PHYSICAL REVIEW VOLUME 170, NUMBER 3 15 JUNE 1968

Polaron in a Magnetic Field*†

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(Received 22 September 1967; revised manuscript received 2 January 1968)

A study is made of the energy spectrum of a polaron in the presence of a magnetic field for the cases of weak and intermediate couplings, using Onsager's theory. This theory makes use of the Bohr-Sommerfeld quantization rule, which has been derived with the WKB approximation and is therefore valid for large quantum numbers. Following an approach first formulated by Argyres, we prove that the energy spectrum of a polaron in a magnetic field obtained by using Onsager's theory is correct even for small quantum numbers like $n=0, 1, 2$, etc.

INTRODUCTION

INVESTIGATIONS of the behavior of an electron moving slowly in the conduction band of a polar crystal and interacting with the polarization field of the crystal lattice have been carried out by several authors[1–6] in the past few years. Such a system is called a polaron. In this brief note we report a calculation of the energy spectrum of a polaron in a magnetic field using a particularly simple approach given by Onsager,[7] and Lifshitz and Kosevich,[8] independently. This approach is based on the use of the Bohr-Sommerfeld quantization rule which is supposed to be valid for large quantum numbers, i.e., in the classical limit. We prove that in the case of a polaron in a magnetic field, the energy spectrum is indeed given quite correctly by Onsager's theory even for small quantum numbers like $n=0, 1, 2$, etc. Our procedure consists in evaluating the first correction term to the usual phase integral, derived from the exact quantization rule by Argyres,[9] for the case of a polaron and showing that it is very small.

THEORY

We consider a single electron whose band effective mass is m and take the electron charge to be $-e$. We assume the electron to be in the conduction band of a polar material and suppose further that the energy surfaces possess minima at the center ($\mathbf{k}=0$) of the Brillouin zone and that they are spherical. The dynamical properties of the system we envisage are given by the Hamiltonian operator[1]

$$H=\frac{p^2}{2m}+\sum_{\mathbf{q}}\left[V_q a_q e^{i\mathbf{q}\cdot\mathbf{r}}+V_q^* a_q^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}\right]+\sum_{\mathbf{q}}\hbar\omega(a_q^\dagger a_q+\tfrac{1}{2}). \quad (1)$$

The first term is the band energy of the electron. The second term gives the interaction Hamiltonian of the electron with the longitudinal optical phonon field. Here a_q and $a_q^\dagger$ are the destruction and creation operators for a phonon of wave vector $\mathbf{q}$ and ω is the optical phonon frequency. The quantity V_q stands for

$$V_q=-\frac{i\hbar\omega}{q}\left(\frac{\hbar}{2m\omega}\right)^{1/4}\left(\frac{4\pi\alpha}{V}\right)^{1/2},$$

where α is the dimensionless coupling constant

$$\alpha=\frac{e^2}{\hbar}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon}\right)\left(\frac{m}{2\hbar\omega}\right)^{1/2},$$

ϵ_∞ and ϵ are the optical and the static dielectric constants of the host lattice, respectively.

We now calculate the energy of our system as a function of the wave vector $\mathbf{k}$ of the electron. In the case of weak coupling ($\alpha\ll 1$) the perturbation theory gives us at $T=0$°K:

$$E(\mathbf{k})=-\alpha\hbar\omega+\frac{\hbar^2k^2}{2m}(1-\alpha/6)-\frac{3}{160}\frac{\hbar^3\alpha k^4}{m^2\omega}, \quad (2)$$

for $k\ll(2m\omega/\hbar)^{1/2}$. For the case of intermediate coupling ($\alpha\leqslant 6$) we have[10]

$$E(\mathbf{K})=-\alpha\hbar\omega+\frac{\hbar^2K^2}{2m}(1+\tfrac{1}{6}\alpha)^{-1}-\frac{3}{160}\frac{\hbar^3\alpha K^4}{m^2\omega}(1+\tfrac{1}{6}\alpha)^{-4}, \quad (3)$$

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* Part of this work was done while the author was at Purdue University and was reported in Semiconductor Research Semiannual Report October 1, 1965 to March 31, 1966 of Purdue University.

† Supported in part by the Advanced Research Projects Agency and the U. S. Army Research Office (Durham) and by the University of Kansas.

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6 A specially useful reference is the book *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Ltd., Edinburgh, 1963).

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for $K \ll (2m\omega/\hbar)^{1/2}$. Here

$$\hbar\mathbf{K} = \hbar\mathbf{k} + \sum_{\mathbf{q}} a_q^\dagger a_q \hbar\mathbf{q}$$

is the polaron momentum.

We now calculate the energy levels of a polaron in a uniform magnetic field using the theory given by Onsager[7] and Lifshitz and Kosevich[8] independently. Suppose we want to study the motion of a charged quasiparticle having the general dispersion relation

$$E = E(p_x, p_y, p_z)$$

in a magnetic field. If the field $\mathbf{B}$ is directed along the z axis of the Cartesian coordinate system, the Hamiltonian of such a particle is obtained by replacing in the above dispersion relation the momentum operator p_i by p_i' such that

$$[p_y', p_x'] = \frac{i\hbar eB}{c};\ [p_y', p_z'] = [p_x', p_z'] = 0. \quad (4)$$

Onsager showed, using the Bohr-Sommerfeld quantization rule, that the energy of the system is given by

$$A(E, p_z) = \int\int dp_x' dp_y' = (n+\gamma)\frac{2\pi\hbar eB}{c}, \quad (5)$$

where $A(E, p_z)$ is the area intercepted on the surface of constant energy by a plane perpendicular to the direction of the magnetic field and γ lies between 0 and 1. We calculate $A(E, k_z)$ for the case of a polaron and find that the energy

$$E_n(k_z, B) = -\alpha\hbar\omega + \hbar\omega_c(1-\tfrac{1}{6}\alpha)(n+\gamma) + \frac{\hbar^2 k_z^2}{2m}(1-\tfrac{1}{6}\alpha) - \frac{3}{40}\left[\alpha\hbar\omega\left(\frac{\omega_c}{\omega}\right)^2(n+\gamma)^2 + 2\alpha\left(\frac{\omega_c}{\omega}\right)\frac{\hbar^2 k_z^2}{2m}(n+\gamma) + \frac{\alpha}{\hbar\omega}\left(\frac{\hbar^2 k_z^2}{2m}\right)^2\right], \quad (6)$$

where $\omega_c = eB/mc$. The cyclotron mass $m_\perp^*$ is defined by the condition

$$\frac{\hbar eB}{m_\perp^* c} = E_{n+1}(k_z, B) - E_n(k_z, B). \quad (7)$$

Simple substitution of Eq. (7) in Eq. (6) gives

$$\frac{m}{m_\perp^*} = 1 - \tfrac{1}{6}\alpha - \frac{3\alpha\omega_c}{20\omega}\left(n+\gamma+\tfrac{1}{2}+\frac{\hbar k_z^2}{2m\omega_c}\right). \quad (8)$$

The expression for $m_\perp^*$ for the case of intermediate coupling is obtained in an analogous fashion.

In calculating the expression for the energy levels of a quasiparticle in the presence of a uniform magnetic field, use has been made of the Bohr-Sommerfeld quantization rule which has been derived by WKB (semiclassical) approximation. This is an asymptotic approximation which is valid only for small values of Planck's constant and large quantum numbers. In the following we prove that in the case of a polaron, the energy spectrum in the presence of a magnetic field is indeed given by Eq. (6) even for small quantum numbers like $n=0, 1, 2$, etc.

Consider a one-dimensional system with a classical Hamiltonian $H(p,q)$ where q is the Cartesian coordinate and p, the conjugate momentum. Assuming that the Hamiltonian of the system is such that at least for a certain range of values of its energy, the classical motion is periodic, Argyres[9] has derived the following exact quantization rule:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dpdq\, S(pq;\epsilon_n) = 2\pi\hbar(n+\tfrac{1}{2}). \quad (9)$$

Here

$$S(pq;\epsilon) = \int_{-\infty}^{\infty} dx \langle q-\tfrac{1}{2}x | \mathcal{S}(\epsilon - H(P+p, Q)) | q+\tfrac{1}{2}x\rangle, \quad (10)$$

where $\mathcal{S}(\epsilon)$ is a step function, P and Q are the momentum and position operators, respectively, and ϵ_n is the nth eigenvalue of H. One can expand $S(pq;\epsilon)$ in power of $\hbar$,

$$S(pq;\epsilon) = S_0(pq;\epsilon) + \hbar^2 S_1(pq;\epsilon) + O(\hbar^4), \quad (11)$$

and calculate $S_0(pq;\epsilon)$ and $S_1(pq;\epsilon)$ explicitly. Argyres finds that $S_0(pq;\epsilon)$ leads to the usual Bohr-Sommerfeld quantization rule, i.e.,

$$\frac{1}{2\pi\hbar}\int\int_{H_c \leqslant \epsilon_n} dpdq = (n+\tfrac{1}{2}) \quad (12)$$

and the expression for $S_1(pq;\epsilon)$ is

$$S_1(pq;\epsilon) = \frac{1}{16}\left[H_c\left(\frac{\delta}{\delta p}\frac{\partial}{\partial q} - \frac{\delta}{\delta q}\frac{\partial}{\partial p}\right)^2 H_c\right]\delta'(H_c - \epsilon) + \frac{1}{24}H_c\left[\frac{\delta}{\delta p}\frac{\partial H_c}{\partial q} - \frac{\delta}{\delta q}\frac{\partial H_c}{\partial p}\right]^2 \delta''(H_c - \epsilon). \quad (13)$$

Here $\mathcal{S}'(\epsilon) \equiv d\mathcal{S}/d\epsilon = \delta(\epsilon)$ is the Dirac δ distribution and $\delta/\delta p$ and $\delta/\delta q$ are differential-operators which operate only on the functions to their left, whereas $\partial/\partial p$ and $\partial/\partial q$ operate only on the functions to their right. The Bohr-Sommerfeld quantization rule gives good results for those values of ϵ_n for which

$$\hbar^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dqdp S_1(pq;\epsilon_n) \ll \int\int_{H_c \leqslant \epsilon_n} dpdq. \quad (14)$$

We now evaluate the phase integral

$$\iint_{H_c \leqslant \epsilon_n} dp dq$$

and

$$\hbar^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_1(pq;\epsilon_n) dp dq$$

for the case of a polaron in a magnetic field and show that the value of the latter expression for most materials of interest is much smaller than that of the former for magnetic fields generally available in the laboratory. Now the expression for the classical Hamiltonian of a polaron in the presence of a magnetic field can be written as

$$H_c = \frac{1}{2m(1+\frac{1}{6}\alpha)}(p_x'^2+p_y'^2+p_z'^2) - \frac{3\alpha}{160\hbar m^2\omega}(p_x'^2+p_y'^2+p_z'^2)^2 \quad (15)$$

and making use of Eq. (4) we can write Eq. (15) as

$$H_c = \beta_1(p^2+\phi^2 q^2) - \beta_2(p^2+\phi^2 q^2)^2, \quad (16)$$

where we have made the following substitutions: $\beta_1 = 1/2m(1+\alpha/6)$, $\beta_2 = 3\alpha/160m^2\hbar\omega$, $p_y' = p$, $p_x' = \phi q$, $e\beta/c = \phi$. Here we have assumed that the energy is measured from $-\alpha\hbar\omega$ and have put $p_z = 0$ to simplify the calculations. As before, the applied magnetic field is along the z axis of the Cartesian coordinate system. Because of the commutation relations (4), q and p in Eq. (16) behave as a pair of conjugate variables. A straightforward calculation yields the following expression for the phase integral:

$$\iint_{H_c \leqslant \epsilon_n} dp dq = \pi \frac{\beta_1 - (\beta_1^2 - 4\beta_2\epsilon_n)^{1/2}}{\beta_2\phi}. \quad (17)$$

To calculate

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} S_1(pq;\epsilon) dp dq$$

we write the integrand $S_1(pq;\epsilon)$ in two parts, i.e.,

$$S_1(pq;\epsilon) = S_1^{(1)}(pq;\epsilon) + S_1^{(2)}(pq;\epsilon), \quad (18)$$

where

$$S_1^{(1)}(pq;\epsilon) = \frac{1}{16}\left[H_c\left(\frac{\delta}{\delta p}\frac{\partial}{\partial q} - \frac{\delta}{\delta q}\frac{\partial}{\partial p}\right)^2 H_c\right]\delta'(H_c-\epsilon) \quad (19)$$

and

$$S_1^{(2)}(pq;\epsilon) = (1/24)H_c\left[\frac{\delta}{\delta p}\frac{\partial H_c}{\partial q} - \frac{\delta}{\delta q}\frac{\partial H_c}{\partial p}\right]^2 \delta''(H_c-\epsilon). \quad (20)$$

We now calculate these two functions for the classical Hamiltonian given by Eq. (16); we have

$$S_1^{(1)}(pq;\epsilon) = \frac{1}{8}\left[\frac{\partial^2 H_c}{\partial p^2}\frac{\partial^2 H_c}{\partial q^2} - \left(\frac{\partial^2 H_c}{\partial p \partial q}\right)^2\right]\delta'(H_c-\epsilon)$$
$$= \tfrac{1}{2}[\beta_1^2\phi^2 - 8\beta_1\beta_2\phi^4 q^2 + 12\beta_2\phi^6 q^4 + p^2(24\beta_2^2\phi^4 q^2 - 8\beta_1\beta_2\phi^2) + 12\beta_2^2\phi^2 p^4]\delta'(H_c-\epsilon). \quad (21)$$

We now express $S_1^{(1)}(pq;\epsilon)$ in terms of H_c and q using Eq. (16)

$$H_c = \beta_1(p^2+\phi^2 q^2), \quad (22)$$

where we have neglected the second term on the right-hand side of Eq. (16) because in the case of a polaron it is much smaller than the first term. Putting y for H_c we get

$$S_1^{(1)}(qy;\epsilon) = \tfrac{1}{2}[\beta_1^2\phi^2 - 8\beta_1\phi^2 y + 12(\beta_2^2\phi^2 y^2/\beta_1^2)]\delta'(y-\epsilon). \quad (23)$$

Therefore

$$\hbar^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} S_1^{(1)}(pq;\epsilon) dp dq = -\hbar^2 \frac{d}{d\epsilon}\int_{a(\epsilon)}^{b(\epsilon)}\left[\beta_1^2\phi^2 - 8\beta_1\phi^2\epsilon - \frac{12\beta_2^2\phi^2\epsilon^2}{\beta_1^2}\right]\frac{dq}{p(\epsilon q)}, \quad (24)$$

where we have changed the variable of integration from p to y and $p(\epsilon q)$ is the Jacobian of transformation; $a(\epsilon)$ and $b(\epsilon)$ are the classical turning points and in our case are given by

$$a(\epsilon) = -(\epsilon/\beta_1)^{1/2} 1/\phi,$$
$$b(\epsilon) = (\epsilon/\beta_1)^{1/2} 1/\phi. \quad (25)$$

In obtaining Eq. (24) we have used the following definition[11] of the derivative of the Dirac's δ-distribution:

$$\int_{-\infty}^{\infty}\delta'(x)F(x)dx = -\int_{-\infty}^{\infty}F'(x)\delta(x)dx, \quad (26)$$

where $F(x)$ is an infinitely differentiable arbitrary function of x. After carrying out the indicated operations on the right-hand side of Eq. (24) we obtain

$$\hbar^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dp dq S_1^{(1)}(pq;\epsilon) = \frac{\hbar^2\pi}{\beta_1}\left(8\beta_2\phi - \frac{24\beta_2^2\phi\epsilon}{\beta_1^2}\right). \quad (27)$$

[11] Hans Bremermann, *Distributions, Complex Variables, and Fourier Transforms* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965), p. 6.

For $S_1^{(2)}(pq;\epsilon)$ we have the expression

$$S_1^{(2)}(pq;\epsilon)=(1/24)y\left(\frac{\delta}{\delta p}\frac{\partial y}{\partial q}-\frac{\delta}{\delta q}\frac{\partial y}{\partial p}\right)^2\delta''(y-\epsilon)=(1/24)\left[\frac{\partial^2 y}{\partial p^2}\left(\frac{\partial y}{\partial q}\right)^2-2\frac{\partial^2 y}{\partial p\partial q}\frac{\partial y}{\partial q}\frac{\partial y}{\partial p}+\frac{\partial^2 y}{\partial q^2}\left(\frac{\partial y}{\partial p}\right)^2\right]\delta''(y-\epsilon) \quad (28)$$

and for our case

$$\begin{aligned}S_1^{(2)}(pq;\epsilon)=(1/24)[&(2\beta_1-12\beta_2p^2-4\beta_2\phi^2q^2)(2\beta_1\phi^2q-4\beta_2\phi^2qp^2-4\beta_2\phi^4q^3)\\&+16\beta_2\phi^2qp(2\beta_1\phi^2q-4\beta_2\phi^2qp^2-4\beta_2\phi^4q^3)(2\beta_1p-4\beta_2p^3-4\beta_2\phi^2q^2p)\\&+(2\beta_1\phi^2-4\beta_2\phi^2p^2-12\beta_2\phi^4q^2)(2\beta_1p-4\beta_2p^3-4\beta_2\phi^2q^2p)^2]\delta''(y-\epsilon). \quad (29)\end{aligned}$$

Simplifying this expression and putting $p^2+\phi^2q^2=y/\beta_1$, we obtain

$$\begin{aligned}S_1^{(2)}(yq;\epsilon)=\frac{1}{3}\Bigg[&\beta_1^2\phi^2y-12\beta_1\beta_2\phi^4q^2y+q^2(y/\beta_1-\phi^2q^2)(12\beta_2^2\phi^4y+32\beta_2^3\phi^4y^2)+\frac{12\beta_2^2\phi^2y^2}{\beta_1}(y/\beta_1-\phi^2q^2)\\&+6\beta_1^2\beta_2q^4\phi^6-\frac{48\beta_2^3\phi^6q^4}{\beta_1}(y/\beta_1-\phi^2q^2)-\frac{16\beta_2^3\phi^8yq^6}{\beta_1}+8\beta_2^3\phi^{10}q^8-\frac{64\beta_2^3\phi^4yq^2}{\beta_1}(y/\beta_1-\phi^2q^2)^2\\&-4\beta_1^2\beta_2\phi^2(y/\beta_1-\phi^2q^2)^2-8\beta_2^3\phi^2(y/\beta_1-\phi^2q^2)^4\Bigg]\delta''(y-\epsilon). \quad (30)\end{aligned}$$

Now to calculate

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}S_1^{(2)}(pq;\epsilon)dpdq$$

we change the variable of integration from p to y, integrate over y and q and get (after some tedius but straightforward calculation) the expression

$$\hbar^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}S_1^{(2)}(pq;\epsilon)dqdp=\frac{\hbar^2\pi}{2\beta_1}\left(-\tfrac{7}{2}\beta_2\phi+\frac{36\beta_2^2\phi\epsilon}{\beta_1^2}+\frac{80\beta_2^3\phi\epsilon^2}{\beta_1^4}\right). \quad (31)$$

Hence

$$\hbar^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}S_1(pq;\epsilon_n)dpdq=\frac{\hbar^2\pi}{2\beta_1}\left(\tfrac{9}{2}\beta_2\phi+\frac{12\beta_2^2\phi\epsilon_n}{\beta_1^2}+\frac{80\beta_2^3\phi\epsilon_n^2}{\beta_1^4}\right). \quad (32)$$

To show that the first-order correction term

$$\hbar^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}S_1(pq;\epsilon_n)dpdq$$

is much smaller than the phase integral

$$\iint_{H_c\leqslant\epsilon_n}dpdq,$$

we calculate the values of these two expressions for a typical ionic material, say, CdTe and compare them. Using the following values of the various physical quantities for CdTe,[12] $m=0.090m_0$, $\alpha=0.4$ and $\hbar\omega=0.0213$ eV, we find that the first-order correction term is about 2% of the phase integral for the magnetic fields of the order of 100 kG. Similar results are obtained for other II-VI and I-VII compounds. Thus the energy spectrum of a polaron in the presence of a magnetic field is correctly obtained by using Onsager's theory even for small quantum numbers like $n=0$, 1, 2, etc.

Investigations of the energy spectrum of a polaron in the presence of a magnetic field have been made by several authors.[13–15] Tulub,[13] for instance, finds that the polaron effective mass for weak magnetic fields is given by that of the field-free mass plus a term proportional to $(\omega_c/\omega)^2$. This result is derived for the case of intermediate coupling, but the effective mass he obtains does not approach the weak coupling result to order α. This is in disagreement with the results of the present work. Hellwarth and Platzman[14] calculate the free energy of polarons in a magnetic field and not the energy spectrum. Hence, the comparison is not immediately possible. Larsen[15] has obtained the ground state and the low-lying excited states of a polaron in a magnetic field using a variational method closely related to the intermediate coupling theory of Lee, Low, and Pines.[10] The results we obtain are quite similar to those obtained by Larsen. Our procedure has the advantage of being simple and direct.

Throughout our work we have assumed that the electron moves in a parabolic conduction band. Using

[12] K. K. Kanazawa and F. C. Brown, Phys. Rev. **135**, A1757 (1964).
[13] A. V. Tulub, Zh. Eksperim. i Teor. Fiz. **36**, 656 (1959) [English transl.: Soviet Phys.—JETP **9**, 392 (1959)].
[14] R. W. Hellwarth and P. M. Platzman, Phys. Rev. **128**, 1599 (1962).
[15] D. M. Larsen, Phys. Rev. **135**, A419 (1964).

Kane's[16] theory we have calculated the variation of the effective mass of an electron with the magnetic field due to the nonparabolicity of the band. In the case of CdTe, for instance, we find that this variation from the zero field mass is about 1.5% at 100 kG. The corresponding variation in the polaron mass is about 4%. For GaAs, however, the change in the effective mass due to the nonparabolicity of the band is about 2% at 100 kG whereas the variation in the polaron mass is about 0.4%. It seems that, in most direct wide-energy-gap ionic semiconductors, the effects due to the nonparabolicity of the conduction band are relatively small.

Cyclotron-resonance experiments in several III-V compounds have been made[17] and a small change in the effective mass of an electron as a function of the magnetic field is observed. In GaAs for instance, we find that the observed variation of the cyclotron mass with field is the same as we have calculated. Similar measurements in II-VI compounds have not yet been made.

ACKNOWLEDGMENTS

The author wishes to thank Professor Sergio Rodriguez for many useful discussions. He would also like to thank his wife, Mrs. Swarn Bajaj, for clarifying some mathematical points.

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PHYSICAL REVIEW VOLUME 170, NUMBER 3 15 JUNE 1968

Raman Scattering in 6*H* SiC†

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Fifteen phonon lines were observed in the first-order Raman spectrum of 6*H* SiC, using laser excitation. Polarized light was used to identify the mode symmetry, and a large-zone analysis was used to classify the modes and to display the results in what appear to be dispersion curves. All observed narrow lines are consistent with our interpretation, and only two of the expected lines remain unobserved. A study of the dependence of phonon energy on propagation direction shows that certain infrared and Raman active modes have extremely little infrared strength (a consequence of the polytype structure of 6*H* SiC). Doublets in the Raman spectrum give accurate measurements of the 4–8-cm^{-1} discontinuities within the large zone.

I. INTRODUCTION

RAMAN measurements have been greatly improved by the use of laser light sources. In recent Raman work the allowed optical phonons of ZnO [1] and CdS [2] have been fully identified. These crystals are uniaxial, with wurtzite structure. 6*H* SiC belongs to the same space group as ZnO and CdS ($P6_3mc$) but has more atoms per unit cell,[3] and therefore has additional weak modes accessible to Raman scattering. As a result of certain special properties of phonons in SiC polytypes it is possible to classify the observed weak modes in 6*H* SiC and to display the results in what appear to be phonon dispersion curves.

Many phonon energies have been reported for 6*H* SiC, but most are zone boundary phonons, measured in luminescence,[4] indirect interband absorption,[5] and two-phonon infrared absorption.[6] Polytype 6*H* has 12 atoms per unit cell, hence 33 long-wavelength optic modes, many of them allowed in first-order Raman scattering, but few of them previously observed. Earlier Raman work on SiC was done without a laser, and apparently without polytype identification; only a few lines were reported.[7] The residual ray reflection spectrum of 6*H* SiC was analyzed by Spitzer *et al.*[8] to give fairly complete information on the strong modes. Recently[9] an additional weak absorption line was found at 19.9 μ. This was subsequently identified as a fundamental lattice line, the key to identification being an analysis of phonon branches in the large zone.[10]

† This work was supported in part by the U. S. Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract No. F33615-67-C1401.

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