(ii) if, on the other hand, the interaction of the dipoles is dominant and $\langle s_z \rangle$ is the order parameter, quadrupolar ordering must occur at the same time.

In solid methane, the lowest-order multipole (octupole) is dominant. The correspondence is with case (ii) of the magnetic example. The (anti-) ordering of higher multipoles, which does not require the breaking of inversion symmetry in case of even-order multipoles ($z \neq 0$ requires site symmetry $4/mmm$), is induced by the octupolar ordering ($y \neq 0$; actual site symmetry $\bar{4}2m$).

The statement that the ordering occurs in the system of the octupoles and that c_{31} or y is the true order parameter, whereas higher-order expansion coefficients (e.g., c_{41} or z) are only secondary quantities, is supported experimentally: Strong critical scattering in phase I[9] is found at the superlattice reflections with indices $h_1h_2h_3$ all odd. The intensities diverge with approaching T_c and scale with the corresponding Bragg intensities below T_c. On the other hand, no evidence of critical scattering was found at superlattice reflections with Miller indices $h_1h_2h_3$ all even (e.g., 660).

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Magnetophonon Effect in n-Type $Hg_{1-x}Cd_xTe$ ($x = 0.212$)†

H. Kahlert and G. Bauer

Ludwig Boltzmann-Institut für Festkörperphysik, and Institut für Angewandte Physik der Universität Wien,
A-1090 Vienna, Austria

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We report measurements of the magnetic field positions of magnetophonon-oscillation peaks on samples of n-type $Hg_{1-x}Cd_xTe$ ($x = 0.212$). The band-edge effective mass $m^*(0) = 0.005m_0$ and the effective g factor $g^*(0) = -172$ are deduced from low-temperature Shubnikov–de Haas measurements. The temperature dependence of the magnetophonon peaks is interpreted using a nonparabolic band model with a temperature-dependent energy gap and a temperature-dependent band-edge effective mass. A large positive temperature coefficient $d\epsilon_g/dT = +7.6\times10^{-4}$ eV/K is required to fit the experimental data.

The small-gap alloy semiconductor $Hg_{1-x}Cd_xTe$ has roused considerable interest because of its semiconductor-semimetal transition and the associated possibility of adjusting the energy gap by varying the alloy composition. In the last years great progress has been made in the knowledge of the band structure of $Hg_{1-x}Cd_xTe$ by measurements of the far-infrared cyclotron resonance[1,2] and of the absorption edge,[3,4] and by Hall and conductivity measurements with and without hydrostatic pressure.[5,6] Raman scattering data[7] have shown that two kinds of longitudinal-optical phonons are found in the alloy system over a wide range of compositions, the one having the frequency of LO phonons in phonons in pure HgTe, $\omega_{0,1}$, and the other having the frequency of LO phonons in pure CdTe, $\omega_{0,2}$.

This Letter reports measurements of the magnetophonon effect in the temperature range from 50 to 130 K. We interpret these data with a nonparabolic band model[8,9] taking into account the temperature variation of the energy gap, which behaves anomalously for a zinc-blende-type semiconductor: The observed energy gap increases with increasing temperature, a fact which has not yet been explained theoretically.[4,10,11]

Magnetophonon resonances have recently been studied in a variety of semiconductors.[12] Among its applications the magnetophonon effect can be employed as a simple method of probing the $\epsilon(k)$ relation of conduction or valence bands if the energy of the LO phonons is precisely known.

The determination of the exact values of the magnetic fields where extrema of the oscillatory magnetophonon resonance occur is difficult. The oscillatory component of the magnetoresistance is superimposed in most cases on a nonoscillatory component with unknown functional dependence on the magnetic field. To overcome this difficulty, electronic differentiating techniques have widely been employed.[13] We have solved the problem of extracting the oscillatory component by amplifying the signal from the potential probes of our samples and feeding it to a Hewlett-Packard 3584 digital voltmeter and to a Hewlett-Packard 9820 calculator, while the magnetic field was swept linearly with time. The voltage drop across the potential probes and the first and second derivatives with respect to the magnetic field are then calculated and plotted versus magnetic field on a Hewlett-Packard 9862 X-Y plotter. Extrema of the second derivative occur at magnetic fields where the oscillatory component of the original curve has a minimum or maximum.

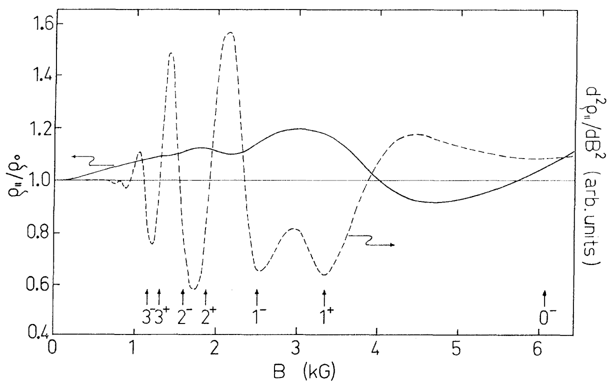

FIG. 1. Dependence of the resistivity (full curve) and its second derivative (dashed curve) on the longitudinal magnetic field at 4.2 K. The arrows indicate the positions calculated for the extrema.

The samples used in the present experiment are n-type $Hg_{1-x}Cd_xTe$ ($x = 0.212$, Cominco) with a mobility of 85 600 cm^2/V sec at 4.2 K. A carrier concentration of $n = 1.6\times 10^{15}$ cm^{-3} was deduced from Hall effect and Shubnikov-de Haas (SdH) measurements at 4.2 K. The SdH data were taken in the longitudinal configuration $B \parallel j$. Figure 1 shows an experimental recording of the SdH oscillations at 4.2 K together with the second derivative of the resistivity ρ with respect to B. The spin splitting of the $L = 1$ extremum is well resolved. By using the expression[9]

$$\epsilon = \frac{\hbar e B}{m^*(0)} \frac{\epsilon_g(\epsilon_g + \Delta)}{3\epsilon_g + 2\Delta}\left(L + \frac{1}{2}\right)\left(\frac{\epsilon}{\epsilon + \epsilon_g} + \frac{1}{\epsilon + \epsilon_g + \Delta}\right) \pm \frac{1}{2}\beta g^*(0) B \frac{\epsilon_g(\epsilon_g + \Delta)}{\Delta}\left(\frac{1}{\epsilon + \epsilon_g} - \frac{1}{\epsilon + \epsilon_g + \Delta}\right), \tag{1}$$

we have calculated the positions of the extrema indicated by the arrows in Fig. 1. From an amplitude analysis of the SdH extrema at 4.2 K and lower temperatures, we have deduced a value of the band-edge effective mass $m^*(0) = (0.005 \pm 0.0003)m_0$. Parameters of the calculation were $\epsilon_g = 93$ meV, $\Delta = 0.96$ eV, the Fermi energy $\epsilon_F = 9.065$ meV, and $g^*(0) = -172 \pm 10$ being the effective spectroscopic splitting factor at the bottom of the conduction band. This value is in good agreement with a value of $g^*(0) = -197$ given by McCombe, Wagner, and Prinz,[14] bearing in mind the smaller band gap of their samples according to a slightly different composition. An evaluation of the g factor assuming a parabolic band as presented by Suizu and Narita[15] from an analysis of SdH measurements seems to be invalid for this small-gap material.

Figure 2 shows experimental recordings of the longitudinal magnetoresistance at various lattice temperatures. Apparently the extrema of the oscillatory component marked by arrows are shifted towards higher magnetic fields with increasing temperature. For an interpretation of these results, we have calculated the positions of magnetophonon extrema using the following expression for the energy of the Landau levels, which for large Δ can be used instead of Eq. (1)[8]:

$$\epsilon_L = \frac{1}{2}\epsilon_g\left[-1 + \left(1 + 4\ L + \frac{1}{2} \pm \frac{1}{4} g^*(0)\left[\frac{m^*(0)}{m_0}\right]\frac{\hbar e B}{\epsilon_g m^*(0)}\right)^{1/2}\right]. \tag{2}$$

The position of the Nth extremum follows from the solution of $\epsilon_{L+N} - \epsilon_L - \hbar\omega_{0,1} = 0$. We have considered transitions to the $L = 0$ Landau level only. The calculated extremal positions of the magnetophonon effect for $N = 1, 2, 3$ as a function of the lattice temperature are shown in Fig. 3 together with the experi-

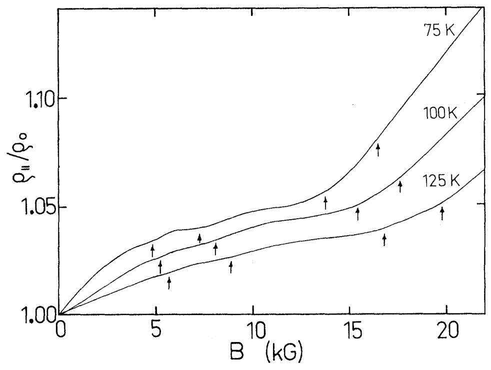

FIG. 2. Longitudinal magnetoresistance versus B. Parameter is the lattice temperature. The arrows indicate the positions of the magnetophonon resonances as obtained from the second derivative of the curves.

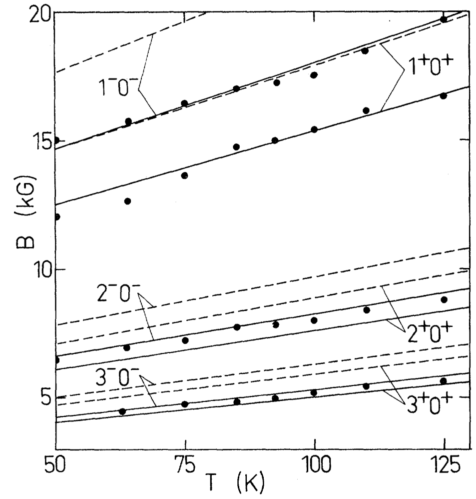

FIG. 3. Temperature dependence of the magnetophonon resonances. Solid lines, calculated for $\hbar\omega_{0,1} = 17.1$ meV; dashed lines, calculated for $\hbar\omega_{0,2} = 19.6$ meV; dots, experimental data.

mental data. The full curves are for $\hbar\omega_{0,1} = 17.1$ meV ("HgTe phonons"), the dashed curves for $\hbar\omega_{0,2} = 19.6$ meV ("CdTe phonons"). Obviously, the observed resonances must be attributed to transitions involving the 17.1-meV HgTe phonons. The spin splitting of the $N = 1$ transition is well resolved. We could not detect resonances belonging to 19.6-meV phonons within our experimental accuracy.

The temperature dependence of the positions arises from the temperature dependence of the energy gap, which we have assumed to be of the form $\epsilon_g = \epsilon_g^0(1 + \alpha T)$ with $\epsilon_g^0 = 0.09$ eV. Consequently, the band-edge effective mass, which according to Kane's theory[8] is proportional to the energy gap, we have applied in the form $m^*(0) = m_0^*(0)(1 + \alpha T)$. As a fitting parameter we have varied the temperature coefficient α. A best fit of the calculated curves to the experimental data in Fig. 3 was obtained with $\alpha = 8.5 \times 10^{-3}$ K^{-1} yielding $d\epsilon_g/dT = \alpha\epsilon_g^0 = 7.6 \times 10^{-4}$ eV/K. Any attempt to fit the temperature dependence of the four experimentally observed lines with transitions involving 19.6-meV phonons was unsuccessful.

Applying the Brooks-Yu theory,[16] Tsay *et al.*[17] were able to calculate theoretically the correct temperature dependence of the band gaps in several III-V semiconductors. However, it was shown by Guenzer and Bienenstock[11] that the Brooks-Yu theory is not capable of explaining the positive temperature coefficient of the band gap in HgTe. Because of the smooth shift of $d\epsilon_g/dT$ with composition in the $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ system, these authors anticipated that the mechanism which leads to the anomalous sign in HgTe also causes the anomalous sign for the alloys with $0.16 \lesssim x \lesssim 0.5$. Hence, their results suggested that the Brooks-Yu theory is inadequate for them as well.

The value of $d\epsilon_g/dT = 7.6 \times 10^{-4}$ eV/K derived from our fitting procedure has to be compared with the directly measured temperature coefficient of the band gap of $d\epsilon_g/dT = 3.5 \times 10^{-4}$ eV/K in alloys with similar composition.[18] However, an explanation of this difference must be deferred until an adequate theory for the anomalous sign of $d\epsilon_g/dT$ in HgTe and $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ is found.

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Surface States and Catalysis on *d*-Band Perovskites[*]

F. J. Morin and T. Wolfram
Science Center, Rockwell International, Thousand Oaks, California 91360

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It is demonstrated that surface states derived from the lower conduction band of d-band perovskites produce a square-root singularity peak in the density of surface states at energies which lie in the forbidden gap. These surface states are highly localized and have nearly pure d-state character. It is suggested that these surface states provide the necessary orbitals to facilitate an important class of symmetry-forbidden chemical reactions.

Considerable attention has been focused recently on transition-metal oxides of the perovskite structure because of their possible utility as catalysts. Pedersen and Libby[1] suggested that the rare-earth cobalt oxides $R\mathrm{CoO}_3$ (R = La, Nd, and Dy) might provide an inexpensive substitute for platinum-based catalysts for the oxidation of pollutants in auto exhaust. More recently, Voorhoeve[2] reported success in oxidizing carbon monoxide and reducing the oxides of nitrogen using transition-metal oxides such as $(\mathrm{La}_{1-x}\mathrm{Pb}_x)\mathrm{MnO}_3$ and $(\mathrm{Pr}_{1-x}\mathrm{Pb}_x)\mathrm{MnO}_3$ which also have the cubic perovskite structure. Although it is generally believed that the catalytic properties of these materials are associated with the d electrons, the detailed mechanisms of catalysis are not well understood.

We had suggested previously[3] that the d-band perovskite insulators such as SrTiO_3 would be simple model materials with which to initiate studies of the catalytic properties of the d-band perovskites since the d-band surface states in these materials are normally empty but may be populated in a controlled manner by photoexcitation. Theoretical calculations by Wolfram, Kraut, and Morin[3] have established that a reasonably realistic, analytical model for the d bands in the perovskites could be derived from a very simple linear-combination-of-atomic-orbitals (LCAO) energy band calculation. The utility of this model was demonstrated by Wolfram[4] who showed that analytic expressions derived for the density of states of the lower conduction bands were in *quantitative* agreement with detailed calculations of Mattheiss.[5] The model has also been used to derive exact expressions for the surface energy bands and wave functions.[3]

In this Letter we demonstrate that (001) surface states derived from the lower conduction bands produce a square-root singularity peak in the density of states in the band gap and that these surface states are of nearly pure d character. We suggest that these states are capable of providing the necessary orbitals to facilitate an important class of symmetry-forbidden chemical reactions.

In a previous Letter,[4] we showed that the lowest conduction bands of a number of d-band perovskites were dominated by the two-center transfer (resonance) integral $(pd\pi)$ which mixes the t_{2g} d orbitals of the transition-metal ion with the p orbitals of the oxygen. These three bands are