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Effect of the magnetic order on the optical-absorption edge in $Cd_{1-x}Mn_xTe$

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The effect of the magnetic order on the optical-absorption edge of the semiconductor $Cd_{1-x}Mn_xTe$ is studied. A magnetic blue shift is observed when the temperature decreases below the Néel temperature. This effect is not affected by the magnetic order at low temperature. With the analysis of the experimental data, it is proposed that the exchange interaction gives rise to a red shift of the absorption edge. This phenomenon, however, decreases with temperature to such an extent that an extra blue shift appears at low temperatures.

I. INTRODUCTION

The absorption edge of semiconductors usually exhibits a blue shift with decreasing temperature. In magnetic semiconductors, this behavior is strongly affected by magnetic phase transitions.[1,2] This effect has been studied in several ferromagnetic crystals such as europium chalcogenides[3–5] and chromium chalcogenide spinels.[6–8] The absorption edge exhibits a bathachromic shift with temperature below the Curie temperature T_C. This results in a substantial reduction of the energy gap by an amount which is about 25% in the case of EuO and 50% in the case of $HgCr_2Se_4$.[8] On the other hand, antiferromagnetic crystals present a different behavior. In the case of EuTe (Ref. 3), MnS and CoO (Ref. 2) magnetic blue shifts were observed, while a red shift was noticed in the case of MnO. This effect had been investigated by several authors using a theory based on a model in which a conduction electron is coupled by exchange interactions with the magnetic moments localized on lattice sites.[9–11]

A similar effect is expected in semimagnetic semiconductors. The main difference between semimagnetic and magnetic semiconductors is that the former are obtained by the introduction of magnetic ions in a semiconductor matrix, resulting in their random distribution, while the latter are periodic spin systems. The most studied semimagnetic semiconductors are the II-VI compounds containing manganese. Among these materials, $Cd_{1-x}Mn_xTe$ is a large-band-gap semiconductor. Its magnetic phase diagram was determined by specific-heat and low-field susceptibility measurements by Galazka *et al.*[12] Three ranges of Mn concentration were distinguished, resulting in different magnetic properties at low temperatures. The range $0.6<x<0.73$ corresponds to an antiferromagnetic structure of the third kind, while a spin-glass phase occurs for $0.2<x<0.6$. For $x<0.2$ the material remains paramagnetic at all temperatures. The absorption edge of $Cd_{1-x}Mn_xTe$ was studied previously.[13–16] At low temperatures two absorption bands, attributed to Mn intraion transitions, perturb the fundamental absorption edge.

In the present work, the absorption spectra of $Cd_{1-x}Mn_xTe$ were determined in the temperature range between 4.4 and 300 K up to $\alpha=20\,000$ cm^{-1}. Taking into account the two absorption bands, the fundamental absorption edge of $Cd_{1-x}Mn_xTe$ was deduced. A blue shift is observed with decreasing temperature for both antiferromagnetic and spin-glass-type samples. The obtained experimental data are analyzed, evaluating the exchange interaction between the magnetic ions and the band electrons.

II. EXPERIMENTAL RESULTS

Absorption measurements were performed on $Cd_{1-x}Mn_xTe$ single crystals prepared by a modified Bridgman technique by Triboulet.[17] Samples with thicknesses of 3 μm—0.3 mm were used to measure the absorption edge as a function of composition. These samples were mechanically polished. Four crystals with manganese compositions corresponding to $x=0.3$, 0.4, 0.63, and 0.73 were studied. To determine the absorption coefficient, the variation of the reflectivity with temperature was neglected. Its room-temperature value, $R=0.3$, was used over the entire range of temperatures. It is assumed that such an approximation does not substantially affect the data obtained.

In Fig. 1 the absorption spectra of $Cd_{0.27}Mn_{0.73}Te$ are depicted at the temperatures of 4.4, 145, and 300 K. A strong increase of the absorption can be noticed above the value of absorption coefficient (α) larger than 5000 cm^{-1}. This is mainly attributed to a valence- to conduction-band transition. In the case of $\alpha<5000$ cm^{-1}, two bands can be observed, A and B, located at 2.43 and 2.63 eV, respectively. To elucidate the influence of the magnetic order on the fundamental absorption edge, it is necessary to eliminate the contribution of these A and B bands from the spectra. It can be seen in Fig. 1 that the contribution of these bands at energies above 21 600 cm^{-1} is less than 2000 cm^{-1}. Below this energy the absorption coefficient of the A and B bands is between 2000 and 3000 cm^{-1}. Taking into account this extra absorption, one can determine the region of the fundamental absorption edge. This is shown by the dotted lines in Fig. 1 at temperatures of 300, 145, and 4.4 K, respectively. To determine the shift

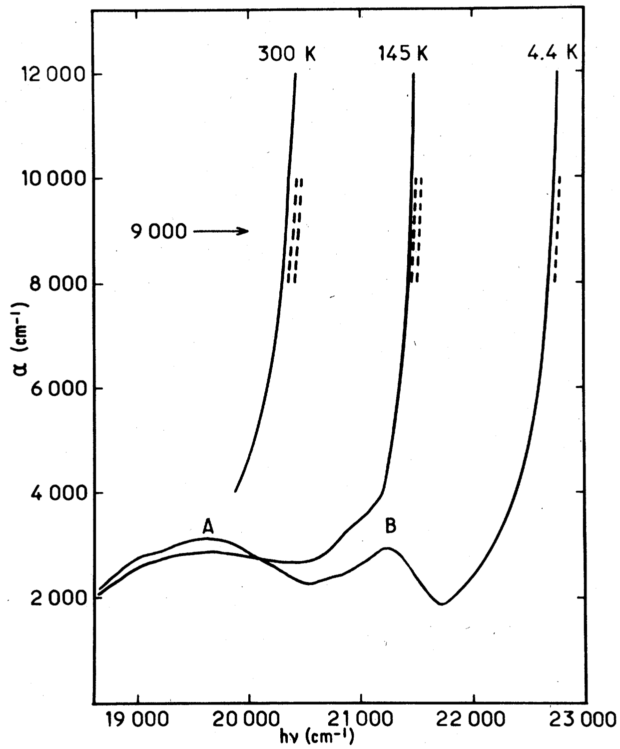

FIG. 1. Absorption spectra of $Cd_{0.27}Mn_{0.73}Te$ at 4.4, 145, and 300 K. The dotted lines represents the extreme possible values for the absorption edge after eliminating the contribution of the A and B bands.

of the fundamental absorption edge, the energy value was arbitrarily taken at $\alpha = 9000\ \text{cm}^{-1}$. The resulting temperature dependence of the fundamental absorption determined by this procedure is shown in Fig. 2. The errors inherent in the above-described technique are indicated by the lengths of the bars. A blue shift is present, as expected, below 70 K. At higher temperatures, the temperature coefficient of the band gap, $dE_g/dT = -9\times10^{-4}$ eV/K, has a value close to that determined by electroreflectance.[18] Using the temperature dependence of a classical semiconductor, $E(T)=E_0 - aT^2/(T+\Theta)$,[19] the dashed curve is obtained by extrapolating, to lower temperatures, the high-temperature data, according to this expression. The difference between the extrapolated and measured curve is attributed to the effect of the magnetic ordering. This blue shift can be estimated to be ~45 meV. The absorption of $Cd_{0.6}Mn_{0.4}Te$ crystal is not significantly influenced by the A and B absorption bands. In Fig. 3 the variation of the band gap, E_g, taken at $\alpha \sim 10\,000\ \text{cm}^{-1}$ as a function of the temperature, is shown. For this sample as well, the result is a hypochromic magnetic shift whose value at 4.4 K is about 17 meV. The same measurements were performed on samples corresponding to manganese concentrations of $x = 0.3$ and 0.6, giving a blue shift of 7 and 31 meV, respectively.

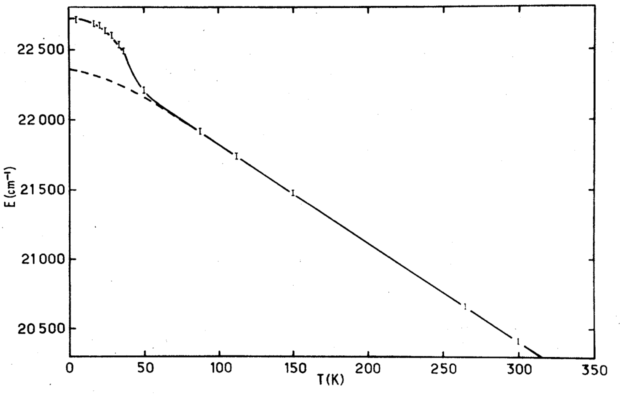

FIG. 2. Absorption edge as function of temperature for $Cd_{0.27}Mn_{0.73}Te$. The dotted curve shows the extrapolation of E_g obtained from high temperatures according to a classical $E_g(T)$ law.

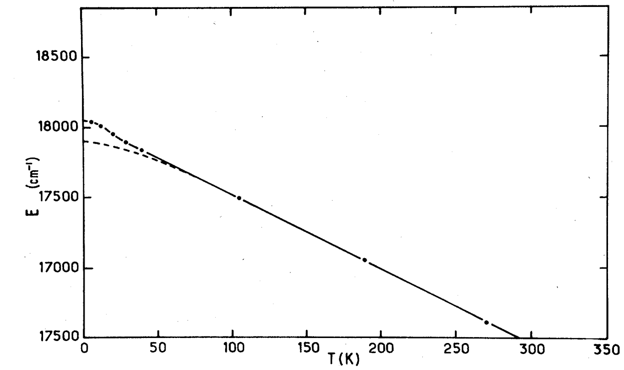

FIG. 3. Absorption edge as function of temperature for $Cd_{0.6}Mn_{0.4}Te$. The dotted curve shows the extrapolation of E_g obtained from high temperatures according to a classical $E_g(T)$ law.

III. DISCUSSION

The magnetic shift of the absorption edge of magnetic semiconductors has been treated by Rys *et al.*,[9] who related this phenomenon to the lowering of the conduction-band energy by exchange interaction of the magnetic ions and conduction electrons. It has been shown that a good approximation of this shift could be obtained by the rigid-ion spin model, at temperatures far below and far above the Curie temperature. A similar treatment is used in this investigation, taking into account the nature of the absorption edge, attributed to the $\Gamma_8-\Gamma_6$ transition. It is assumed that the magnetic blue shift is the sum of valence- and conduction-band displacements, and temperatures much lower or much higher than the Néel temperature T_N will be considered.

The exchange interaction between Mn^{2+} and band electrons is described by the usual Heisenberg Hamiltonian with the following modifications:

$$H_{\text{ex}} = -x\frac{V}{N}\sum_j J(\mathbf{r}-\mathbf{r}_j)\mathbf{s}\cdot\mathbf{S}_j \ , \qquad (1)$$

where $\mathbf{S}_j$ is the localized spin at site $\mathbf{R}_j$, $\mathbf{s}$ is the spin of the band electron and $\mathbf{r}$ its position, $J(\mathbf{r}-\mathbf{R}_j)$ is the exchange integral which varies rapidly over a unit cell, V/N is the volume per magnetic ion, and x is the fraction of cation sites occupied by Mn^{2+} ions. According to the virtual-crystal approximation, the summation is extended over all the cation positions.

Expression (1) is considered to be a perturbation of the system of one electron and N spins, with respect to the nonperturbed system:

$$|\mathbf{k},\sigma\rangle=\frac{1}{\sqrt{V}}e^{-i\mathbf{k}\cdot\mathbf{r}}|\sigma\rangle\ , \tag{2}$$

where $\mathbf{k}$ is the wave vector and $|\sigma\rangle$ represents the spin part of the wave function.

Then the first-order correction is

$$\Delta E^{(1)}(\mathbf{k},\sigma)=\langle\mathbf{k},\sigma|H_{\mathrm{ex}}|\mathbf{k}\sigma\rangle\ . \tag{3}$$

By introducing $J_0=\int J(\mathbf{x})d^3x$ to replace the summation in Eq. (1), we obtain

$$\Delta E^{(1)}(\mathbf{k},\sigma)=-x\sigma J_0\frac{1}{N}\sum_j S_{jz}\ . \tag{4}$$

In the case of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, $\sum_j S_{jz}=0$ at all temperatures. Consequently, the energy correction will be given by the second-order term,

$$\Delta E^{(2)}(\mathbf{k},\sigma)=\sum_{\mathbf{q}(\neq 0)}\sum_{\sigma'}\frac{|M_{q,\sigma,\sigma'}|^2}{E_0(\mathbf{k})-E_0(\mathbf{k}-\mathbf{q})}\ , \tag{5}$$

where $E_0(\mathbf{k})$ is the unperturbed electron energy and

$$M_{\mathbf{q},\sigma,\sigma'}=\langle\mathbf{k},\sigma|H_{\mathrm{ex}}|\mathbf{k}-\mathbf{q},\sigma'\rangle\ . \tag{6}$$

Using the Fourier transform of the exchange coupling,

$$J_{\mathbf{q}}=\int d^3x\,J(\mathbf{x})e^{-i\mathbf{q}\cdot\mathbf{x}}\ , \tag{7}$$

we have

$$\langle\mathbf{k}|J(\mathbf{r}-\mathbf{R}_j)|\mathbf{k}-\mathbf{q}\rangle=\frac{1}{V}e^{-i\mathbf{q}\cdot\mathbf{R}_j}J_{\mathbf{q}}\ . \tag{8}$$

The range of the exchange coupling, $J(\mathbf{x})$, is determined by the size of the $3d$ shell. The Fourier transform $J_{\mathbf{q}}$ can be approximated by[9]

$$J_{\mathbf{q}}=\begin{cases}J_0 & \text{for } |\mathbf{q}|<q_{\max}\ ,\\ 0 & \text{for } |\mathbf{q}|>q_{\max}\ .\end{cases} \tag{9}$$

A. Energy correction at $T \ll T_N$ for antiferromagnetic $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$

In a rigid antiferromagnet of the third kind, the spins are ordered in the fcc lattice as shown in Fig. 4. In this case,

$$S_{jx}=0\ ,\quad S_{jy}=0\ ,\quad S_{jz}=S_j=\pm S\ .$$

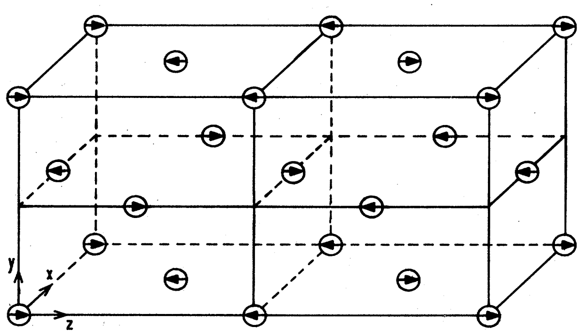

FIG. 4. Magnetic cell for type-III antiferromagnetic ordering.

Using (8), Eq. (6) can be given as

$$M_{\mathbf{q},\sigma,\sigma'}=-\frac{xJ_{\mathbf{q}}}{N}\sum_j\langle\sigma|\mathbf{s}\cdot\mathbf{S}_j|\sigma'\rangle e^{i\mathbf{q}\cdot\mathbf{R}_j}\ , \tag{10}$$

where

$$\langle\sigma|\mathbf{s}\cdot\mathbf{S}_j|\sigma'\rangle=\langle\sigma|s_zS_j|\sigma'\rangle=\sigma S_j\delta_{\sigma,\sigma'}\ .$$

Therefore,

$$M_{\mathbf{q},\sigma,\sigma'}=-\frac{xJ_q}{N}\sigma\delta_{\sigma,\sigma'}\sum_j S_j e^{i\mathbf{q}\cdot\mathbf{R}_j}\ . \tag{11}$$

Using the Fourier transform of S_i,

$$S(\mathbf{q})=\sum_j S_j e^{i\mathbf{q}\cdot\mathbf{R}_j}\ , \tag{12}$$

the matrix element becomes

$$M_{\mathbf{q},\sigma,\sigma'}=-\frac{xJ_{\mathbf{q}}}{N}\sigma\delta_{\sigma,\sigma'}S(\mathbf{q})\ . \tag{13}$$

It it known that $S(\mathbf{q})=0$, except for $\mathbf{q}=\mathbf{q}_0+\mathbf{Q}$, where $\mathbf{q}_0$ is a vector which characterizes the antiferromagnetic order and $\mathbf{Q}$ is any vector of the reciprocal lattice. In an antiferromagnetic of the third kind, $\mathbf{q}_0=(2\pi/a)(0,1,\frac{1}{2})$ or $(2\pi/a)(1,0,\frac{1}{2})$, and then we obtain

$$|M_{\mathbf{q},\sigma,\sigma'}|^2=\frac{x^2}{4}J_{\mathbf{q}}^2\sigma^2S^2\delta_{\sigma,\sigma'}\delta_{\mathbf{q},\mathbf{q}_0+\mathbf{Q}}\ . \tag{14}$$

Finally, the second-order perturbation correction is

$$\Delta E^{(2)}(\mathbf{k},\sigma)=\tfrac{1}{2}x^2\sigma^2S^2\sum_{\mathbf{q}\,(=\mathbf{Q}+\mathbf{q}_0)}\frac{J_{\mathbf{q}}^2}{E_0(\mathbf{k})-E_0(\mathbf{k}-\mathbf{q})}\ . \tag{15}$$

Assuming the same approximation[9] for $J_{\mathbf{q}}^2$ of both conduction and valence bands, the shift of the extrema of the two bands at $k=0$, in the parabolic approximation, can be given as

$$\Delta E_c^{(2)}=-x^2\frac{1}{4}\frac{m_c^*}{\hbar^2}S^2\sum_{\mathbf{q}\,(=\mathbf{Q}+\mathbf{q}_0)}\frac{J_{\mathbf{q}c}^2}{\mathbf{q}^2} \tag{16}$$

and

$$\Delta E_v^{(2)}=-x^2\frac{9}{4}\frac{m_v^*}{\hbar^2}S^2\sum_{\mathbf{q}\,(=\mathbf{Q}+\mathbf{q}_0)}\frac{J_{\mathbf{q}v}^2}{\mathbf{q}^2} \tag{17}$$

for conduction and valence band, respectively, where m_c^* and m_v^* are the effective masses of the conduction- and valence-band electrons.

The lowest value of $|\mathbf{q}|$ is obtained for $\mathbf{Q}=\mathbf{0}$ and it is $q=|\mathbf{q}_0|=0.58$ a.u. The $\mathbf{q}$ dependence of $J_{\mathbf{q}}$ is needed to evaluate $\Delta E_g=\Delta E_c^{(2)}+\Delta E_v^{(2)}$. In this investigation the classical approximation (9) is used with an appropriate value of $q_{\max}$. This is certainly smaller than 0.58 a.u., as will be shown in the following. On one hand, ΔE_g, for $q=0.58$ a.u. is 0.3 eV, which is incompatible with experimental data which give $\Delta E_g=0.045$ eV. On the other hand, the comparison between $J_{\mathbf{q}}$ for Mn^{2+} and $J_{\mathbf{q}}$ for

Eu^{2+} ($q_{\max}=0.72$) using the δ interaction and an adequate atomic wave function for these two cases, leads to $q_{\max}<0.4$ a.u. for Mn^{2+}. Therefore it can be concluded that the optical gap of $Cd_{1-x}Mn_xTe$ in the case of $0.6<x<0.73$ is not significantly affected by the exchange coupling at $T=0$.

B. High-temperature energy correction ($T\gg T_N$)

The square of the matrix element in expression (6) includes a double sum over the ion positions denoted by the indices l and m. At temperatures much higher than the Néel temperature, the correlation between ion spins can be neglected and only the $l=m$ terms contribute to $|M_{\mathbf{q},\sigma,\sigma'}|^2$. Consequently,

$$\sum_{\sigma'}|M_{\mathbf{q},\sigma,\sigma'}|^2 = x^2\frac{J_{\mathbf{q}}^2}{N^2}\sum_{\sigma'}\sum_{l}\sum_{m}\langle\sigma|\mathbf{s}\cdot\mathbf{S}_l|\sigma'\rangle\langle\sigma'|\mathbf{s}\cdot\mathbf{S}_m|\sigma\rangle \times e^{-i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_m)} \tag{18}$$

becomes

$$\sum_{\sigma'}|M_{\mathbf{q},\sigma,\sigma'}|^2 = x^2\frac{1}{4N}J_{\mathbf{q}c}^2S(S+1) \tag{19}$$

for the $s=\frac{1}{2}$ conduction band, and

$$\sum_{\sigma'}|M_{\mathbf{q},\sigma,\sigma'}|^2 = x^2\frac{5}{4N}J_{\mathbf{q}v}^2S(S+1) \tag{20}$$

for the $s=\frac{3}{2}$ valence band.

Hence, in the parabolic approximation, the second-order perturbation shift is

$$\Delta E_g^{(2)}=\Delta E_c^{(2)}+\Delta E_v^{(2)} = \frac{x^2S(S+1)}{2N\hbar^2}\sum_{\mathbf{q}\,(\neq 0)}\frac{m_c^*J_{\mathbf{q}c}^2+5m_v^*J_{\mathbf{q}v}^2}{\mathbf{q}^2}\ . \tag{21}$$

Now, replacing $\sum_{\mathbf{q}}$ by

$$\int\frac{V}{(2\pi)^3}d^3q$$

and using

$$\int\frac{1}{\mathbf{q}^2}J_{\mathbf{q}}^2d^3q=4\pi J_0^2q_{\max}\ ,$$

expression (21) becomes

$$\Delta E_g^{(2)}=-x^2\frac{VS(S+1)}{N(2\pi)^2\hbar^2}(m_c^*J_{0c}^2q_{c\max}+5m_v^2J_{0v}^2q_{v\max})\ . \tag{22}$$

C. Application of the results to $Cd_{1-x}Mn_xTe$

The effect of the magnetic order on the fundamental absorption edge can be obtained by taking the difference between the second-order correction at temperatures much below and much above the Néel temperature, respectively. As it was shown above, $\Delta E_{T\ll T_N}^{(2)}\sim 0$. Therefore

$$\Delta E_g=\Delta E_{T\gg T_N}^{(2)}-\Delta E_{T\ll T_N}^{(2)}\sim\Delta E_{T\gg T_N}^{(2)}\ .$$

This can be evaluated, for example, for $x=0.73$, by using the following constants: The lattice constant $a=0.638$ nm, the volume per magnetic ion, $V/N\sim 158$ a.u., the exchange coupling constants, $J_{0c}=N_0\alpha=16.2\times10^{-3}$ a.u. and $J_{0v}=N_0\beta/3=21.6\times10^{-3}$ a.u.,[20] and the effective masses $m_c^*=0.1m_0$ and $m_v^*=0.65m_0$,[21] with $m_0=0.5$ a.u. We obtain

$$\Delta E_g\sim[(9.7\times10^{-3})q_{c\max}]+0.19q_{v\max}\ , \tag{23}$$

where ΔE_g and $q_{\max}$ are, respectively, given in eV and a.u. Comparing with the experimental value of ΔE_g and assuming the same order of magnitude $q_{\max}$ for $q_{v\max}$ and $q_{c\max}$, we obtain $q_{\max}\sim 0.24$ a.u. This type of behavior can be expected to be valid for different compositions of this semimagnetic semiconductor with the same value, $q_{\max}=0.24$ a.u. In Table I the calculated value of the magnetic shift for different compositions are given and compared with the measured values. One can see that the agreement is quite acceptable.

TABLE I. Comparison between measurements and calculated value of the magnetic blue shift using $q_{\max}=0.24$ for different concentrations.

Concentration	ΔE (meV)	
x	Calculated	Measured
0.73	45	45
0.63	31	33
0.4	17	13
0.3	7	7

IV. CONCLUSION

In the case of $Cd_{1-x}Mn_xTe$, a blue shift of the fundamental absorption was measured as a function of the magnetic ion concentration. An analysis of the experimental data was carried out using the rigid-ion spin model.

In this case a second-order perturbation correction can be evaluated at temperatures $T\ll T_N$ and $T\gg T_N$. The calculations indicate that in the first case there is no significant effect due to magnetic order, but at temperatures high compared to the transition temperature there is a significant correction. Using the calculated values the blue shift of the fundamental absorption could be satisfactorily attributed to magnetic disorder.

For completely disordered ion spins, the ion-electron spin exchange shifts the absorption edge toward the red. This phenomenon, however, decreases with temperature due to magnetic ordering and increased rigidity of the lattice, thus leading to the extra blue shift at low temperatures.

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[1] See references cited in P. Wachter, *Handbook on the Physics and Chemistry of Rare Earths* (North-Holland, New York, 1979), Vol. 2, p. 554.

[2] H. H. Chou and H. Y. Fan, Phys. Rev. B **10**, 901 (1974).

[3] G. Busch and P. Wachter, Phys. Kondens. Mater. **5**, 232 (1966); Solid State Commun. **8**, 1133 (1970).

[4] G. Busch, P. Junod, and P. Wachter, Phys. Lett. **12**, 11 (1964).

[5] B. E. Argyle, J. C. Suits, and M. Freiser, Phys. Rev. Lett. **15**, 822 (1965).

[6] G. Harbeke and H. Pinch, Phys. Rev. Lett. **17**, 1090 (1966).

[7] G. Harbeke, S. B. Berger, and F. P. Emmenegger, Solid State Commun. **6**, 533 (1968).

[8] H. W. Lehmann and F. P. Emmenegger, Solid State Commun. **7**, 965 (1969).

[9] F. Rys, J. S. Helman, and W. Baltensperger, Phys. Kondens. Mater. **6**, 105 (1967).

[10] J. Alexander, J. C. Helman, and J. Balberg, Phys. Rev. B **13**, 304 (1975).

[11] T. Kambara and Y. Tanabe, J. Phys. Soc. Jpn. **28**, 628 (1970).

[12] R. R. Galazka, S. Nagata, and P. H. Keesom, Phys. Rev. B **22**, 3344 (1980).

[13] Nguyen The Koi and J. A. Gaj, Phys. Status. Solidi. B **83**, K133 (1977).

[14] M. El Amrani, J. P. Lascaray, and J. Diouri, Solid State Commun. **45**, 351 (1983).

[15] G. Rebman, C. Rigaux, G. Bastard, M. Menant, R. Triboulet, and W. Giriat, in *Proceedings of the Sixteenth International Conference on the Physics of Semiconductors, Montpellier, 1982,* edited by M. Averous (North-Holland, Amsterdam, 1983).

[16] J. P. Lascaray, J. Diouri, M. El Amrani, and D. Coquillat, Solid State Commun. **47**, 709 (1983).

[17] R. Triboulet and G. Didier, J. Cryst. Growth **52**, 614 (1980).

[18] K. Zanio, Semicond. Semimet. **13**, 99 (1978).

[19] Y. P. Varshni, Physica (Utrecht) **34**, 149 (1967).

[20] J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).

[21] A. Twardowski and J. Ginter, Phys. Status. Solidi. B **110**, 47 (1982).