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Magnetic order effects on electric susceptibility hole mass of Sn$_{1-x}$Mn$_x$Te

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Résumé. — Nous reportons les valeurs expérimentales de la masse optique $m_s$ des porteurs libres en fonction de la température entre 4,2 et 300 K pour SnTe et le semiconducteur magnétique Sn$_{0.923}$Mn$_{0.077}$Te avec des concentrations en porteurs de $6.6 \times 10^{20}$ et $6.2 \times 10^{20}$ cm$^{-3}$ respectivement. Les valeurs sont déduites de l’analyse de la réflectivité sous incidence normale dans le domaine infrarouge. La différence entre les valeurs de $m_s$ pour les deux échantillons n’excède jamais l’erreur expérimentale, et est inférieure à 3 %, pour des températures supérieures à 13 K. Ceci montre que les effets d’alliage dus à l’introduction d’impuretés Mn dans la matrice SnTe ne conduisent à aucun changement significatif de la structure de bande de SnTe, et sont donc négligeables. Toutefois, pour l’échantillon dopé au Mn, l’apparition de l’ordre ferromagnétique à $T \leq 11$ K, mis en évidence par des mesures de l’aimantation à l’aide d’un magnétomètre vibrant entraîne une décroissance supplémentaire de $m_s$ d’un taux de 8 % corrélé à un accroissement de la constante diélectrique. Nous attribuons cet effet à la levée de dégénérescence de spin de la bande de valence, associée à une déformation de la structure complexe de la bande de valence. L’analyse est faite sur la base d’un modèle ne faisant intervenir qu’une seule bande non parabolique avec plusieurs vallées. Les surfaces d’énergie constante, semblables à celles de Cohen, sont allongées dans la direction (111) et partent du bord de zone. Un bon accord est trouvé avec les données expérimentales.

Abstract. — Experimental values of the electric susceptibility mass $m_s$ of free carriers are reported as function of temperature in the whole range 4.2 to 300 K, for SnTe and the magnetic semiconductor Sn$_{0.923}$Mn$_{0.077}$Te having carrier concentrations $6.6 \times 10^{20}$ and $6.2 \times 10^{20}$ cm$^{-3}$ respectively. The values are deduced from the analysis of the normal reflectivity in the infrared region. The difference between the values of $m_s$ for the two samples never exceeds the experimental uncertainty and is smaller than 3 % at temperatures higher than 13 K. This shows that alloying effects due to the introduction of Mn impurities in the matrix SnTe does not lead to any significant change in the band structure of SnTe, and are then negligible. However, for the Mn doped sample, the occurrence of a ferromagnetic arrangement of the Mn spins at $T \leq 11$ K, evidenced by measurements of the magnetization with a vibrating sample magnetometer, leads to a further decrease of $m_s$ by an amount of 8 % correlated with an increase of the optical dielectric constant. This effect is assigned to the spin splitting of the valence band, associated with a deformation of the complex valence band structure. The analysis is made on the basis of a single band non parabolic multivalley model. The energy surfaces, taken to be Cohen like, are (111) prolate surfaces located at the edges of the Brillouin zone. Semiquantitative agreement with experiment is obtained.

1. Introduction. — The p-type semiconductor SnTe provides a suitable matrix in which to dilute magnetic ions, and to study the interaction between the localized spins and the free carriers (holes). The aim of previous works on the Sn$_{1-x}$Mn$_x$Te system was to study this interaction in the case of Mn ions by investigating the magnetic and transport properties of this material. The first of these studies was performed by Cohen et al. [1] who reported, in particular, that the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange [2] between the Mn spins leads to a ferromagnetic order at low temperatures. However, no optical experiments have been performed on this material to our knowledge, and it is the purpose of this paper to report the frequency dependence of the spectral reflectivity, in the infrared region, of a sample Sn$_{0.923}$Mn$_{0.077}$Te, and of a check sample SnTe. The objective was to deduce from these measurements the electric susceptibility hole mass $m_s$ as a function of temperature, and then investigate the effects of the magnetic interactions induced by Mn ions on the band structure of SnTe. Our measurements on the SnTe sample are a complement to the study of the temperature dependence of $m_s$ reported by Bis and Dixon [3], since the experimental uncertainties are smaller and the number of temperatures investigated much larger.
than in reference [3]. Hall constant measurements showed that our samples are p-type as expected [4], owing to Sn vacancies.

Both samples investigated were chosen to have roughly the same hole concentration, i.e.

$$6.4 \times 10^{20} \text{ cm}^{-3}$$

so as to enable quantitative comparisons to be made between SnTe and SnTe-MnTe, and to isolate the effects strictly induced by Mn ions from the effects induced by change of the carrier concentration, such as variations of \( m_s \) due to the strong non parabolicity of the bands [5]. Otherwise, the Mn concentration \( x = 7.7 \text{ at. } \% \) is the best compromise between the necessity of dealing with a small \( x \) so as to be free from any alloying effect and Mn-Mn direct interactions, beyond the scope of the present work, and the necessity of dealing with a large \( x \) in order to increase as much as possible the magnetic effects induced by Mn. Our experimental method is described in section 2. The dispersion relations for photons, from which \( m_s \) is determined, are given in section 3. Optical and magnetic measurements are reported in section 4, while section 5 is devoted to the analysis and discussion of the results.

2. Experiments. — The bulk single crystals SnTe and SnTe-MnTe were grown in our laboratory. The homogeneity was controlled and the Mn concentration measured by electron microprobe analysis. Values of the hole concentrations \( p \) and conductivity mobilities \( \mu_e \) were determined from measurements of the low field Hall coefficient \( R_0 \) and the conductivity \( \sigma \) using the relations:

\[
p = r/(R_0 \, e)
\]

\[
\mu_e = R_0 \, \sigma / r
\]

\( r = R_r / R_0 \) where \( R_r \) is the high field Hall coefficient. We have chosen for the anisotropy factor \( r \) the value \( r = 0.6 \) established experimentally by Houston et al. [6] for SnTe over a wide range of carrier concentrations, including that of our samples. We have assumed that this value is still the same in the Mn doped sample, which amounts to neglecting distortion of the band structure of SnTe by addition of Mn ions. This point will be discussed later. The values of \( p \) at \( T = 300 \text{ K} \) are \( p = 6.6 \times 10^{20} \text{ cm}^{-3} \) for the SnTe sample, and \( p = 6.2 \times 10^{20} \text{ cm}^{-3} \) for the Sn_{0.923}Mn_{0.077}Te sample, and can be considered as independent of the temperature within 5 \% [7].

The measured reflectivities of the samples were dependent upon the method used to prepare the optical surfaces. When mechanical polishing techniques were employed, reflectivities in the wavelength region of the reflectivity minimum were not reproducible. Reproducible results, however, were obtained by etching after polishing, according to the method developed by Norr [8].
losses of the apparatus. The angle of incidence of the extreme rays upon the sample was approximatively 6°. The reflectivity at this angle is expected to differ from that obtained at normal incidence by 0.1 %. The reflectivity was determined by comparing the light reflected from the sample with that from a front surface aluminum mirror.

3. Dispersion theory. — Let us first recall the dispersion relations for photons in order to connect the frequency dependence of the reflectivity \( R \) measured at normal incidence, with the band parameters and in particular with \( m_s \). \( R \) is given in terms of the index of refraction \( n \) and the extinction coefficient \( k \) by:

\[
R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]

while the dielectric constant takes the form:

\[
e = (n + ik)^2 = \varepsilon_{\infty} + 4 \pi \chi_{\text{FC}}.
\]

The \( \chi \)'s are the electric susceptibilities corresponding to dispersion mechanisms involving bound carriers \( \chi_{\text{BC}} \), lattice vibrations \( \chi_{\text{LV}} \) and free carriers \( \chi_{\text{FC}} \). In the spectral region which we study, near the plasma frequency, we can neglect the frequency dependence of \( \chi_{\text{BC}} \) and \( \chi_{\text{LV}} \) with respect to that of \( \chi_{\text{FC}} \) and eq. (3.2) takes the form:

\[
(n + ik)^2 = \varepsilon_{\infty} + 4 \pi \chi_{\text{FC}}.
\]

According to the Maxwell equations, \( \chi_{\text{FC}} \) in a medium characterized by a conductivity \( \sigma \) is:

\[
\chi_{\text{FC}} = i \sigma / \omega.
\]

The conductivity tensor \( \sigma \) derived from the first order iteration of the classical Boltzmann transport equation may be written:

\[
\sigma = \frac{e^2}{\hbar} \frac{1}{2 \pi^3} \int d^3k \frac{v_k v_k}{1 + i \bar{\gamma} / \omega} \frac{\partial f_0}{\partial E}.
\]

\( \gamma \) is the damping coefficient, \( E \) the energy of the carriers, \( v_k = \sqrt{E / \hbar} \) the group velocity, and \( e \) the electronic charge. \( f_0 \) is the distribution function. Since we deal with a crystal having cubic symmetry, the conductivity tensor \( \sigma \) reduces to a scalar \( \sigma \). When \( \gamma / \omega \ll 1 \), the integrand of the imaginary part of \( \sigma \) reduces to a scalar \( \gamma \). It is thus customary to define the plasma frequency \( \omega_p \) by:

\[
\frac{4 \pi \text{Im}(\sigma)}{\omega \varepsilon_{\infty}} = \frac{\omega_p^2}{\omega^2}
\]

and by analogy with the free electron plasma, to define the susceptibility mass \( m_s \) by:

\[
m_s = 4 \pi e^2 / (\varepsilon_{\infty} \omega_p^2).
\]

With these notations, eq. (3.3), when we neglect the frequency dependence of the damping coefficient, becomes [9]

\[
(n + ik)^2 = \varepsilon_{\infty} \left(1 - \frac{\omega^2}{\omega_p^2} \frac{1 - i \gamma / \omega}{\omega^2 + \gamma^2}\right)
\]

while eq. (3.5) leads to [10]:

\[
\frac{p_1}{m_s} = -\frac{1}{3} \frac{1}{4 \pi^2} \frac{1}{\hbar} \int_0^\infty \frac{\partial f_0}{\partial E} \int_{S_k} v_k \, dS_k.
\]

We have considered here the case of a number \( \Gamma \) of multivalleys. \( p_1 = p / \Gamma \) is the hole concentration in one valley and \( S_k \) one of the equivalent surface energies in \( k \) space. \( \gamma \) is related to the optical mobility \( \mu \), according to the relation:

\[
\mu = e' / (m_s \gamma).
\]

When \( \gamma / \omega \ll 1 \), and \( k \ll n \), eqs. (3.1) to (3.8) reduce to the well known equations [11]:

\[
R = (n - 1)^2 / (n + 1)^2
\]

\[
n^2 = \varepsilon_{\infty} - \frac{e^2}{\pi c^2 m_s} \lambda^2
\]

where \( \lambda \) is the wavelength.

4. Results. — Typical results of reflectivity measurements of our samples are shown in figure 2. The experimental points obtained are separated from one another by only 0.05 \( \mu \) and only some of the experimental points have been reported in figure 2, to improve clarity. The curves have common characteristics. At short wavelengths, the reflectivity decreases to a minimum, which results from the contribution of free carriers. At longer wavelengths, the reflectivity becomes uniformly high, indicating a metallic reflection. When the minimum reflectivity is small, eq. (3.11) can be used at wavelengths between the

Fig. 2. — Reflectivity \( R \) as a function of the wavelength \( \lambda \) at typical low temperatures for SnTe (a), and Sn_{0.92}Mn_{0.08}Te (b). Open circles are experimental points. The full curves are theoretical fits.
absorption edge and the reflectivity minimum. In such a case, the experimental curve \( n^2 \) vs. \( \lambda^2 \) is a straight line, whose slope yields \( m \), while the intercept with the \( Y \) axis yields \( \varepsilon_{\infty} \). Unfortunately, this method failed to give results with the required accuracy, because a discrepancy between our theory and experiment occurs at short wavelength (\( \lambda < 2.5 \mu \)), arising from a frequency dependent contribution of bound carriers to the reflectivity, while at larger wavelengths (\( \lambda > 3.2 \mu \)) the damping factor cannot be neglected. The results deduced from this analysis were then uncertain up to \( 10\% \) at low temperature (\( T < 77 \) K) and increased at higher temperatures where the optical mobility is smaller. That is the reason why we have used eqs. (3.1), (3.7) and (3.8) taking the carrier scattering into account in order to determine \( \varepsilon_{\infty}, m \), and \( \gamma \). The plot \( n^2(\lambda^2) \) was used only to find trial values of \( \varepsilon_{\infty} \) and \( m \), serving as a first step in the procedure which consists in finding by trial calculations the values of \( \varepsilon_{\infty}, m \), and \( \gamma \) which give the best fit to the experimental reflectivity curves.

Usually, the procedure involving a fit of three parameters is rather intricate, as far as the uniqueness of the solution is questionable. In this present case, however, this uniqueness is insured by the distinct effects of any variation of each of the parameters on the reflectivity curves. The parameter \( \gamma \) for example, determines the width of the dip near the plasma frequency, and \( \varepsilon_{\infty} \) determines the absolute value of the reflectivity at wavelengths equal or smaller to the value of \( \lambda \) corresponding to the minimum of the curve. Also, this position of the minimum of reflectivity is essentially determined by the product \( m, \varepsilon_{\infty} \). Quite good agreement was found with experimental data, and the discrepancy did not exceed \( 2\% \) for wavelengths \( \lambda > 2.5 \mu \), and was even much smaller near the minimum of reflectivity for \( 3 < \lambda < 5 \mu \). At shorter wavelengths, the discrepancy increases due to the onset of bound carrier dispersion. The correction for the lattice dispersion, calculated as

![Fig. 3. Reduced electric susceptibility mass as a function of temperature. The full curve and experimental points denoted by crosses stand for SnTe. The broken curve and open circles stand for the Mn doped sample. To improve clarity, we have reported experimental uncertainties for only two points, since they are the same for all the other points.](image1)

![Fig. 4. Optical dielectric constant \( \varepsilon_{\infty} \) as a function of temperature. The full curve and experimental points shown as crosses refer to SnTe. The broken curve and white circles refer to the Mn doped sample. The experimental uncertainties are reported for only two points but are the same for the other points.](image2)

![Fig. 5. Optical mobility as a function of the magnetic field \( H \) for SnTe (full curve, right scale) and Sn\(_{0.923}\)Mn\(_{0.077}\)Te (broken curve, left scale). Experimental uncertainties on each curve are identical to those for the example shown.](image3)
in reference [9] is lower than 0.1 % and is then negligible, because of the high hole concentration. The computed values of \( \varepsilon_{\text{opt}} \), \( m_e \) and \( \mu_l \) are reported in figures 3, 4 and 5. The accuracy with which these parameters are derived is better than 3.5 % at all temperatures. A good agreement was found between optical and conductivity mobilities measured at \( T = 300 \text{ K} \), which indicates that the carrier scattering is not different at the surface and in the bulk of the material. The values of \( m_e \) are in good agreement with the values determined by Bis and Dixon [3] for SnTe with similar hole concentrations, at 300, 80, and 10 K. Moreover, no difference between the values of \( m_e \) for the Mn doped and the undoped samples could be evidenced between 13 K and 300 K. The objection can be raised, that if the very good accuracy in measurements of the temperature dependence of \( m_e \) for a given sample can be insured by the limitation of the thermal shift of the sample as mentioned above, the comparison of \( m_e \) between two different samples is more doubtful, and is subject to an error reaching a few per cent, since it is subject to their respective surface states which may affect the absolute value of the reflectivity. This is why alloying effects when Mn impurities are substituted to Sn atoms lead to variations of \( m_e \) within the experimental uncertainties and are only evidenced in figure 5 by the lowering of the optical mobility in the Mn doped sample. The point of interest is that around 13 K, a jump of about 10 % of \( m_e \) can be evidenced on the Mn doped sample, correlated with a hollow in the mobility curve. Such effects are expected to be generated by magnetic interactions induced by Mn ions. To check this, we have measured the magnetization of this sample as a function of the magnetic field at various temperatures, with a vibrating sample magnetometer (Fig. 6). The Curie temperature deduced from the magnetization at low fields as a function of \( T \) is \( T_c = 11 \pm 1 \text{ K} \). This poor accuracy in the determination of \( T_c \) is due to the rather small temperature dependence of the magnetization around \( T_c \), which reveals important magnetic fluctuations, up to 2 \( T_c \) or 3 \( T_c \). This value of \( T_c \) is in agreement with the expected values for such a Mn concentration [12]. The magnetization per Mn ion deduced from the saturation magnetization at 4.2 K is 5 \( \mu_B \) as expected for Mn\(^{++} \) in a S state with a spin 5/2.

The hollow in the optical mobility curve in figure 5, near \( T_c \), is not surprising, and can be imputed to a scattering of the carriers by the magnetic fluctuations [13]. The variations of \( \varepsilon_{\text{opt}} \) near \( T_c \) are only slightly greater than the uncertainty in each experimental value, and thus cannot be discussed further, so that we shall focus our attention on the variations of \( m_e \).

5. Temperature dependence of \( m_e \). — Let us investigate in which way the magnetic interactions can induce a change of \( m_e \). They can be described by the usual Hamiltonian:

\[
-H = - \sum_n J S_n \cdot s(R_n)
\]  

(5.1)

\( S_n \) is the spin of the Mn ion at the site \( R_n \) and \( s \) the spin of the free carrier. \( J \) is the exchange integral. This interaction leads to a change in the energy spectrum of the carriers, resulting in a change of \( m_e \). To the first order of perturbation, the energy of the carriers becomes:

\[
E(k)^\pm = E^0(k) \pm \frac{1}{2} x JS \sigma
\]  

(5.2)

where \( \sigma = S^z/S \) is the spin polarization of the Mn ions, and \( x \) the relative concentration of Mn entering the formula Sn\(_{1-x}\)Mn\(_{x}\)Te. \( E^0(k) \) is the unperturbed energy of the free carriers. \( E(k)^+ \) refers to a carrier with spin up, and \( E(k)^- \) to a spin down. In the molecular field approximation, the second order perturbation Hamiltonian is [2]:

\[
\mathcal{H}_{\text{ex}}'' = - \left( \frac{J}{2 N^0} \right)^2 \sum_{i,j} S_i^z S_j^z \sum_k \sum_q \frac{e^{i q (R_i - R_j)}}{E^0(k) - E^0(k + q)} \times
\]

\[
\times (n_{k+} + n_{k-})
\]  

(5.3)

where \( N^0 \) is the number of unit cells, i.e. of Te atoms, while \( n_{k,\pm} \) are occupation numbers for a hole with the wavevector \( k \), and spin \( \uparrow \) and \( \downarrow \) respectively. This expression takes the form \( \mathcal{H}_{\text{ex}}'' = - \sum_{i,j} J_{\text{eff}}(R_{ij}) S_i \cdot S_j \) which defines the effective coupling constant \( J_{\text{eff}}(R_{ij}) \) of the indirect exchange. This is the interaction responsible for the ferromagnetism, the Curie temperature being defined by:

\[
T_c = \frac{2(S(S + 1))}{3 k_B} J_{\text{eff}}(0)
\]  

(5.4)

where \( J_{\text{eff}}(0) \) is the Fourier transform at \( k = 0 \) of \( J_{\text{eff}}(R_{ij}) \) and \( k_B \) the Boltzman constant. The Fourier
integral has been calculated [14] in the case of a parabolic band at $T = 0$, and leads to:

$$T_e = \frac{S(S + 1)}{8 k_B} (J\Omega)^2 \frac{nN_M}{E_F}$$  \hspace{1cm} (5.5)

where $N_M$ is the concentration of Mn ions, and $\Omega$ the volume of the unit cell of the lattice. According to eq. (5.3), the second order correction to the energy of the free carriers is:

$$\Delta E(k) = \left(\frac{J}{2 N^0}\right)^2 \sum_{ij} S_i^b S_j^b \sum_q e^{i q (\mathbf{R}_i - \mathbf{R}_j)} \frac{E^0(k) - E^0(k + q)}{E^0(k)}$$  \hspace{1cm} (5.6)

and the full change of the energy spectrum of the carriers is:

$$E(k) = E^0(k) \pm \frac{1}{2} xJS \sigma + \Delta E(k).$$  \hspace{1cm} (5.7)

The dependence on $k$ of the renormalizing energy in eq. (5.7) is entirely contained in the term $\Delta E(k)$. Its effect on the mass has been calculated in the case of a parabolic band by Rys et al. [15]. In this case we can write the renormalized susceptibility mass $m_s^* = m_s + \gamma xJS \sigma$. At low temperature when the correlation function $S_\mathbf{k} S_\mathbf{q} = S^2$, eq. (5.7) leads to:

$$\frac{m_s}{m_s^*} = 1 + x^2 \frac{4 m_s^2 S^2 J^2}{3 h^4} \sum_{q \neq 0}^{1} \frac{1}{Q^2}$$  \hspace{1cm} (5.8)

$Q$ is a wavevector of the reciprocal lattice. The numerical calculation, in which $J$ is deduced from eq. (5.5), gives a lowering of $m_s$ by an amount of about 0.1%. This effect is then negligible, which is expected to be a special feature of magnetic semiconductors with dilute magnetic spins. In effect, eq. (5.7) can be considered as a perturbation expansion of the energy as a function of $x$ since $\Delta E(k) \propto x^2$. That is why the correction on $m_s$ due to $E(k)$ is two orders of magnitude smaller than in magnetic semiconductors like EuO [15] where $x = 1$. Since $\Delta E(k)$ is much smaller than the spin splitting energy, we shall only consider the correction of the energy as given by eq. (5.2). The break of the spin degeneracy due to the exchange interaction in the ferromagnetic configuration implies that we cannot deal with a single band as is supposed in section 3, but with two bands separated by $JS \sigma$. The generalization of the classical dispersion relation given by eq. (3.8) to the case of a multiple-band system is [9]:

$$(n + ik)^2 = \epsilon_n \sum_j \left(1 - \omega_{pq}^2 \frac{1 - i \gamma_{pq} \omega}{\omega^2 + \gamma_{pq}^2}ight)$$  \hspace{1cm} (5.9)

where $\omega_{pq}$ and $\gamma_{ij}$ are related to the properties of the free carriers of type $j$. However, the fact that we have obtained a good agreement between our reflectivity data and the results calculated on the basis of the single band relation suggests that the dispersion parameters associated with each of the bands are such that eq. (5.9) takes on the form of the single band relation of eq. (3.8). This is why we shall take $\gamma_{ij}$ to be independent of $j$, i.e. independent of the spin index. In this case, eq. (5.9) reduces to eq. (3.8) with $\omega_{ij}^2 = \sum_j \omega_{ij}^2$ or, according to eq. (3.7)

$$\frac{1}{m_s} = \sum_j \frac{f_j}{m_{sj}}$$  \hspace{1cm} (5.10)

where $f_j$ is the fraction of carriers of type $j$. The calculation of $m_{sj}$ requires a dispersion law for the carriers, and thus a valence band model for SnTe. This problem has received much attention [16]. Although there is some evidence supporting the existence of multivalence bands in SnTe, it has been shown in reference [3] that optical measurements at 300 K could be accounted for by a single band model involving only a Cohen type valence band, i.e. a valence band with non parabolic approximately ellipsoid energy surfaces first described by M. H. Cohen [17] for bismuth. Although some recent calculations [18] indicate that the top of the valence band is located near the edge of the Brillouin zone in the $<111>$ direction, rather than at the edge, we shall make the usual approximation according to which the extremum of the band is placed at the L point. Because of the high symmetry at L, this induces simplifications in the equation determining the four equivalent energy surfaces, given by eq. (26) of reference [17], which can be written:

$$E(k) = \frac{1}{2} \left[ E_s + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_l} - \frac{1}{m_T} \right) \right] +$$

$$+ \frac{1}{2} \left\{ \left[ E_s + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_l} + \frac{1}{m_i} \right) \right]^2 + 4 E_s \frac{\hbar^2 k^2}{2 m_T} \right\}^{1/2}.$$  \hspace{1cm} (5.11)

The notations $m_l$ and $m_i$ have been used in place of $m_2$ and $m_3$ of reference [17], because they stand for the longitudinal masses of the valence band and of the interacting conduction band respectively. $m_T$ is the transverse mass at the bottom of the valence band. $E_s$ is the interaction gap. The susceptibility mass defined by eq. (3.9) associated with such surfaces, given by eq. (5.11) has been calculated by Dixon and Riedl [19]. We shall write the result in the condensed form:

$$m_s = F(p, m_l, m_i, m_T, E_s, T)$$  \hspace{1cm} (5.12)

where $F$ stands for the function defined by eqs. (13) to (16) of reference [19]. At $T = 300$ K, as it has been already established [3], a good agreement
between the value of \( m_s \) calculated according to eq. (5.12) and the experimental results is obtained for the set of band parameters deduced from the data given by Tsu et al. [20] :

\[
\frac{m_l}{m_0} = 0.07 \quad \frac{m'_l}{m_0} = 0.28 \quad \frac{m_T}{m_0} = 0.015 \quad F_g = 0.2 \text{ eV}.
\]

(5.13)

\( m_e \) is the free electron mass. However, it is important to notice that these band parameters are not independent of one another. This can be evidenced by using the procedure of Kane [21] for InSb to derive the dispersion law of the valence band. This procedure, as followed by Tsu et al. [20] gives, when free electron terms are neglected, the dispersion law given by eq. (5.11) provided that we make the identification :

\[
m_T = \frac{\hbar^2 F_g}{2 \beta^2} \quad (5.14)
\]

where \( \beta \) is the Kane matrix element. We can deduce from the data in eq. (5.13) the value of \( \beta \) :

\[
P = 7.05 \times 10^{-8} \text{ eV} \times \text{cm}.
\]

(5.15)

To the same order of approximation, \( m_l \) and \( m'_l \) do not depend on \( E_g \). For SnTe, at \( T < 77 \text{ K} \), \( m_s \) like band parameters is almost temperature independent. For \( \text{Sn}_{0.923}\text{Mn}_{0.077}\text{Te} \) however, at \( T > T_c \), the band is split into two subbands, whose dispersion relations are, according to eqs. (5.2), (5.11) and (5.14) :

\[
E(k)^j = \left( j - \frac{3}{2} \right) \times JS\sigma - \frac{1}{2} \left[ E_g^j + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_l} - \frac{1}{m_l'} \right) \right] +

\frac{1}{2} \left[ E_g^j + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_l} + \frac{1}{m_l'} \right) \right]^2 + 4 F_g^j \frac{\hbar^2 k^2}{2 m_T^j} \right\}^{1/2}
\]

(5.16)

\( j = 1 \) refers to the spin up subband and \( j = 2 \) to the spin down subband. These eqs. (5.16) involve one of the most drastic approximations of our model, that is the neglect of the unknown spin splitting of the conduction band. In effect, the \( k.p \) interaction only couples bands which have the same spin. This means that the parameter \( E_g^j \) in the expression of \( E(k)^j \) is the energy gap between the conduction and valence subbands which have the same spin, as defined by \( j \). We have chosen, however, a value of \( E_g^j \) in a model where the conduction band is not split and the valence band split as if it was a pure s band. Since the conduction band ought to be split in some way, and since there is strong evidence that the valence states are a mixture of s and p type states, it is very difficult to discuss the validity of our expression for \( E_g^j \) more especially as no available experimental determination exists for this parameter which still remains unknown. It is worth noticing that the distortion of the bands according to eq. (5.16), which are not rigidly shifted when \( \sigma \) is varied, is strictly due to interband interactions responsible for the dependence of \( E(k) \) on \( E_g \). The nature of this distortion is then entirely different from the distortion due to \( \Delta E(k) \) in eq. (5.7), which has been found to be negligible and due to a RKKY exchange interaction.

The value of \( J \) deduced from eq. (5.5) is [22] :

\[
J = 0.4 \text{ eV}. \quad \text{However, this derivation is made with the assumption of parabolic spherical energy bands, so that this value must be considered first order in nature. The value used for the scattering problem is usually } J = 0.6 \text{ eV} \quad [23]. \quad \text{We shall thus take an intermediate value } J = 0.5 \text{ eV}. \quad \text{We have computed } m_s \text{ given by eqs. (5.10) and (5.12), for the set of parameters } m_l/m_0 = 0.07, m'_l/m_0 = 0.028, E_g^0 = 0.2 \text{ eV, } P = 7.05 \times 10^{-8} \text{ eV} \times \text{cm. and } \rho = 6.6 \times 10^{20} \text{ cm}^{-3}. \quad \text{The computed electric susceptibility mass is found to decrease by an amount of about 10\% when } \sigma \text{ varies from 0 to 1, in good agreement with our experimental data.}

However, this agreement should not mask other disagreements resulting from the oversimplified structure of the valence band in our model. In particular, it is not possible to explain the variations of \( m_s \) and \( \varepsilon_\infty \) in the range of temperatures \( 77 < T < 300 \text{ K} \) by varying the band parameters of eq. (5.11). To account for such variations of \( m_s \) and \( \varepsilon_\infty \) with \( T \), we must assume that \( dE_g/dT \) is positive, although metal insulator semiconductor tunelling experiments indicate that \( dE_g/dT \) is negative [24]. Burke and Riedl [25] have proposed an explanation of this inconsistency, supported by recent calculations [18, 26], which demonstrated the complexity of the Fermi surfaces including regions of both positive and nega-
tive temperature coefficient. The variations of $\varepsilon_c$ and $m$, with $T$ for $T > 77$ K are thus beyond the scope of the present model, and follows from a dispersion relation of the holes much more intricate than those of eq. (5.11). The same conclusion applies to the temperature dependence of $\varepsilon_c$, whose origin is expected to be the same as for $m$.

6. Conclusion. — Measurements performed on SnTe and Sn$_{0.923}$Mn$_{0.077}$Te with a carrier concentration $6.4 \times 10^{21}$ cm$^{-3}$ have revealed a lowering of the electric susceptibility mass $m_s$ below $T_c$ in the Mn doped sample due to magnetic interactions. The analysis of the results has been performed in the framework of a very simplified valence band model assuming the existence of only one multi-valley Cohen type band at the L point of the Brillouin zone. Although this model is too crude to account for the variations of $m_s$ at high temperature ($T > 77$ K), it accounts for the lowering of $m_s$ at $T < T_c$. This agreement, however, cannot be considered as a proof for the validity of our model regarding this effect, mainly because we have neglected the spin splitting of the conduction band and the $p$ character of the valence states. Nevertheless, we are inclined to attribute this renormalization of $m_s$ at $T < T_c$ to a spin splitting of the non rigid valence band, since among the various processes which we have considered, it turned out to be the only one capable of a renormalization of $m_s$ with the proper order of magnitude. This effect does not exist when dealing with a rigid parabolic spherical valence band. It is then due to the fact that this semiconductor has a small gap, the interband interaction being responsible for this complexity of the energy surfaces. Moreover, this effect is a first order effect with respect to the relative concentration of localized spins $x$, and overbalance the deformation of the band due to the RKKY contribution to the energy, which is only of second order in $x$, because we deal with dilute spins ($x \ll 1$). The nature of the effect evidenced in this paper should then be considered as a specific effect of small gap magnetic semiconductors with dilute spins.

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References
