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ANISOTROPY IN THE TWO-PHOTON ABSORPTION SPECTRUM IN CdS

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An expression for the two-photon inter-band absorption coefficient $K_2(\omega_2)$ in a CdS crystal has been obtained for polarized as well as unpolarized light beams. The frequency dependence of $K_2(\omega_2)$ in CdS was measured at room temperature for various light beam polarizations and for unpolarized light. The experimentally-observed anisotropy of two-photon absorption can essentially be explained by the theory proposed. A change in the frequency dependence of $K_2(\omega_2)$ from the usual form $K_2(\omega_2) \sim (\hbar\omega_1 + \hbar\omega_2 - E_g)^{1/2}$ for CdS to the form $K_2(\omega_2) \sim (\hbar\omega_1 + \hbar\omega_2 - E_g)^{3/2}$ under certain conditions of variation of the light beam polarizations has been observed and explained for the first time. The effective electron mass $m_j = 0.3m$ in the conduction bands lying 6.2 eV above the top of the upper valence band was determined. The experimentally measured two-photon absorption cross section for CdS is $\sigma_2 \approx 1.4 \cdot 10^{-47}$ cm^4 sec.

1. INTRODUCTION

THE inter-band two-photon absorption in CdS was first observed by Braunstein and Ockman[1]. Later, Konyukhov, Kulevskiĭ, and Prokhorov[2] measured the two-photon absorption coefficient K_2 in CdS at the ruby-laser frequency dependence of $K_2(\omega_2)$ of the two-photon absorption coefficient in CdS, using a neodymium laser and a xenon flash lamp as light sources. Independently, Regensburger and Panizza[4] made similar studies and in addition measured the absorption anisotropy for the two polarization directions of the laser ($\mathbf{e}_1$) and the xenon lamp radiation ($\mathbf{e}_2$) with respect to the optical axis c of the CdS crystal. However, the case $\mathbf{e}_1 \perp \mathbf{c}$ and $\mathbf{e}_2 \perp \mathbf{c}$ could not be interpreted in[4] unambiguously. Regensburger and Panizza[4] made no distinction between the two alternatives $\mathbf{e}_1 \parallel \mathbf{e}_2$ and $\mathbf{e}_1 \perp \mathbf{e}_2$, when $\mathbf{e}_1 \perp \mathbf{c}$ and $\mathbf{e}_2 \perp \mathbf{c}$, although from crystal symmetry considerations alone it would follow that the absorption coefficients may differ considerably when $\mathbf{e}_1 \parallel \mathbf{e}_2$ and $\mathbf{e}_1 \perp \mathbf{e}_2$. This difference was established experimentally.

The experimental data for two-photon absorption in semiconductors are usually compared with the calculated K_2 values derived on the basis of the Braunstein theory[1,5]. This particular theory has two basic disadvantages. First, only the conduction bands are considered from the outset as intermediate bands, although in theory the intermediate valence bands may contribute even more to the two-photon absorption than the conduction bands. The other drawback of the Braunstein theory is the incorrect approximation of the composite matrix element (for details see next section).

This paper, which is a continuation of earlier studies[2,3], will discuss the experimental and theoretical aspects of the two-photon inter-band absorption anisotropy in CdS.

2. CALCULATION OF THE TWO-PHOTON ABSORPTION COEFFICIENT

Let two light beams propagate in a crystal, one with frequency ω_1, wave vector $\mathbf{q}_1$, and polarization $\mathbf{e}_1$ from a laser and the other with frequency ω_2, wave vector $\mathbf{q}_2$, and polarization $\mathbf{e}_2$ from a conventional source (xenon lamp). The respective photon densities are denoted by N_1 and N_2. Furthermore, κ_1 and κ_2 will represent the dielectric constant of the crystal at the respective frequencies ω_1 and ω_2. For simplicity, we shall regard κ as a scalar quantity.

The general expressions for the two-photon absorption coefficient $K_2(\omega_2)$ can be easily obtained from the theory of two-quantum transitions[6]. In the dipole approximation we have:

$$K_2(\omega_2) = \frac{\sqrt{\varkappa_2}}{cN_2} W, \tag{1}$$

$$W = \frac{1}{\hbar}\left(\frac{e}{m}\right)^4 \frac{\hbar N_1}{\omega_1\varkappa_1}\frac{\hbar N_2}{\omega_2\varkappa_2}\sum_{cv}\int |M_{cv}(\mathbf{k})|^2 \times \delta[\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k}) - \hbar(\omega_1+\omega_2)]\,d\mathbf{k} \tag{2}$$

where the composite matrix element is given by

$$M_{cv}(\mathbf{k}) = \sum_j \left[\frac{(\mathbf{e}_1\mathbf{p}_{cj}(\mathbf{k}))(\mathbf{p}_{jv}(\mathbf{k})\mathbf{e}_2)}{\varepsilon_j(\mathbf{k}) - \varepsilon_v(\mathbf{k}) - \hbar\omega_2} + \frac{(\mathbf{e}_2\mathbf{p}_{cj}(\mathbf{k}))(\mathbf{p}_{jv}(\mathbf{k})\mathbf{e}_1)}{\varepsilon_j(\mathbf{k}) - \varepsilon_v(\mathbf{k}) - \hbar\omega_1}\right]. \tag{3}$$

The subscripts c and v denote the conduction and valence bands between which a two-quantum transition can take place. The summation in (3) extends over all intermediate bands j, including bands c and v. $\mathbf{p}_{jj'}(\mathbf{k})$ represents the matrix element of the electron momentum for a transition between the energy bands j′ and j at the point $\mathbf{k}$ of the Brillouin zone. Furthermore, $\epsilon_j(\mathbf{k})$ is the energy of an electron with wave vector $\mathbf{k}$ in the band j. The remaining subscripts are standard.

In a noncentrosymmetric crystal, such as CdS, there exist for each pair of bands c and v intermediate bands j for which the matrix elements $\mathbf{p}_{cj}(0) \equiv \mathbf{p}_{cj}$ and $\mathbf{p}_{jv}(0) \equiv \mathbf{p}_{jv}$ both differ from zero. Assuming that the vector $\mathbf{k}$, determined from the δ function in Eq. (2) is close to the center of the Brillouin zone ($|\mathbf{k}| \ll 1/d$, where d is the lattice constant), the matrix elements $\mathbf{p}_{cj}(\mathbf{k})$ and $\mathbf{p}_{jv}(\mathbf{k})$ in Eq. (3) can be replaced by $\mathbf{p}_{cj}$ and $\mathbf{p}_{jv}$. Disregarding thus the bands j for which $\mathbf{p}_{cj}$ or $\mathbf{p}_{jv}$ are zero (except for bands c and v themselves) and assuming that the effective masses of the electrons and holes are isotropic, the following expression for the composite matrix element can be obtained:

$$M_{cv}(\mathbf{k})=\sum_j\left[\frac{(\mathbf{e}_1\mathbf{p}_{cj})(\mathbf{p}_{jv}\mathbf{e}_2)}{\varepsilon_j(\mathbf{k})-\varepsilon_v(\mathbf{k})-\hbar\omega_2}+\frac{(\mathbf{e}_2\mathbf{p}_{cj})(\mathbf{p}_{jv}\mathbf{e}_1)}{\varepsilon_j(\mathbf{k})-\varepsilon_v(\mathbf{k})-\hbar\omega_1}\right]$$

$$+\hbar\frac{m}{m_{cv}}\left[\frac{(\mathbf{e}_1\mathbf{k})(\mathbf{p}_{cv}\mathbf{e}_2)}{\hbar\omega_1}+\frac{(\mathbf{e}_2\mathbf{k})(\mathbf{p}_{cv}\mathbf{e}_1)}{\hbar\omega_2}\right] \qquad (4)$$

where m_{cv} is the reduced mass of the electron in the conduction band c and of the hole in the valence band v. The summation over j in Eq. (4) extends over all conduction and valence bands, except for bands c and v.

As mentioned in the introduction, in the first calculations of the two-photon absorption coefficient in semiconductors made by Braunstein[5], and specifically for CdS by Braunstein and Ockman[1], only one conduction band differing from the band c has been considered as an intermediate band, i.e., both the second term and all but one term in the sum over j were neglected in the right-hand side of Eq. (4). The incorrectness of this procedure was pointed out by Bunkin[7] in connection with Kleinman's work[8], in which a similar approach was followed for a calculation of the two-photon absorption by impurity centers. On the other hand, the calculations[9] in which the composite matrix element $M_{cv}(k)$ is approximated only by the second term of Eq. (4) obviously underestimates the absorption coefficient $K_2(\omega_2)$, in particular when the total quantum energy $\hbar(\omega_1 + \omega_2)$ is not large.

The band spectrum of a CdS crystal has been studied, in particular, by Thomas and Hopfield[10]. Equations for the periodic parts u of the Bloch functions near **k** = 0 are given below; they can be derived from the data of Thomas and Hopfield[10] (with the conventional subscripts for the bands).

$$c\Gamma_7:\ u_1=S_c\alpha,\quad u_2=S_c\beta,\quad \varepsilon_c(0)=\varepsilon_g=2{,}58\ \mathrm{eV}^{1)};$$

$$v\Gamma_9A:\quad u_1=\sqrt{\frac{1}{2}}(X_v+iY_v)\alpha,\quad u_2=-\sqrt{\frac{1}{2}}(X_v-iY_v)\beta,$$
$$\varepsilon_v(0)=\varepsilon_A=0;$$

$$v\Gamma_7B:\quad u_1=\sqrt{\frac{1}{6}}(X_v+iY_v)\beta-\sqrt{\frac{2}{3}}\frac{Z_v+\gamma_vS_v}{\sqrt{1+\gamma_v^2}}\alpha,$$

$$u_2=-\sqrt{\frac{1}{6}}(X_v-iY_v)\alpha-\sqrt{\frac{2}{3}}\frac{Z_v+\gamma_vS_v}{\sqrt{1+\gamma_v^2}}\beta,$$
$$\varepsilon_v(0)=\varepsilon_B=-0{,}016\ \mathrm{eV};$$

$$v\Gamma_7C:u_1=\sqrt{\frac{1}{3}}(X_v+iY_v)\beta+\sqrt{\frac{1}{3}}\frac{Z_v+\gamma_vS_v}{\sqrt{1+\gamma_v^2}}\alpha,$$

$$u_2=\sqrt{\frac{1}{3}}(X_v-iY_v)\alpha-\sqrt{\frac{1}{3}}\frac{Z_v+\gamma_vS_v}{\sqrt{1+\gamma_v^2}}\beta,$$
$$\varepsilon_v(0)=\varepsilon_C=-0.073\ \mathrm{eV}. \qquad (5)$$

Here, S is a function similar to the atomic s function, X, Y, and Z are functions similar to the atomic p functions, α and β are spin functions, and γ_V is the "mixing" parameter of the functions Z_V and S_V.

Higher conduction bands and lower valence bands have been studied experimentally in[11,12]. Of all bands located in the interval of approximately ± 10 eV above and below the top of the valence band A, the three conduction bands located 6.2 eV above the top of the band A can contribute the most. The symmetry of these bands is similar to that of bands A, B, and C. Therefore, the functions u are determined from the same formulas (5), in which it is only necessary to replace S_V, X_V, Y_V, Z_V and γ_V respectively by S_j, X_j, Y_j, Z_j, γ_j, and ϵ_A, ϵ_B, ϵ_C by ϵ_j. The contributions of other bands in the sum over j in (4) were neglected.

Straightforward but cumbersome calculations lead to an equation for the two-photon absorption coefficient $K_2(\omega_2)$ for various light beam polarizations $\mathbf{e}_1$ and $\mathbf{e}_2$, as well as for the unpolarized light from a conventional (second) source.[2)] It follows that if the effective masses m_j for all three bands j are considered equal, as well as $\epsilon_j(0)$ = 6.2 eV, then the absorption coefficient $K_2(\omega_2)$ is determined by the four unknown parameters:

$$m_j,\quad |\gamma_j|,\quad |\zeta_{cj}\zeta_{jv}|\ \text{and}\ |\zeta_{vj}\zeta_{jc}|,$$

where

$$\zeta_{cj}\equiv\langle S_c|p_z|Z_j\rangle,\quad \zeta_{jv}\equiv\langle S_j|p_z|Z_v\rangle,\quad \zeta_{vj}\equiv\langle S_v|p_z|Z_j\rangle.$$

These four parameters can be determined from four experimental values of $K_2(\omega_2)$, and then theoretical plots of $K_2(\omega_2)$ can be drawn for various $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{q}_1$, $\mathbf{q}_2$.

The remaining parameters necessary for the calculation of the two-photon absorption coefficient are either known or can be determined from experiments on one-photon absorption in CdS[1,10]:

$$m_c=0.2m,\quad m_A=m_B=m_C\equiv m_v=-5m,$$

$$\sqrt{\varkappa_1}=\sqrt{\varkappa_2}=2.6,\quad |\gamma_v|=0{,}15,\quad |\zeta_{cv}|=5\cdot10^{-20}\ \text{g-cm/sec},$$

where m_A, m_B and m_C are the effective electron masses in the valence bands and $\zeta_{cv}\equiv\langle S_c|p_z|Z_v\rangle$.

We have also analyzed the contribution of the exiton intermediate states to $K_2(\omega_2)$. It proved to be purely resonant and could be disregarded in our case.

3. DESCRIPTION OF THE EXPERIMENT

Two light sources were used in the experimental study of the polarization dependence of the two-photon absorption coefficient in CdS, in the frequency interval corresponding to a total quantum energy $\hbar(\omega_1 + \omega_2)$ from 2.5 to 3.5 eV. One of them was a Q-switched neodymium-glass laser (quantum energy $\hbar\omega_1$ = 1.17 eV) with an output energy 1.5 J and a pulse length 30 nsec. Another source was a xenon flash lamp (IFK-2000).

In order to obtain a fully polarized laser radiation output, a pile of plane-parallel plates was inserted at the Brewster angle in the laser resonator. Light from the flash lamp was polarized by means of a Glan prism. Otherwise, the experimental setup was the same as that described previously[3].

Measurements of the two-photon absorption coefficient were made[3)] for five different relative orientations of the vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ of the radiation polarization and the optical axis c of the CdS crystal. Results from these measurements are presented in Fig. 1 and 2.

[1)] The width of the forbidden band ϵ_g in CdS at room temperature is 2.45 eV.

[2)] The dependence of K_2 on the polarization can be determined from the equations of Inoue and Toyozawa [13] if only one intermediate band makes a substantial contribution to the two-photon absorption. However, this is not the case for CdS.

[3)] All the measurements were made at room temperature.

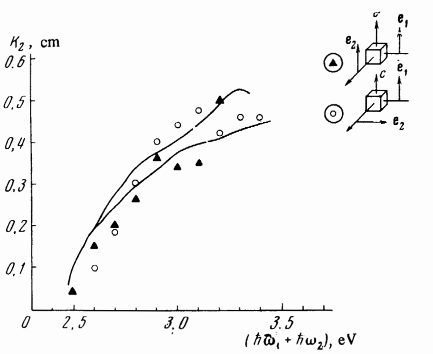

FIG. 1. The dependence of two-photon absorption coefficient K_2 on the total quantum energy $\hbar\omega_1+\hbar\omega_2$ for various polarizations of the light beams, The solid curves depict the theoretical dependence.

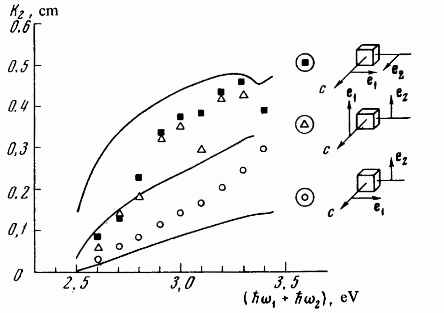

FIG. 2. The dependence of the two-photon absorption coefficient K_2 on the total quantum energy $\hbar\omega_1+\hbar\omega_2$ for various polarizations of the light beams. The solid lines show the theoretical dependence.

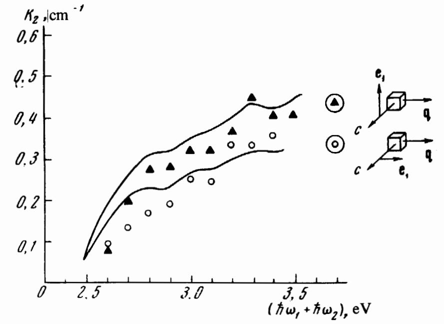

FIG. 3. The dependence of the two-photon absorption coefficient K_2 on the total quantum energy $\hbar\omega_1+\hbar\omega_2$ for unpolarized radiation of a xenon flash lamp. The solid lines depict the theoretical dependence.

In addition, the two-photon absorption coefficient was measured for the unpolarized light at two directions q_2 of the lamp radiation with respect to the vector e_1 and the axis c. The results are given in Fig. 3.

Furthermore, the angular dependence of the two-photon absorption coefficient of ruby laser radiation ($\hbar\omega$ = 1.79 eV) was investigated. The appropriate experimental arrangement is straightforward and is therefore not described here. The experimental results are shown in Fig. 4. It should be noted that the experimental accuracy of the absorption coefficient is 15% at a photon energy $\hbar\omega_2$ = 1.7–1.8 eV and deteriorates to 25% at the ends of the frequency range under study.

4. DISCUSSION OF THE RESULTS

An analysis of the results of the experimental and theoretical investigations of the two-photon absorption spectrum in a CdS crystal, shown in Figs. 1–4, leads to the following conclusions:

1. For both light sources, an appreciable absorption anisotropy occurred for the polarization directions of both radiations with respect to the optical crystal axis c (Fig. 1, 2), including the cases $e_1 \perp c$, $e_2 \perp c$, $e_1 \perp e_2$ and $e_1 \perp c$, $e_2 \perp c$, and $e_1 \parallel e_2$ (Fig. 2), which are not differentiated in the work by Regensburger and Panizza[4].

2. The frequency dependence of the absorption coefficient $K_2(\omega_2)$ at $e_1 \perp c$, $e_2 \perp c$, and $e_1 \perp e_2$ differs considerably from the $K_2(\omega_2)$ dependence for other cases. This can be explained in the following manner: In general, the two-photon absorption coefficient in CdS can be presented in the form

$$K_2(\omega_2)=\alpha[\hbar(\omega_1+\omega_2)-\varepsilon_g]^{1/2}+\beta[\hbar(\omega_1+\omega_2)-\varepsilon_g]^{3/2}, \qquad (6)$$

where the coefficients α and β depend on the polarization directions of both radiations, as well as on the frequency ω_2. However, for low frequencies ω_2, the dependence of α and β on ω_2 is quite weak and can be disregarded. In all cases except $e_1 \perp c$, $e_2 \perp c$, and $e_1 \perp e_2$, the first term in the right-hand side of Eq. (6) makes the essential contribution to $K_2(\omega_2)$. The contribution of the second term is only noticeable when $\hbar \gtrsim 2$ eV. Thus, for not too high ω_2 we have

$$K_2(\omega_2)\sim[\hbar(\omega_1+\omega_2)-\varepsilon_g]^{1/2}.$$

However, when $e_1 \perp c$, $e_2 \perp c$, and $e_1 \perp e_2$, the first term in Eq. (6) for $K_2(\omega_2)$ is small compared to the second, so that

$$K_2(\omega_2)\sim[\hbar(\omega_1+\omega_2)-\varepsilon_g]^{3/2}.$$

3. The two-photon polarization anisotropy exists also for the unpolarized radiation at various directions q_2 of lamp radiation with respect to the optical axis c and the direction e_1 of the laser radiation (Fig. 3). This anisotropy has not been studied in[4].

4. A manifest anisotropy (Fig. 4) occurs for the two-photon absorption of ruby-laser radiation in CdS. As the calculation shows, the angular dependence of the absorption coefficient is given in this case by the expression

$$K_2(\varphi)\sim[0.98+0.30\cos^2\varphi-0.84\cos^4\varphi], \qquad (7)$$

where φ is the angle between the polarization direction of the ruby-laser emission and the optical axis of the crystal.

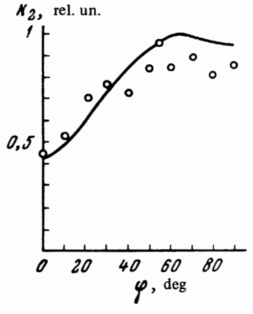

FIG. 4. The dependence of the two-photon absorption coefficient K_2 of ruby laser radiation on the angle between the radiation polarization direction and the optical axis of the crystal. The solid lines depict the theoretical dependence.

5. The two-photon absorption cross section is

$$\sigma_2(\omega_2) = \frac{\pi^2\hbar^2 K_2(\omega_2)}{3F_1\Delta\omega_2|m_{cv}|\{2m_{cv}[\hbar(\omega_1+\omega_2) - \varepsilon_g]\}^{1/2}} \tag{8}$$

where F_1 is the photon flux density of the laser radiation, and $\Delta\omega_2$ is the spectral interval, corresponding to the given $K_2(\omega_2)$ and equals $1.4 \cdot 10^{-47}$ cm^4-sec if $\hbar\omega_2 = 1.6$ eV and $F_1 = 1.8 \cdot 10^{26}$ cm^{-2}-sec^{-1}, ($e_1 \parallel c$).

6. Special note should be taken of the possibility of employing two-photon spectroscopic procedures for finding certain semiconductor energy-structure parameters that are often difficult to determine by one-photon spectroscopic techniques. For example, in this particular experiment the following characteristic parameters were obtained for three conduction bands, Γ_7, Γ_8, Γ_9 located 6.2 eV above the top of the highest valence band Γ_9A: the effective electron mass $m_j = 0.3m$, and the "mixing" parameter $|\gamma_j| = 0.8$ of the functions Z_j and S_j in these bands. For the matrix elements of the transitions v → j → c and c → j → v we found $|\zeta_{cj}\zeta_{jv}| = 5 \times 10^{-38}$ g^2-cm^2-sec^{-2} and $|\zeta_{vj}\zeta_{jc}| = 1 \cdot 10^{-37}$ g^2-cm^2-sec^{-2}.

7. If one considers, on the one hand, the number of simplifying assumptions made in the calculation of the two-photon absorption coefficient (i.e, the isotropy of the effective electron masses in all bands under investigation, the isotropy of the dielectric constant κ, the neglect of the remaining intermediate bands, etc.), and on the other hand the relatively low accuracy of the absorption-coefficient measurements, which furthermore determines the accuracy of theoretical $K_2(\omega_2)$ curves drawn in Figs. 1 to 4, then the agreement between theoretical and experimental data can be regarded as satisfactory in all the cases studied. It should be pointed out that our calculation can not claim good agreement with the experimental data at sufficiently high values of ω_2. In fact, a simple estimates show that already at $\hbar(\omega_1 + \omega_2) \approx 3$ the wave vector of the electron (and the hole) is $|\mathbf{k}| = 2 \times 10^7$ cm^{-1}, i.e., it is quite far from the center of the Brillouin zone. In this case it is necessary to take into account the non-parabolic character of the bands, and accordingly take into account the dependence of the periodic parts u of the Bloch functions on the wave vector **k**.

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[1] R. Braunstein and N. Ockman, Phys. Rev. **134**, A499 (1964).

[2] V. K. Konyukhov, L. A. Kulevskiĭ and A. M. Prokhorov, Dokl. Akad. Nauk SSSR **164**, 1012 (1965) [Sov. Phys. Dokl. **10**, 943 (1966)].

[3] V. K. Konyukhov, L. A. Kulevskiĭ and A. M. Prokhorov, Dokl. Akad. Nauk SSSR **173**, 1048 (1967) [Sov. Phys.-Dokl. **12**, 354 (1967)].

[4] R. J. Regensburger and E. Panizza, Phys. Rev. Lett. **18**, 113 (1967).

[5] R. Braunstein, Phys. Rev. **125**, 475 (1962).

[6] W. Heitler, The Quantum Theory of Radiation, Oxford, 1953.

[7] F. V. Bunkin, Zh. Eksp. Teor. Fiz. **50**, 1685 (1966) [Sov. Phys.-JETP **23**, 1121 (1966)].

[8] D. Kleinman, Phys. Rev. **125**, 87 (1962).

[9] N. G. Basov, A. Z. Grasyuk, I. G. Zubarev, V. A. Katulin and O. N. Krokhin, Zh. Eksp. Teor. Fiz. **50**, 551 (1966) [Sov. Phys.-JETP **23**, 366 (1966)].

[10] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[11] M. Cardona and G. Harbeke, Phys. Rev. **137**, A1467 (1965).

[12] N. B. Kinding and W. E. Spicer, Phys. Rev. **138**, A561 (1965).

[13] M. Inoue and Y. Toyozawa, J. Phys. Soc. Japan **20**, 363 (1965).

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