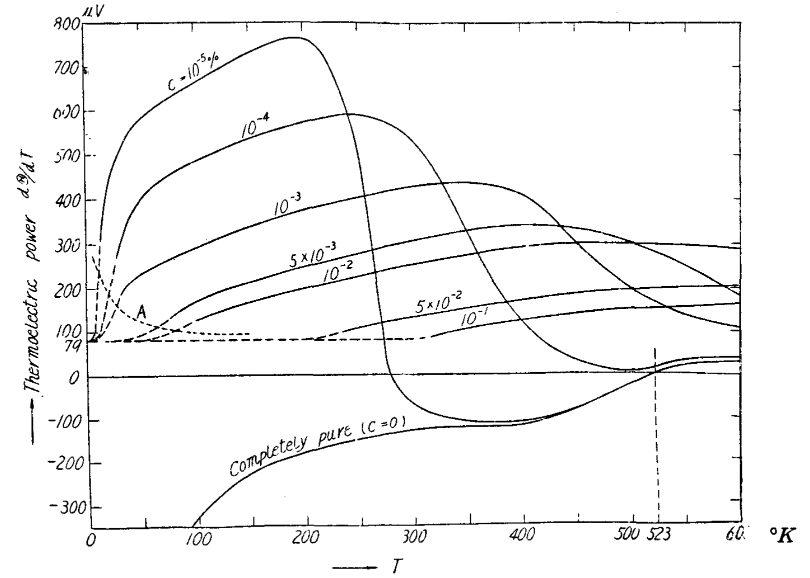

Fig. 6. The calculated characteristics of thermoelectric power versus temperature. C designates the acceptor concentration in atomic per cent. The dashed parts show the uncertain portions due to the approximation of $\Delta E_h=0$. The dotted curve **A** shows the curve for $\Delta E_h=0.001$ eV neglecting the intrinsic excitation, that is, $\frac{d\Theta}{dT}=\frac{k}{|e|}\left(2+\frac{\phi}{kT}-\frac{\beta}{2k}\right)$, $\phi=\frac{\Delta E_h}{2}+\frac{kT}{2}\log\frac{\nu_h}{N}$, where $\nu_h=\frac{2(2\pi m_h kT)^{3/2}}{h^3}$ and N is the acceptor density.

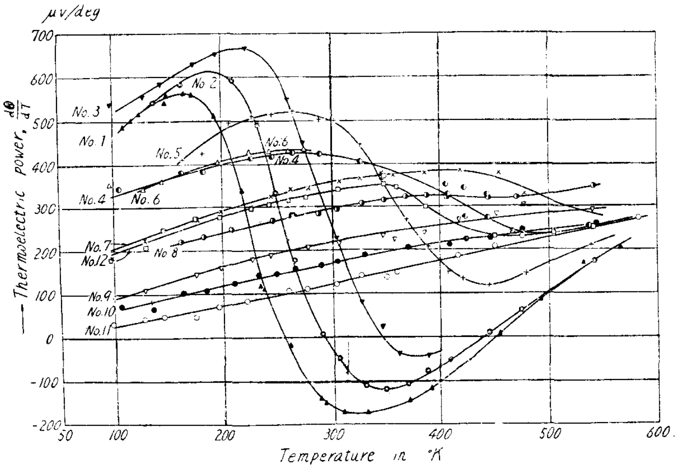

Fig. 7. The thermoelectric power of antimony-doped tellurium specimens against copper measured at various temperatures.

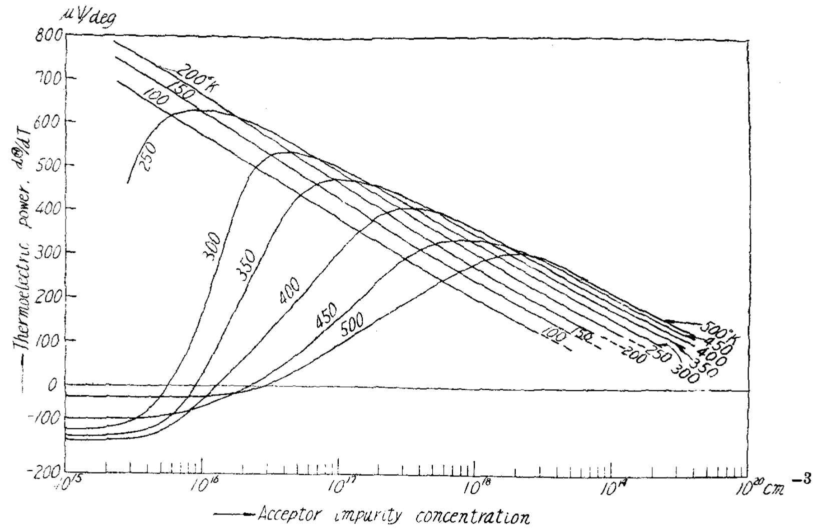

Fig. 8. Variation of thermoelectric power as a function of the density of acceptor levels as derived from Fig. 6.

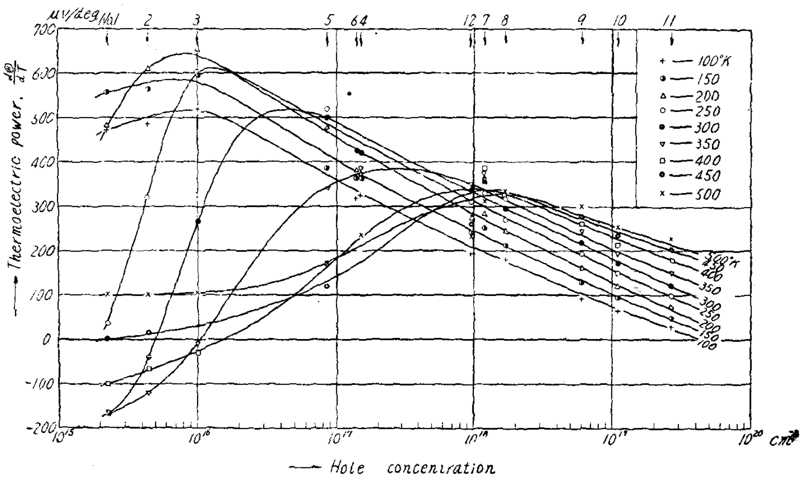

Fig. 9. The measured thermoelectric power plotted against the hole density at room temperature, which is approximately equal to the acceptor density.

parts referred to above should tend to transfer at very low temperatures to some curves similar to the dotted curve A. But the basic assumption of the classical statistics is no longer valid in such lowest temperature range, hence some part of the above discussion would become inadequate. Most of this range, however, is lower than that under examination here. In Fig. 8, the curves of thermoelectric powers versus acceptor concentration, taking temperature as parameter, are replotted from Fig. 6 in order to get facility for the comparison with the experimental results.

V. Comparison with experiments

In the previous paper,(7) we described the experiment on the electrical properties of pure tellurium crystals and tellurium crystals alloyed with antimony to various concentrations. From this, the part related to thermoelectric powers is referred to again in Table 1. The first and second columns show the number of specimens and the antimony concentration respectively, and the third to sixth columns indicate the density of holes obtained from the Hall effect data at room and liquid air temperatures; blanks in the table correspond to the composite or intrinsic cases where the hole density is incapable of being determined in terms of Hall coefficient alone. As seen in this table, there is no large difference between the hole density at room temperature and at liquid air temperature of the same specimen, which fact indicates that almost all of the acceptor levels are ionized, thus yielding holes even at liquid air temperature because of the smallness of the excitation energy, ΔE_h, in all specimens. Consequently the hole concentration ta room temperature is almost equivalent to the effective acceptor concentration and it is permissible to use the former in lieu of the latter. On the other hand, the added antimony concentration and the effective acceptor concentration are generally very different from each other owing to the fact that only a small fraction of the added antimony atoms seem to cause the formation of effective acceptor centres.

Table 1.

specimen number	added antimony concentration (atomic%)	hole concentration				θ* in degree
		at ca 15°C		at liq. nitrogen temp.		
		C atomic%	n_h/cm^3	C atomic%	n_h/cm^3	
1	0	(7.7×10^{-6})	(2.3×10^{15})	6.4×10^{-6}	1.9×10^{15}	6
2	0			1.5×10^{-5}	4.4×10^{15}	20
3	0.0018			3.4×10^{-5}	1.0×10^{16}	poly cryst.
4	0.0045	5.0×10^{-4}	1.5×10^{17}	3.2×10^{-4}	9.6×10^{16}	45
5	0.0105	2.9×10^{-4}	8.5×10^{16}	2.4×10^{-4}	7.1×10^{16}	0
6	0.0157	4.8×10^{-4}	1.4×10^{17}	3.9×10^{-4}	1.2×10^{17}	poly cryst.
7	0.0439	4.2×10^{-3}	1.2×10^{18}	—	—	15
8	0.0943	5.9×10^{-3}	1.7×10^{18}	5.6×10^{-3}	1.6×10^{18}	5
9	0.454	1.9×10^{-2}	5.7×10^{18}	1.9×10^{-2}	5.8×10^{18}	$\theta' < 10$
10	1.048	3.6×10^{-2}	1.1×10^{19}	3.8×10^{-2}	1.1×10^{19}	70
11	5.227	7.6×10^{-2}	2.3×10^{19}	9.1×10^{-2}	2.7×10^{19}	$\theta' \gtrsim 80$
12**	0.0079	3.2×10^{-3}	9.5×10^{17}	3.2×10^{-3}	9.5×10^{17}	35

* θ is the angle between the principal axis of single crystal and the longitudinal axis of the specimen. θ' is the angle of preferred orientation found in a polycrystalline specimen which consists of crystallites having nearly parallel axes.

** No. 12 contains 18.3 atomic per cent selenium.

So that the impurity concentration involved in the calculation of the previous section is capable of being compared adequently with the said hole concentration at room temperature.

The thermoelectric power against copper of the twelve kinds of specimens measured over the range from liquid nitrogen to about 300°C is shown in Fig. 7, in deference to the sign convention depicted in Fig. 1. This is to be compared with the calculated result in Fig. 6, in which, strictly speaking, the absolute thermoelectric power of copper involved in the observed result in Fig. 7 should be taken into account, though because of the negligible smallness of the said power we can leave it out of consideration here. Inasmuch as the estimated acceptor concentration adopted in Fig. 7 is not in agreement with the impurity concentration denoted by C in Fig. 6, which fact entails the inconvenience in direct comparison of these figures, the former is replotted in Fig. 9 in which thermoelectric power is depicted as a function of acceptor concentration taking temperatures as a parameter. On comparing Figs. 8 and 9, a sufficient agreement is recognized between the theoretical and the experimental characteristics, except for some partial discrepancies to be discussed below.

The specimen No. 12 contains about 18 per cent selenium and 0.008 per cent antimony. As in Figs. 7 and 9, the thermoelectric power of this specimen is somewhat smaller at high temperatures than that expected. The cause of this difference may probably be due to the difference of the quantity b, the ratio of electron to hole mobility, in the temperature range in question because of the possible difference of lattice vibration due to the selenium addition.

Now we reflect again upon the approximations used in the present calculation. The assumptions which become objectionable in general when the temperature is lowered are that (i) the application of classical statistics, (ii) the scattering process which is responsible for impurity atoms or ions is ignored in calculating the mean free path integrals, and (iii) the excitation energy $\Delta E_h = 0$. Among them, the assumption (ii) may be the most dubious one for highly impure specimens at low temperature range. However, since the observed and the calculated results for such specimens are in substantial agreement with each other, the result obtained by putting 2 instead of $\frac{1}{kT}\frac{K_2}{K_1}$ in Eq. (20), i. e. the calculation pursuant to the assumption (ii) is unlikely to bring forth serious error in the present case. The experiment at extremely low temperatures is considered to be of very interest in view of the expectance that it may provide the more accurate data for discussing these assumptions. The Hall coefficient of an *intrinsic semiconductor* is given by

$$A_H = \frac{3\pi}{8c|e|n}\,\frac{1-b}{1+b}\,, \tag{30}$$

while the expression of thermoelectric power can be reduced to the form

$$\frac{d\Theta}{dT} = \frac{k}{|e|}\left\{\left(2 + \frac{\Delta E(0)}{2kT}\right)\frac{1-b}{1+b} + \frac{3}{10}\log b\right\}, \tag{31}$$

by substituting $\frac{\partial\chi}{\partial T} = \frac{\beta}{2}$ and $b \fallingdotseq \left(\frac{m_e}{m_h}\right)^{-5/2}$ in Eq. (22). When the value of b takes unity Eqs. (30) and (31) become zero simultaneously. This notwithstanding, the observed characteristic of the thermoelectric power of specimen No. 1 crosses over the abscissa axis at 180°C instead of 250°C at which the Hall effect of the same specimen becomes zero.(8) Furthermore, the magnitude of the thermoelectric power in the higher temperature range of this reversal are fairly larger than the calculated ones and this tendency is also found in the other impure specimens. These facts seem to imply that Eqs. (30) as well as (31) are not so accurate formulae that are capable of representing well such details.

Apropos of these results, we must recollect other assumptions hitherto made in order to deduce the above formulae, that is to say, (iv) the material is isotropic and homogeneous, and (v) the simple composite semiconductor energy band model, consisting of single conduction and valence bands together with an impurity level midway between them, represents the electronic structure of a tellurium crystal. As these assumptions are generally linked to each other and as the tellurium crystal is remarkably anisotropic, in the next section let us tentatively make allowance for the anisotropy effect by assigning a dual bands structure to the conduction band.

VI. Thermoelectric power of an intrinsic semiconductor to which the dual structure of conduction band is assumed

The quantitative disagreement between the theory and the experiment is recognized in the higher intrinsic range. Now, let us consider a crystal free from impurity and assume a dual conduction band scheme as the electronic energy structure of tellurium which consists of two overlapping conduction bands whose bottoms are somewhat shifted each other. For simplicity's sake, let us disregard all temperature effect to the band structure. And denote the energy levels of the top of one valence band and the bottoms of two conduction bands by E_1, E_2 and E_3 as shown in Fig. 10. Next, we assume that the current carriers in the valence band, in the lower conduction band and in the upper conduction band have fixed energy-independent effective masses m_1, m_2 and m_3 respectively. Hereupon let us presume the next relation with regard to the magnitude of m's as the basis of the following argument,

$$m_2 < m_1 < m_3 - c\,, \tag{32}$$

where c is a suitable positive constant, then the mobilities μ_1, μ_2 and μ_3 become,

$$\mu_2 > \mu_1 > \mu_3 \tag{33}$$

Let the effective mass of electrons excited to the conduction band be m_e, when the dual conduction band structure is reduced back again to the original single conduction band model. Then m_e may be an average mass of m_2 and m_3 calculated by taking into account the excited electron densities n_2 and n_3, hence it is not a constant but varies with temperatures. At low temperatures, m_e is smaller than m_1 or to the same thing smaller than m_h by Eq. (32), because the most part of conduction electrons belong to the lower conduction band due to the smallness of kT, and m_e, the mean effective mass of all conduction electrons, is nearly equal to m_2; but with the rise of temperature, electrons excited up to the upper conduction band will be increased, accordingly m_e increases with temperature and approaches to a constant value at sufficiently high temperatures in case that $E_3 - E_2 \ll kT$. Then if c in Eq. (32) is not too small, the value of m_e must exceed m_h at an intermediate temperature. In this way, qualitative as the explanation may be, the temperature dependent abnormal behaviour of m_e in Fig. 3 can be interpreted. Furthermore the thermoelectric power rewritten in accordance with the dual conduction band model is obtained as follows from Eq. (12) using the relation $n_1 = n_2 + n_3$,

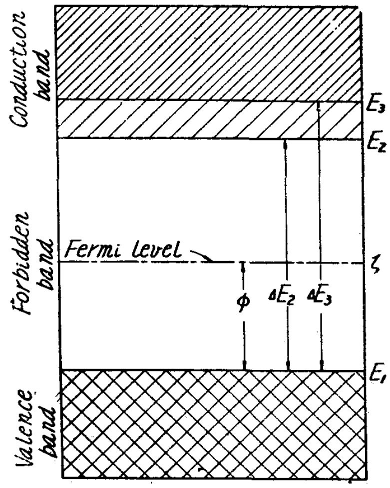

Fig. 10. The energy band model of the dual conduction band without regarding the impurity levels and the temperature effect towards the band edges.

$$\frac{d\Theta}{dT} = \frac{k}{|e|}\left\{\frac{n_2(\mu_1-\mu_2)+n_3(\mu_1-\mu_3)}{n_2(\mu_1+\mu_2)+n_3(\mu_1+\mu_3)}\left(2+\frac{E_2+E_3-2E_1}{4kT}\right)+\delta\right\}, \tag{34}$$

$$\delta = \frac{(n_2+n_3)\mu_1\varepsilon+(n_2\mu_2-n_3\mu_3)\dfrac{E_3-E_1}{2}}{n_2(\mu_1+\mu_2)+n_3(\mu_1+\mu_3)}\cdot\frac{1}{kT}\,. \tag{35}$$

And

$$\phi = \frac{1}{4}\,(E_2+E_3-2E_1)+\varepsilon\,, \tag{36}$$

$$\varepsilon = \frac{kT}{2}\log\frac{m_1^{3/2}}{m_2^{3/2}\exp\left(\dfrac{E_3-E_2}{2kT}\right)+m_3^{3/2}\exp\left(\dfrac{E_2-E_3}{2kT}\right)}\,. \tag{37}$$

If m_1, m_2 and m_3 are of the same order of magnitude and $E_3 - E_2 \lesssim 2kT$, δ in Eq. (34) is small.

While the Hall effect expression for this model is calculated as described below. When the magnetic field H is applied, along the z direction, perpendicularly to the specimen current $\vec{J}_x$ which is derived by the longitudinal electric field F_x, the transverse electric field F_y is set up in the y direction under the condition of no transverse current. The Boltzmann's equation yields the next relationship(12) under the conditions that $J_y = \sum_{i=1}^{3} J_{yi} = 0$, the *isothermal* state $\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = 0$, and the magnitude of H is not very large,

$$\sum_{i=1}^{3} \int_0^{\infty} \frac{\partial f_{0i}}{\partial \eta} \left[F_y l_i \frac{2\eta}{m_i} + HF_x e_i \frac{l_i^2}{m_i} \left(\frac{2\eta}{m_i} \right)^{1/2} \right] d\eta = 0\,. \tag{38}$$

If the assumptions (i) and (ii) described in Section **II**, namely the classical assemblage of carriers and the energy independent mean free path in each band, are also applied, the above equation gives the following expression for the isothermal Hall coefficient A_H, denoting the conductivity in the magnetic field by $\sigma\,(H)$,

$$A_H = \frac{F_y}{HJ_x} = \frac{F_y}{HF_x \sigma(H)}\,, \tag{39}$$

$$\sigma(H) \doteqdot \sigma(0) = \sum_{i=1}^{3} n_i \,|\, e_i \,|\, \mu_i\,, \tag{40}$$

$$\begin{aligned} A_H &= \frac{3\pi}{8|e|} \; \frac{n_1 \mu_1{}^2 - n_2 \mu_2{}^2 - n_3 \mu^2{}_3}{(n_1 \mu_1 + n_2 \mu_2 + n_3 \mu_3)^2}\,, \\ &= \frac{3\pi}{8|e|} \; \frac{n_2(\mu_1{}^2 - \mu_2{}^2) + n_3(\mu_1{}^2 - \mu_3{}^2)}{\{n_2(\mu_1 + \mu_2) + n_3(\mu_1 + \mu_3)\}^2}\,. \end{aligned} \tag{41}$$

The ratio of electron densities in the conduction bands, using the classical statistics as well, is deduced from Eq. (10),

$$\frac{n_3}{n_2} = \left(\frac{m_3}{m_2} \right)^{3/2} \exp\left(\frac{E_2 - E_3}{kT} \right). \tag{42}$$

Now, let us denote the sign reversal temperatures of the thermoelectric power and the Hall coefficient by $T(d\Theta/dT)$ and $T(A_H)$ respectively, the next relation follows from Eqs. (34), (41) and (42),

$$\begin{aligned} &\left(\frac{n_3}{n_2} \right)_{T(d\Theta/dT)} \Big/ \left(\frac{n_3}{n_2} \right)_{T(A_H)} = \exp\left\{ \frac{E_2 - E_3}{k} \left(\frac{1}{T(d\Theta/dT)} - \frac{1}{T(A_H)} \right) \right\} \\ &\doteqdot \frac{\mu_2 - \mu_1}{\mu_3 - \mu_1} \Big/ \frac{\mu_2{}^2 - \mu_1{}^2}{\mu_3{}^2 - \mu_1{}^2} = \frac{\mu_1 + \mu_3}{\mu_1 + \mu_2}\,. \end{aligned} \tag{43}$$

From Eq. (32), the right-hand side of Eq. (43) is less than unity. Namely,

$$T(d\Theta/dT) < T(A_H)\,. \tag{44}$$

As described above, the reversal temperatures are observed as follows,

$$T(d\Theta/dT) = 180^\circ\mathrm{C} = 453^\circ\mathrm{K}\,, \qquad T(A_H) = 250^\circ\mathrm{C} = 523^\circ\mathrm{K}\,,$$

therefore the suggested energy band model also lends itself to account qualitatively for the temperature disagreement in question.

We wish to express thanks to Assist. Prof. A. Morita for his useful discussions. A part of expenditures for this work owes to the Scientific Research Fund of the Ministry of Education.

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