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Orientation Dependence of *K*-Absorption Extended Fine Structure of a Single Crystal of Germanium†

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The fine structure of the *K*-absorption spectrum of a Ge single crystal was investigated with 90% polarized radiation. A single-crystal spectrometer and a fine focus x-ray tube were used. Absorption curves were obtained up to 300 eV from the main edge for five different positions of the absorber. No shifts of the extrema of the fine structure were observed. This experimental result is in agreement with theoretical considerations given here which show that absorption is independent of orientation for cubic symmetry and also for other cases of symmetry.

INTRODUCTION

VARIOUS theories were proposed to explain the extended fine structure on the short-wavelength side of the *K*-absorption edge in solids. Kronig's theory[1] is based on the band model of solids assuming that the absorption coefficient depends mainly on the density of unoccupied states and that the variations of the transition probability may be neglected. The density of states is influenced mainly by the fact that certain wave vectors of the photoelectron are forbidden. In a cubic crystal, these forbidden states are defined by

$$E=(h^2/8ma^2\cos^2\theta)(\alpha^2+\beta^2+\gamma^2)\,. \qquad (1)$$

Here h is the Planck constant, a is the lattice constant, m is the mass of the electron, and θ is the angle of incidence of the photoelectron on the $(\alpha\beta\gamma)$ plane. It follows from (1) that the minimum energy for each $(\alpha\beta\gamma)$ plane is given by

$$E_{\min}=(h^2/8ma^2)(\alpha^2+\beta^2+\gamma^2)\,. \qquad (2)$$

According to Kronig's theory, the fluctuations are located in the neighborhood of the $E_{\min}$ values given by (2). He calculates the fluctuation for polycrystalline material. Evidently, in this case, the absorption coefficient is independent of orientation.

Hayasi[2] approaches the problem from another point of view. He predicts fine structure due to standing waves located in the neighborhood of the absorbing atom. According to him, an absorption maximum can occur when the de Broglie wave of the photoelectron satisfies Bragg reflection condition from a $(\alpha\beta\gamma)$ plane for normal incidence, i.e.,

$$n\lambda=2d_{\alpha\beta\gamma}\,. \qquad (3)$$

Then, for $n=1$, in case of a simple cubic lattice the energy corresponding to this wavelength is given by

$$E=(h^2/8ma^2)(\alpha^2+\beta^2+\gamma^2)\,. \qquad (4)$$

We see that Eq. (4) is identical with Eq. (2), but contrary to Kronig's theory, absorption maximum is predicted at this point.

Shiraiwa *et al.*[3] took into account changes of transition probability (relative to the case of a free atom) due to neighboring atoms which scatter the electron wave. They considered both elastic and inelastic scattering and also scattering of higher orders. Using Kronig's equation for molecular gas,[4] they calculated the transition probability for polycrystalline material averaging over all directions of ejection. Under some simplifying assumptions they obtained for energies more than 30 eV above the edge an explicit equation

$$(k)=\frac{2mV_0a^3}{\hbar^2}\left[\frac{\cos 2ka}{(2ka)^2}-\frac{\sin 2ka}{(2ka)^3}\right]\sum_s\frac{N_s}{r_s{}^2}(\sin 2kr_s)e^{-\mu r_s} \qquad (5)$$

where V_0 is the depth of the potential well of each atom, a is the radius of the well, k is the wave number of the electron wave, N_s is the number of atoms which are at equal distances r_s from the absorbing atom, and μ is equal to $(\sigma_{\mathrm{el}}+\sigma_{\mathrm{inel}})\rho$ where σ_{el} and σ_{inel} is the cross-section for elastic and inelastic scattering, respectively, and ρ the number of atoms per unit volume.

Kozlenkov,[5] like Shiraiwa[3] and Kostarev,[6] assumes that the fine structure is due to the presence of neighboring atoms. He bases his calculations of the fine structure on nonmonotonous changes of the transition probabilities due to scattering in the field of the absorbing atom and its neighbors. He calculates more accurately than did Shiraiwa and Kostarev the amplitudes of the final eigenfunction and the phase shifts. To simplify the calculations, he averages the fields over-all directions and so his calculations are good for polycrystalline material only. He shows that results of Shiraiwa and Kostarev are only approximations to his work.

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[4] R. De L. Kronig, Z. Physik **75**, 468 (1932).

[5] A. I. Kozlenkov, Bull. Acad. Sci. USSR Ser. Phys. **25**, 968 (1961).

[6] A. I. Kostarev, Zh. Eksperim. i Teor. Fiz. **11**, 60 (1941); *ibid.*, **19**, 431 (1949); *ibid.*, **21**, 917 (1951); *ibid.*, **22**, 628 (1952).

TABLE I. The extrema of the fine structure measured from the main edge in eV.

Extrema	Present measurements 90% polarization					Singh[a] 38.2% polarization		El-Hussaini and Stephenson[b] 7% polarization			Doran and Stephenson[c] 7% polarization	Hulubei and Cauchois[d]
	k parallel to [1 1 1] axis			*k* parallel to [1 1 0] axis		*k* parallel to [1 1 1] axis		*k* parallel to [1 1 1] axis Unknown orientations			*k* parallel to [1 1 1] axis	Polycrystalline material
	A at 15° to $[1\bar{1}0]$	A parallel to $[1\bar{1}0]$	A at 30° to $[1\bar{1}0]$	$A\|[1\bar{1}0]$	$A\|[001]$	A at 15° to $[1\bar{1}0]$	A at 30° to $[1\bar{1}0]$					
A	6	6	6			6	6.5	6		6	6.2	5.7
a	8	8	8			8	9					
B	9	9	9			12	13					
b	15	18	17		19	21	19	17.7		17.7	15.7	14.6
C	23	24	24		24	27	22	24		25	25.2	20
c	30	33	31	31	31	31	25	34		36	31.7	28
D	38	38	36	36	38	35	33					
d	41	42	39	41	42	39	40					
E	48	51	50	52	51	47	52	45	48	47	51	39
e	60	64	59	60	61	55	72	59	60	61	61	47
F	75	78	76	76	76	70	88	79	78	73	79	77
f	89	93	93	92	91	83	96					
G	98	98	100	99	99	99	108					
g	114	111	116	111	113	115	126	113	114	108	114	108
H	133	135	136	136	133	157	143	151	138	138	147	157
h	177	168	171	177	175	175	177	196	185	169	186	193
I	216	214	216					227	222	192	223	225
i	254	251	249					278	254	211	271	
J	276	273	282									
j												287

[a] Ref. 9. [b] Ref. 8. [c] Ref. 10. [d] Ref. 11.

Leder *et al.*[7] tried to connect the fluctuations near the edge with plasma oscillations.

In all the above mentioned theoretical papers, comparison with experiment has been carried out for polycrystalline material only. Kronig, however, already stated (Ref. 1, p. 205) that "for a single crystal and polarized radiation changes in the distribution will occur." It has generally been concluded from Kronig's theory and from the other theories that, for a single crystal absorber, changes in the absorption coefficient will occur with change of direction of the polarization vector in the absorbing crystal, since, in a single crystal, the probability of ejection of a photoelectron in a given direction depends on the direction of the polarization vector relative to the crystal axes.

Experiments with single crystals were carried out by El-Hussaini and Stephenson[8] and by Singh[9] with a Ge absorber. El-Hussaini and Stephenson used a double crystal spectrometer and the Ge was cut parallel to the (1 1 1) plane, brought to a thickness of 12 μ and put between the two reflecting crystals of the spectrometer. The reflection was from the cleavage planes of calcite. The polarization was 7% and the width of W $L\gamma_1$ line at the half-maximum of the intensity was 10.6 eV. They measured 28 counts/sec without absorber. For each point 5000 counts with and without absorber were taken. They reported considerable shifts of absorption extrema (see Table I) for three different orientations of the Ge crystal). The Ge crystal was rotated from the initial position by 45° and by 90°. They thought this result surprising because of the small polarization.

Singh[9] in his work used a double crystal spectrometer with quartz as the first crystal [reflection from the $(2 0 \bar{2} 3)$ plane] and calcite as the second crystal [reflection from the (2 1 1) plane]. A thin single crystal of Ge cut parallel to the (1 1 1) plane was put between the two crystals of the spectrometer. The full width of the W $L\gamma_1$ line at the half-maximum of the intensity was 13.4 eV. With these crystals he obtained without absorber 15 counts/sec and reported 38.2% polarization. 2000 counts without and 1000 counts with the absorber were taken for each point on the curve. Singh examined the fine structure for two orientations: (1) When the polarization vector was at 16°±2° with the $[1\bar{1}0]$ direction and (2) when it was 29°±2°. He again reported considerable shifts of the peaks of the order of magnitude of 10 eV and compared the results with calculations according to Kronig's theory. The total number of fluctuations which he reported was larger than that reported by El-Hussaini and Stephenson,[8] Doran and Stephenson[10] and Hulubie and Cauchois.[11]

However, as will be shown in the Appendix, it follows from symmetry considerations that no shifts are to be expected in a cubic crystal, or in the cases when the x-ray beam is parallel to a 3-, 4-, or 6-fold symmetry

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[7] L. B. Leder, H. Mendlowitz, and L. Marton, Phys. Rev. **101**, 1460 (1956); L. Marton, Rev. Mod. Phys. **28**, 172 (1956).

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[9] J. N. Singh, Phys. Rev. **123**, 1724 (1961).

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[11] H. Hulubei and Y. Cauchois, Compt. Rend. **211**, 316 (1940).

axis. Thus, to substantiate this claim, we carried out similar (but more accurate) measurements than those of El-Hussaini and Stephenson[8] and Singh.[9] No shifts were observed.

EXPERIMENTAL

A. Spectrometer

The investigation was carried out with a single crystal spectrometer adapted to a fine focus tube (Hilger and Watts, London). The effective width of the focus was about 0.01 mm and the length 1 mm. A single spectrometer slit of 0.065±0.01 mm width was used. Distance between the focus and the slit was 30±0.5 cm; the angular aperture was thus less than 1 min. The distance from the slit to the reflecting crystal was 15 cm. The radiation was detected by a G.E. krypton-filled proportional counter with detecting unit (2 S.P.G. counter tube, scaler, power supply, ratemeter, and preamplifier). Continuous radiation from a wolfram anticathode was used. The x rays were reflected from the (4 2 0) plane of a LiF crystal (supplied by Semiconductor Incorporated) having external planes (1 0 0). Thus, the Bragg angle for the region of the spectrum investigated is from $38.3°-37°$. The degree of polarization as calculated from $(1-\cos^2 2\theta)/(1+\cos^2 2\theta)$, is therefore 89.8% at the absorption edge—going down to 86% at the end of the region. In order to avoid second-order radiation and to reduce incoherent scattering, a voltage of only 22 kV was applied. A tube current of 3.6 mA gave a counting rate of 80 counts/sec without the absorber, in the relevant wavelength range.

Under these conditions, the full width of the W $L\gamma_1$ line at the half-maximum of intensity was 10.5 eV. Background counting rate was 7.5 counts/sec.

Work with this apparatus proved superior to experiments carried out in this laboratory with a double crystal spectrometer, a conventional closed x-ray tube and the same detection arrangement. Using two quartz crystals with reflecting planes (3 1 0) the polarization was 80% but the counting rate in the investigated region was only 3.7 cps. Using a Calcite crystal as the first crystal of the double crystal spectrometer and the *a/m* quartz reflector as the second crystal, the counting rate was 30 cps but the resolution was unsatisfactory.

The resolution of the single-crystal arrangment with a fine focus can be judged by comparing the width of the W $L\gamma_1$ line with that reported by Williams[12] (10.4 eV). Using this arrangement with the (3 1 0) plane of quartz instead of the (4 2 0) plane of LiF we obtained 9.5 eV for W $L\gamma_1$.

B. Absorber

The Ge crystal was ground and polished up to a thickness of 0.1 mm and then etched up to a thickness of less than 15 μ, parallel to the (1 1 1) plane. The composition of the etch was 1 cc HNO_3 70%, 2 cc HF 40% and 100 mg $Cu(NO_3)_2$ in 2 cc H_2O.

The homogeneity of the thickness was tested by measuring x-ray absorption in different points of the absorber. Variations of absorption were within the experimental error.

C. Measurements

The absorption spectrum was measured for three different orientations relatively to the polarization vector **A** of the incident beam (Fig. 1, curves a, b, c). The angle between the polarization vector and the [1 $\bar{1}$ 0] direction was (a) 15°±2°; (b) 0°±2°; (c) 30°±2°. In all these measurements the beam was parallel to the [1 1 1] axis of the absorbing crystal.

For each point of the absorption curve 4×4000 counts were taken without the absorber and 3×4000 with the absorber. These measurements without and with the absorber were taken alternatively. The distance between successive points on the absorption curve were as follows:

1 eV for the range up to 50 eV from the edge
1.33 eV for the range 50 eV–85 eV
2 eV for the range 85 eV–300 eV.

Each curve was repeated at least twice. The reproducibility was within the statistical error ($\sigma\sim 2\%$).

The results are given in Fig. 1 curves a, b, c. We concluded from these experiments that no shifts exist.

In order to ascertain that these results are not due to the high symmetry of the (1 1 1) plane, further measurements were taken with the incident beam parallel to the [1 1 0] axis. In this position, the spectrum was measured in two orientations of the absorber relatively to the polarization vector [Fig. 1 (d), (e)].

Part (d) The polarization vector **A** parallel to the [1 $\bar{1}$ 0] direction.
Part (e) The polarization is parallel to the [0 0 1] direction.

Two runs were taken in each position from about 15 eV up to 200 eV from the edge. The reproducibility was again very good. Here, too, the positions of the extrema were the same as in the former measurements.

Figure 1 shows the absorption curves obtained for the different orientations of the crystal. The maxima are designed by capital letters and the minima by small letters.

Part (a) shows the absorption curve of the Ge crystal when the incoming radiation is parallel to the [1 1 1] axis of the crystal, and the polarization vector **A** makes an angle of 15° with the [1 $\bar{1}$ 0] axis in the (1 1 1) plane.

Similarly, Parts (b) and (c) give the absorption curve with the polarization vector parallel to and inclined by an angle of 30° with the [1 $\bar{1}$ 0] axis of the crystal, respectively.

In (c) two curves are shown. The upper curve represents a run in the same position of the polarization

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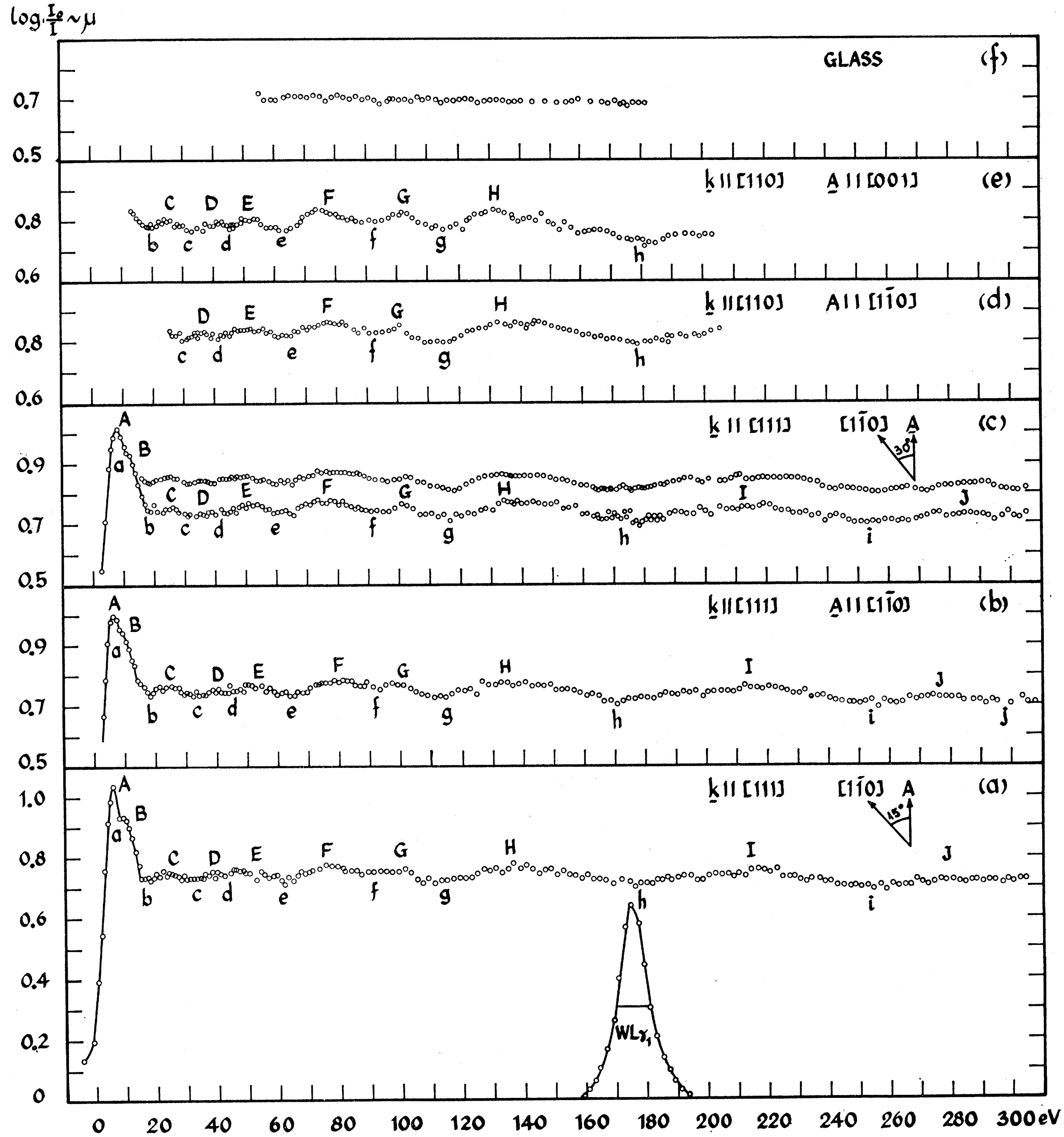

FIG. 1. The extended K-absorption curve of Ge single crystal. Parts (a), (b), and (c) have the incoming radiation parallel to the [1 1 1] axis, and the polarization vector inclined by 15°, parallel to, and inclined by 30° to the [1 $\bar{1}$ 0] axis, respectively. Parts (d) and (e) have the incoming radiation parallel to the [1 1 0] axis and the polarization vector parallel to the [1 $\bar{1}$ 0] and [0 0 1] axes, respectively. Part (f) shows the absorption through a plate of glass. The zero is taken from the center of the edge. The W $L\gamma_1$ emission line is indicated.

vector as the lower curve; it is shifted arbitrarily in the vertical direction and is given here to show the reproducibility obtained.

Parts (d) and (e) give the absorption curves with the incoming radiation parallel to the [1 1 0] axis, and the polarization vector parallel to the [1 $\bar{1}$ 0] and [0 0 1] axes in the (1 1 0) plane, respectively.

Part (f) gives an absorption curve of a thin glass plate. This experiment was carried out in order to test systematic errors of the apparatus and its statistical spread.

The W $L\gamma_1$ line is shown.

The results are summarized in Table I and results found in literature are reproduced for comparison. The positions of the maxima and the minima are given in eV, measured from the center of the edge.

We estimate the error in the positions of the extrema as ±2 eV for the sharp extrema and ±5 eV for the very flat ones.

CONCLUSION

No shifts of the positions of the maxima or minima in the extended fine structure of the K-absorption edge of Ge single crystal were observed when the direction of the polarization vector relatively to the absorber was changed. This observation is in agreement with symmetry considerations for cubic crystals as given in the Appendix. We have no explanation of different results reported by previous authors. Experiments are under way in this laboratory measuring the extended fine structure of the K-absorption edge, in noncubic single crystals.

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The authors thank Z. H. Kalman for very valuable help in all stages of this work. They are indebted to Professor J. W. M. DuMond for the donation of a double crystal spectrometer[13] to M. Wix of the United Kingdom who presented the fine focus x-ray unit to this laboratory, and to Sylvania Electric Products Incorporated for the excellent Ge crystals.

APPENDIX A

Let a plane-polarized monochromatic x-ray beam traverse a cubic crystal. Then it can be shown that the photoelectric K-absorption coefficient $\mu(\lambda)$ is independent of the direction of the polarization vector $\mathbf{A}$ of the beam in the crystal.

To show this, it is enough to prove that

$$P=\sum_{t=1}^{m} P(\mathbf{n}_t)$$

is independent of the direction of $\mathbf{A}$, where $P(\mathbf{n}_t)$ is the probability of a photoelectron ejection in an arbitrary direction $\mathbf{n}_t$, and the summation is to be taken over the set of all the m directions symmetrically equivalent to one of them.

Proof:

$$P(\mathbf{n}_t)=C\left|\mathbf{A}\cdot\int\Psi_{\mathbf{n}_t}{}^*(x,y,z)e^{2\pi i(\mathbf{r}_0+\Delta\mathbf{r})\cdot\mathbf{k}}\nabla\Psi_{\text{in}}(x,y,z)d\tau\right|^2. \tag{A1}$$

Here $\Psi_{\mathbf{n}_t}(x,y,z)$ is the eigenfunction of the electron ejected in the $\mathbf{n}_t$ direction, $\mathbf{k}$ is the wave vector of the photon, $\Psi_{\text{in}}(x,y,z)$ is the initial wave function of the ejected electron (in our case it is a $1s$-type eigenfunction and, therefore, is spherical symmetric), $d\tau=dx\,dy\,dz$, $\mathbf{r}_0$ is the radius vector from the origin of the coordinate system to the center of the absorbing atom, $\Delta\mathbf{r}$ is the radius vector from the center of the absorbing atom to the point (x,y,z).

Now, in case of K absorption, the term $e^{2\pi i\Delta\mathbf{r}\cdot\mathbf{k}}$ can generally[4] be replaced by unity (i.e., for Ge Ψ_{in} is appreciably different from zero for $|\Delta r|\approx 2.10^{-10}$ cm and $\lambda\approx 10^{-8}$ cm so that $2\pi\Delta rk\approx 0.1$) and then the equation (A1) becomes

$$P(\mathbf{n}_t)=C\left|\mathbf{A}\cdot\int\Psi_{\mathbf{n}_t}{}^*(x,y,z)\nabla\Psi_{\text{in}}(x,y,z)d\tau\right|^2. \tag{A2}$$

Let

$$\int\Psi_{\mathbf{n}_t}{}^*\nabla\Psi_{\text{in}}d\tau=\mathbf{e}_t\left|\int\Psi_{\mathbf{n}_t}{}^*\nabla\Psi_{\text{in}}d\tau\right|$$

and

$$\int\Psi_{\mathbf{n}_i}{}^*\nabla\Psi_{\text{in}}d\tau=\mathbf{e}_i\left|\int\Psi_{\mathbf{n}_i}{}^*\nabla\Psi_{\text{in}}d\tau\right|.$$

Now, because of the symmetry of the crystal we have[14]:

$$|\Psi_{\mathbf{n}_t}{}^*\nabla\Psi_{\text{in}}d\tau|=|\Psi_{\mathbf{n}_i}{}^*\nabla\Psi_{\text{in}}d\tau|,$$

and $(\mathbf{e}_i)=(T)(\mathbf{e}_t)$, where (T) is the symmetry transformation $(\mathbf{n}_i)=(T)(\mathbf{n}_t)$.

It follows, therefore, that

$$\begin{aligned}P=\sum_{t=1}^{m}P(\mathbf{n}_t)&=C\sum_{t=1}^{m}\left|\mathbf{A}\cdot\int\Psi_{\mathbf{n}_t}{}^*\nabla\Psi_{\text{in}}d\tau\right|^2\\&=C\left|\int\Psi_{\mathbf{n}_t}{}^*\nabla\Psi_{\text{in}}d\tau\right|^2\sum_{t=1}^{m}(\mathbf{A}\cdot\mathbf{e}_t)^2\\&=C\left|\int\Psi_{\mathbf{n}_t}{}^*\nabla\Psi_{\text{in}}d\tau\right|^2\Big[A_x^2\sum_{t=1}^{m}e_{tx}^2+A_y^2\sum_{t=1}^{m}e_{ty}^2\\&\quad+A_z^2\sum_{t=1}^{m}e_{tz}^2+2A_xA_y\sum_{t=1}^{m}e_{tx}e_{ty}\\&\quad+2A_xA_z\sum_{t=1}^{m}e_{tx}e_{tz}+2A_yA_z\sum_{t=1}^{m}e_{ty}e_{tz}\Big].\end{aligned} \tag{A3}$$

Now, for every direction (e_{tx}, e_{ty}, e_{tz}), there exists in a cubic crystal an equivalent direction $(-e_{tx}, e_{ty}, e_{tz})$ (choosing x,y,z in the directions of the main axes). Therefor, $2A_xA_y\sum_{t=1}^{m}e_{tx}e_{ty}=0$ and $2A_xA_z\sum_{t=1}^{m}e_{tx}e_{tz}=0$. Similarly, $2A_yA_z\sum_{t=1}^{m}e_{ty}e_{tz}=0$.

All the equivalent directions of $(\mathbf{e}_t)$ are of a form (e_{ix},e_{iy},e_{iz}) which is some permutation of $\pm e_{tx}$, $\pm e_{ty}$, $\pm e_{tz}$. Consider the three equivalent directions (e_{ux},e_{uy},e_{uz}), (e_{vx},e_{vy},e_{vz}), and (e_{wx},e_{wy},e_{wz}), where $e_{ux}=e_{vy}=e_{wz}$; $e_{uy}=e_{vz}=e_{wx}$; $e_{uz}=e_{vx}=e_{wy}$. Since $e_{ux}^2+e_{uy}^2+e_{uz}^2=e_{ux}^2+e_{vx}^2+e_{wx}^2=1$ etc., we have

$$A_x^2\sum_{t=1}^{m}e_{tx}^2=\tfrac{1}{3}mA_x^2,\quad A_y^2\sum_{t=1}^{m}e_{ty}^2=\tfrac{1}{3}mA_y^2,$$

$$A_z^2\sum_{t=1}^{m}e_{tz}^2=\tfrac{1}{3}mA_z^2.$$

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[13] J. W. M. DuMond and A. Hoyt, Phys. Rev. 36, 1702 (1930).

[14] This treatment implies that the atom is located at a point with the full symmetry of the crystal. However, if this is not the case, the same result is obtained by summing over all the atoms in the unit cell equivalent to this one.

Therefore, from Eq. (A3) we have

$$P=\tfrac{1}{3}mCA^2\left|\int \Psi_{\mathrm{n}_t}{}^*\nabla\Psi_{\mathrm{in}}d\tau\right|^2,$$

which is independent of the direction of **A**.

Equation (A3) holds generally. Thus, (provided only Ψ_{in} has spherical symmetry and $e^{2\pi i\Delta\mathbf{r}\cdot\mathbf{k}}$ can be replaced by unity) the absorption coefficient $\mu(\lambda)$ is independent on the direction of **A** not only for cubic crystals but whenever the term in the square brackets in (A3) is independent of the direction of **A**. It should be noted that for the purpose of this calculation the space group and not the point group is of importance, because here an n-fold screw axis is equivalent to an n-fold rotation axis and a glide plane is equivalent to a plane of symmetry, considering the summation over-all equivalent atoms.

Thus, $\mu(\lambda)$ will be the same for all those directions of **A** which give equal values of the expression in the square brackets of Eq. (A3). For example, from Eq. (A3) follows that when the investigated crystal possesses only a three-fold (or a higher) symmetry axis and the beam is parallel to this axis, then $\mu(\lambda)$ is independent of the direction of **A**.

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Electronic Structure of Copper Impurities in ZnO

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We have measured the near infrared absorption, Zeeman effect, and electron spin resonance of Cu^{2+} ions introduced as a substitutional impurity into single-crystal ZnO. From the g values of the lowest Γ_6 component of the T_2 state (the ground state), $g_{\parallel}=0.74$ and $g_{\perp}=1.531$, and from the g values of the $\Gamma_4\Gamma_5$ component of the E state, $g_{\parallel}=1.63$ and $g_{\perp}=0$, we have determined the wave functions of Cu^{2+} in terms of an LCAO MO model in which overlap only with the first nearest neighbor oxygen ions is considered. These wave functions indicate that the copper $3d$ (t_2) hole spends about 40% of its time in the oxygen orbitals, and that the copper t_2 orbitals are expanded radially with respect to the e orbitals. Corroboration for the radial expansion of the t_2 orbitals is obtained from an analysis of the hyperfine splitting. It is concluded from our model that the large values of the hyperfine constants, $|A|=195\times10^{-4}$ cm^{-1} and $|B|=231\times10^{-4}$ cm^{-1}, are due to the contribution from the orbital motion of the t_2 hole.

I. INTRODUCTION

ALTHOUGH much work has been done on the spin resonance and optical spectra of transition metal impurities in compound semiconductors,[1-4] the nature of the states remains obscure. The energy levels of these impurities are deep, so the hydrogenic model based on the effective mass formalism is not applicable.[5] An alternative point of view exists, that of the ligand field theory, which was originally developed for transition ions in ionic lattices.[6] The formalism of ligand field theory is based primarily on symmetry considerations, though its usefulness depends on the degree of localization of the center. The transition from ionic to covalent bonding is taken into account by allowing the parameters used in the theory to vary. The calculation of these parameters is the task of a microscopic theory, and to our knowledge no case has so far been reported of their successful calculation for the case of strong covalent bonding such as occurs in a semiconductor.[7,8]

In this paper we report a detailed investigation of the optical spectrum, Zeeman effect, and spin resonance of copper in hexagonal zinc oxide.[9,10] It appears that copper substitutes for zinc, entering a slightly distorted tetrahedral site. When the Fermi level is low enough, the copper is divalent, having a single d hole which in its ground state is in a triply degenerate t_2 orbital. Such an orbital is of the correct symmetry to make σ bonds with the coordinating oxygen ions. We interpret our results in terms of a tight-binding LCAO (linear combination of

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