

where the change in $2\langle\Delta\rangle$, $\delta(\Delta_{>} + \Delta_{<})$, is plotted versus temperature for a junction on a glass substrate. These data were taken in the low-power regime where Methods 1 and 2 were indistinguishable. At each of the two frequencies (9.9 and 11.9 GHz), there was an enhancement for $T \lesssim T_{\nu}$ while $\langle\Delta\rangle$ was depressed for $T \gtrsim T_{\nu}$. This result is consistent with the observation by Tredwell and Jacobsen³ that the critical current of aluminum microbridges was enhanced by 10-GHz phonons only when $h\nu < 2\Delta_c$. The depression of $\langle\Delta\rangle$ for $T \gtrsim T_{\nu}$ suggests that 10-GHz microwaves do not enhance the transition temperature of aluminum by Method 2. Since Klapwijk and co-workers⁴ found that T_c was enhanced by 3-GHz microwaves, the degree of enhancement is evidently strongly frequency dependent.

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¹G. M. Eliashberg, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 186 (1970) [JETP Lett. **11**, 114 (1970)]; B. I. Ivlev and G. M. Eliashberg, Pis'ma Zh. Eksp. Teor. Fiz. **13**, 464 (1971) [JETP Lett. **13**, 33 (1971)]; G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **61**, 1254 (1971) [Sov. Phys. JETP **34**, 668 (1972)]; B. I. Ivlev, S. G. Lisitsyn, and G. M. Eliashberg, J. Low Temp. Phys. **10**, 449 (1973).

²A. F. G. Wyatt, V. M. Dmitriev, W. S. Moore, and F. W. Sheard, Phys. Rev. Lett. **16**, 1166 (1966); A. H. Dayem and J. J. Wiegand, Phys. Rev. **155**, 419 (1967).

³T. J. Tredwell and E. H. Jacobsen, Phys. Rev. Lett. **35**, 244 (1975), and Phys. Rev. **13**, 2931 (1976).

⁴T. M. Klapwijk and J. E. Mooij, Physica (Utrecht) **81B**, 132 (1976); T. M. Klapwijk, J. N. van den Bergh, and J. E. Mooij, J. Low Temp. Phys. **26**, 385 (1977).

⁵B. R. Fjordbøge, T. D. Clark, and P. E. Lindelof, Phys. Rev. Lett. **37**, 1302 (1976).

⁶J.-J. Chang and D. J. Scalapino, to be published.

⁷J.-J. Chang and D. J. Scalapino [Phys. Rev. Lett. **37**, 522 (1976)] have recently discussed tunneling as a probe of nonequilibrium superconductors.

⁸C. C. Chi and D. N. Langenberg, Bull. Am. Phys. Soc. **21**, 403 (1976); C. C. Chi, private communication.

⁹W. L. McMillan, and J. M. Rowell, *Superconductivity* (Dekker, New York, 1969), Vol. 1, p. 589.

¹⁰A. H. Dayem and R. J. Martin, Phys. Rev. Lett. **8**, 246 (1962); P. K. Tien and J. P. Gordon, Phys. Rev. **129**, 647 (1963).

¹¹J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

¹²S. Shapiro, Phys. Rev. Lett. **11**, 80 (1963).

Observation of a Charge Transfer During Bi Oxidation as Noted from the Final-State Changes*†

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By monitoring the change in the conduction-band optical density of states (CBODOS) and the bonding shifts of the core levels, we observe an electronic transfer from Bi to oxygen atoms during Bi oxidation. Similar analysis of the CBODOS of other Bi and Pb chalcogenides indicates a partial ionicity in these compounds which correlates with electronegativities and the chemical shifts of the core levels.

The observation of changes in electronic structure during chemisorption and/or oxidation has been confined primarily to monitoring the changes of the occupied, i.e., valence-band, density of states (VB DOS) and core-level shifts. However, a charge redistribution of valence electrons, reflecting formation of new bonds, can also result in changes in the conduction band. We report here the first observation of changes in the (empty) conduction-band density of states (CB DOS), noted during the oxidation of Bi. Because of a strong spin-orbit (SO) splitting of the conduction band (CB) of bismuth oxide, we can determine

the predominant total-angular-momentum component of Bi valence electrons which are transferred to oxygen atoms during formation of Bi_2O_3 . Specifically, during formation of Bi_2O_3 , we observe in the CB DOS the onset of a dominant peak due to states of mainly $6p_{1/2}$ character which in the atomic ground state are fully occupied. These empty $6p_{1/2}$ states in Bi_2O_3 , reflecting the redistribution of Bi valence electrons, are strongly localized at Bi atoms as evidenced by their very small width [~ 0.5 eV full width at half-maximum (FWHM)]. The bonding shifts (1.9 eV) of the core levels, observed simultaneously with the onset of

empty $p_{1/2}$ -like states during Bi_2O_3 formation, indicate that the specific form of the observed charge redistribution is indeed a charge transfer, reflecting the formation of (at least partially) ionic bonds in Bi_2O_3 . Furthermore, the above observation of the narrow, resonancelike *empty* density-of-states (DOS) peak is in agreement with recent calculation of Lang and Williams¹ for the case of chemisorptive *cationic* bonding. The information on the CBDOS was obtained by an application of synchrotron radiation which monitors the CBDOS by measuring the electron emission at fixed kinetic energy E_k resulting from the Auger decay of optically excited core holes. The Auger emission is proportional to the optical transition rate from a flat core level to the CB, and thus provides the CBDOS multiplied by the optical (dipole) matrix elements between the core level and conduction band, and hence, is the CBODOS. This technique, known as CFS² (constant final-energy spectroscopy), is a modification of photoyield spectroscopy³ and allows some control of surface sensitivity by varying E_k , and hence, the escape depth λ , of detected electrons. Thus this work indicates that the application of synchrotron radiation allows monitoring during a chemical reaction the changes occurring in (i) valence states, (ii) empty states, and (iii) core levels.

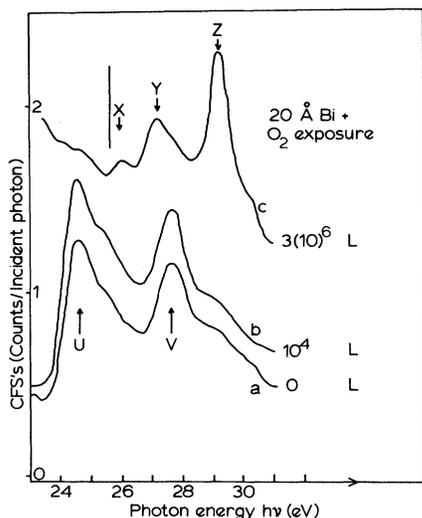


FIG. 1. CFS's between $h\nu = 23$ and $h\nu = 31$ eV normalized and corrected for the varying light flux out of the monochromator. The core-level indications reflect the instrumental resolution at these photon energies as opposed to the visible onset of the peaks. Curve *a* is for pure Bi, curve *b* for Bi+ chemisorbed oxygen, and curve *c* is for Bi_2O_3 . (1 L = 10^{-6} Torr sec.)

The large (~ 3.1 eV) SO splitting of the $5d$ core levels of Bi allows the application of selection rules to determine the angular momentum character of empty states in the optical transitions from the $5d$ cores to the conduction band. Besides considerable SO splitting of core states in Bi and its compounds, Bi was chosen for this study because of interesting properties of oxidation kinetics. Specifically, the onset of the true oxidation of Bi (as determined by changes in the VB, CB and a 1.9-eV bonding shift of the core levels) is preceded by and sharply separated from a precursor stage of oxygen chemisorption below a certain critical exposure L_c .⁴ This separation of the chemisorptive and oxidation phases makes the system attractive for direct studies of charge transfer. The experimental details and interpretation of the ultraviolet photoelectron spectroscopy observation are presented elsewhere.⁴ In Fig. 1 we present the CFS's for three representative systems: (i) a pure Bi film, deposited *in situ* (curve *a*), (ii) Bi+ chemisorbed oxygen at an exposure less than the critical oxidation exposure (curve *b*), and (iii) oxidized Bi, termed Bi_2O_3 (curve *c*). For comparison, in Fig. 2, we present the VB DOS for the three corresponding cases indicating that the chemisorption of O_2 results in attenuation of metallic Bi emission from the upper VB peak.⁵ Upon oxidation,

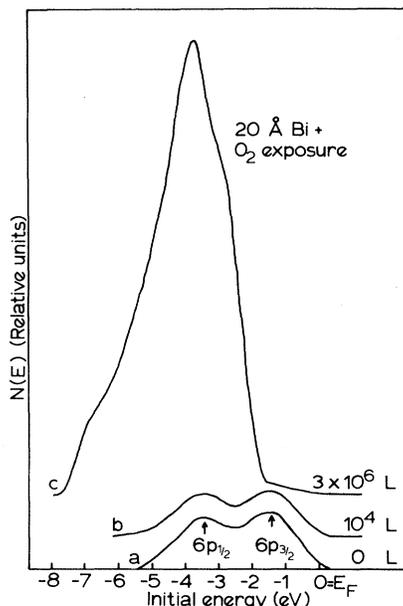


FIG. 2. Corrected valence-band emission from EDC's at $h\nu = 18.0$ eV (inelastic peak subtracted). The three curves *a*, *b*, and *c* correspond to the same oxygen exposures as in Fig. 1.

the formation of the valence-band edge at ~ -1.9 eV below the Fermi level E_F is obvious.

The main interpretation of the data is based on extracting the angular momentum character of the *final states* from selection rules for the transitions from $5d_{5/2}$ and $5d_{3/2}$ to the empty states for the two distinct cases for Bi metal and Bi_2O_3 . Curve a of Fig. 1 clearly indicates that the basic features of the CBODOS of Bi metal are nearly identical as "seen" from the two SO-split $5d$ core levels. This implies that the CB states cannot be separated into $|p_{1/2}\rangle$ - and $|p_{3/2}\rangle$ -like regions, nor are atomiclike selection rules applicable. Similar conclusions hold for Bi+chemisorbed O_2 (curve b). Curve c for Bi_2O_3 , however, presents an entirely different situation, where the CB "seen" from $5d_{5/2}$ level is strikingly different from that "seen" from the $5d_{3/2}$ level.

Such a situation can be explained in terms of spin-orbit splitting of the empty states into $6p_{1/2}$ - and $6p_{3/2}$ -like states⁶ and at least partial restoration of atomiclike selection rules in Bi_2O_3 . On the basis of energies and relative intensities of transitions from chemically shifted Bi $5d$ core states, the following assignments of prominent features of Fig. 1(c) are made. The region between $h\nu = 25.7$ and 28.8 eV represents the CBDOS as coupled to the Bi $5d_{5/2}$ core level. The weak peak X at $h\nu = 26.2$ eV and broader peak Y at $h\nu = 27.3$ eV are interpreted to be due to transitions to primarily $6p$ - and $6p_{3/2}$ -like states, respectively. The region above $h\nu = 28.8$ eV shows the same portion of the CBDOS, but as coupled to the Bi $5d_{3/2}$ core level. The lower part (p -like) of the conduction band is now strongly coupled to the $5d_{3/2}$ core level in contrast to the weakly coupled $5d_{5/2}$ core level, as evidenced by the strong peak Z at $h\nu = 29.3$ eV, which clearly dominates the spectrum. The remainder of the conduction band is only weakly coupled to the $5d_{3/2}$ level (shoulder at $h\nu = 30.7$ eV). We consider the strong⁷ peak of $p_{1/2}$ -like character occurring in the empty states

of Bi_2O_3 , but not of Bi, as evidence of a charge redistribution during formation of Bi_2O_3 . Simultaneous observation of the 1.9 eV increase in the binding energies of the Bi $5d$ core levels⁴ clearly indicates that the observed charge redistribution, manifesting itself through the onset of the strong $p_{1/2}$ -like empty DOS peak, is indeed a charge transfer reflecting formation of (at least partially) ionic bonds in Bi_2O_3 . The small half-width of the peak Z (~ 0.5 eV FWHM) further indicates a strong localization of the *empty* $p_{1/2}$ -like state at the Bi site, and is consistent with the charge-transfer phenomenon. Significantly, the observation of the resonancelike empty $p_{1/2}$ -like peak just above the Fermi level is in agreement with the recent calculation¹ of Lang and Williams for chemisorptive cationic bonding, and can be thus considered as further evidence of the charge transfer during Bi_2O_3 formation. Table I shows transition strengths calculated for the various couplings as if all levels were strictly atomic. The most obvious breakdown of the "strictly atomic" assertion is that the transition $d_{5/2} \rightarrow p_{1/2}$ does occur, showing that despite the small half-width of the peak Z, the localization of final conduction-band states in Bi_2O_3 is not perfect (nor is it expected to be).

TABLE I. Strengths of optical transitions between atomic d and p states.

| Transition | Strength (relative) | Corresponding peak |
|-------------------------------|---------------------|--------------------|
| $d_{5/2} \rightarrow p_{1/2}$ | 0 | X |
| $d_{5/2} \rightarrow p_{3/2}$ | 1 | Y |
| $d_{3/2} \rightarrow p_{1/2}$ | 5/9 | Z |
| $d_{3/2} \rightarrow p_{3/2}$ | 1/9 | |

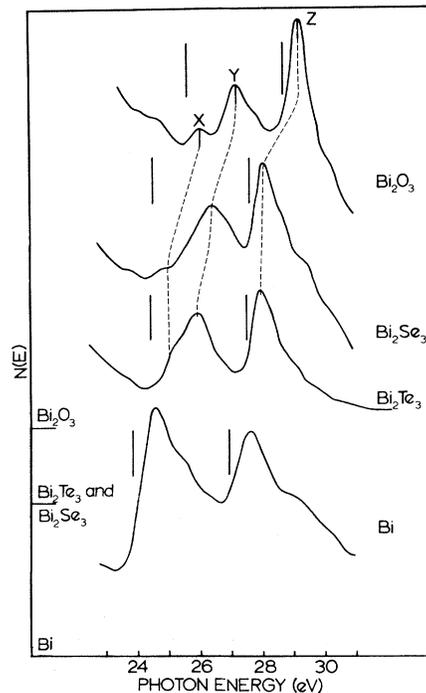


FIG. 3. The CFS's for pure Bi and the three Bi chalcogenides.

Similar charge redistribution is noted to occur, albeit to a lesser extent, in the compounds Bi_2Te_3 ⁶ and Bi_2Se_3 , which are isoelectronic to Bi_2O_3 . CFS's for Bi and the three other compounds are shown in Fig. 3. For Bi_2Te_3 and Bi_2Se_3 , we see that the shapes of the CBODOS for coupling to two separate core levels are not the same, indicating again the SO-split portions of the empty states. However, because of a much lesser degree of the charge redistribution, the separation of the $p_{1/2}$ - and $p_{3/2}$ -like portions (i.e., of structures X, Y) in the telluride and selenide is much weaker than in the oxide. (Actually, the peak X in the oxide is changed into a weak but definite shoulder in the telluride and selenide.) The relevant structures and their onsets in the CFS's are shifted in photon energy for the four solids, because the Bi 5*d* core levels are all chemically shifted in the compounds (Table II). Note that for the entire sequence of Bi chalcogenides there is a correspondence between (i) the size of the chemical shift, (ii) the degree of SO splitting of the CB appearing in the CFS's, (iii) the degree of localization of the final states, and (iv) the electronegativity of the chalcogen, indicating progressively larger transfer of the bismuth electrons to the chalcogen site from Te to O.

In Table II we show the 5*d* core levels referenced to the Fermi energy. These binding energies may be compared to the CFS's in Fig. 3, with Bi metal as a neutral case. As the Bi ion becomes more and more positive, the core levels shift in response to a slightly more attractive potential. We consider the correlation of the SO splitting of the empty states with the bonding shifts of the core levels as evidence of (at least) *partial* ionicity in all three Bi chalcogenides. The ionicity in Bi_2Te_3 and Bi_2Se_3 is indeed much less than in Bi_2O_3 , and the width of the peak Z is much larger suggesting more delocalization dur-

ing the electron redistribution. The narrowness of the peak Z (as well as of X) and the separation of peaks X and Y in Fig. 3 correlates with the relative magnitude of these structures, and with the relative degree of ionicity in these compounds.⁸ There is a special significance to this experimental evidence for the partial ionicity in the cases of Bi_2Te_3 and Bi_2Se_3 because the strongly anisotropic bonding in this layered solid necessitates the existence of an intermediate, partially ionic bond, which was previously postulated on theoretical grounds.⁹

Finally, the above analysis can be carried over to the case of lead chalcogenides. There, a similar spin-orbit splitting of the final state was observed,¹⁰ which in view of the above analysis can be interpreted as a result of a partial ionicity in the lead compounds, consistent with their rock salt structure.

In summary, we have shown that the CFS technique with synchrotron radiation can be used during oxidation to monitor the charge redistribution by allowing observation of the onset of a narrow, dominant $p_{1/2}$ -like empty DOS peak of features similar to those described in calculations¹ for chemisorptive cationic bonding. Simultaneous observation of the 1.9-eV increase of the binding energy of Bi core levels indicates formation of an ionic bond in Bi_2O_3 and suggests that the onset of the empty $p_{1/2}$ -like peak in the CFS's reflects at least partial transfer of $p_{1/2}$ -like electrons from Bi to oxygen sites. Indeed, this charge-transfer evidence sheds light on the previously observed sharp distinction between the system Bi + chemisorbed O_2 (probably weak, covalentlike bonds) and Bi_2O_3 .⁴ Evidence of much weaker and broader $|p_{1/2}\rangle$ empty states has been found for other Bi (and Pb) chalcogenides and is interpreted as an indication of the partial ionicity expected on bonding grounds to occur in these compounds. The relative intensity and the half-width of the empty $p_{1/2}$ peak can be related to the bonding shifts of core electrons and to the degree of partial ionicity.

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TABLE II. Binding energies (below E_F) of Bi 5*d* core levels in Bi, in the three Bi chalcogenides, and the electronegativities.

| | $5d_{3/2}$ (eV) | $5d_{5/2}$ (eV) | Electronegativities |
|--------------------------|--------------------|--------------------|---------------------|
| Bi | 23.8 | 26.9 | 2.0 (Bi) |
| Bi_2Te_3 | 24.5 | 27.6 | 2.1 (Te) |
| Bi_2Se_3 | 24.6 | 27.7 | 2.4 (Se) |
| Bi_2O_3 | 25.7 | 28.8 | 3.5 (O) |

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¹N. D. Lang and A. R. Williams, Phys. Rev. Lett. **37**, 212 (1976).

²For a more detailed discussion of the CFS technique see G. J. Lapeyre, A. D. Baer, J. Hermanson, J. Anderson, J. A. Knapp, and P. L. Gobby, Solid State Commun. **15**, 1601 (1974). See also Z. Hurych, J. C. Shaffer, D. L. Davis, T. A. Knecht, G. J. Lapeyre, P. L. Gobby, J. A. Knapp, and C. G. Olson, Phys. Rev. Lett. **33**, 830 (1974).

³W. Gudat and C. Kunz, Phys. Rev. Lett. **29**, 169 (1972).

⁴R. L. Benbow and Z. Hurych, Phys. Rev. B **14**, 4295 (1976).

⁵It has been indicated that the splitting of the VB of Bi into peaks labeled $6p_{1/2}$ and $6p_{3/2}$ is due *primarily* to the SO interaction. L. Ley, R. A. Pollak, S. Kowalczyk, F. R. McFeely, and D. A. Shirley, Phys. Lett. **41A**, 429 (1972), and Phys. Rev. B **8**, 641 (1973), and references therein.

⁶Similar SO structure in the CBODOS has been reported previously in Bi_2Te_3 . Hurych *et al.*, Ref. 2.

⁷The relative strengths of the empty $p_{1/2}$ - and $p_{3/2}$ -

like peaks are difficult to estimate since the two peaks are overlapping, but some qualitative estimates can still be made. Two facts indicate a sharp maximum of the empty $p_{1/2}$ -like DOS: (i) The transition $d_{5/2} \rightarrow p_{1/2}$ of a very small matrix element (zero for atomiclike case) is clearly discernible as the peak X, and (ii) the transition of $d_{3/2} \rightarrow p_{1/2}$ (peak Z) dominates the spectrum despite having smaller atomic matrix element (see Table I) than the $d_{5/2} \rightarrow p_{3/2}$ transition (peak Y).

⁸Observation of the above features of the CBODOS in all Bi chalcogenides and lack of these features in Sb_2Te_3 (which has the same crystal structure as Bi_2Te_3) suggest that the SO splitting rather than the crystal-field effects is the dominant factor in determining the above features of CBODOS in Figs. 1 and 3. Likewise, the fact that the sharpest structures in Fig. 3 occur for (presumably) polycrystalline Be_2O_3 , grown on polycrystalline Bi films, rather than for single crystals of Bi_2Te_3 or Bi_2Se_3 , supports our interpretation of the CBODOS (Fig. 3) in terms of partial ionicity.

⁹J. R. Drabble and C. H. Goodman, J. Phys. Chem. Solids **5**, 142 (1958).

¹⁰G. Martinez, M. Schluter, M. L. Cohen, R. Pinchaux, P. Thiry, D. Dagneaux, and Y. Petroff, Solid State Commun. **17**, 5 (1975), and references therein.

Selection Rules in Raman Scattering from Surface Polaritons

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Raman-scattering selection rules for surface polaritons have been studied by experiments using a thin ($\approx 20 \mu\text{m}$) single-crystal slab of GaP of known orientation. The dispersion of the observed mode has been determined by varying the scattering angle, and comparison is made with the theoretically predicted dispersion of surface polaritons at the surface of a semi-infinite GaP crystal. The observed selection rules are consistent with the results of an analysis using the bulk Raman tensors.

Recently, surface polaritons (SP) have been observed by Raman scattering from polycrystalline films of GaAs.¹ In these experiments, the authors observed scattering from the upper and lower SP modes characteristic of a two-interface, or slab, configuration where the thickness of the slab is comparable to the penetration depth of the surface mode.² Thus far, however, no successful observations have been made of Raman scattering from SP with a single crystal of known orientation. Consequently, the polarization selection rules for SP have not previously been determined. We report in this Letter the first determination of Raman-scattering selection rules for surface polaritons.

We have performed near-forward Raman scattering measurements on a thin ($\approx 20 \mu\text{m}$) slab of

single-crystal GaP with (111) faces with known orientation in the plane. A peak in the Raman spectrum has been observed, whose frequency lies between the bulk TO and LO phonon frequencies for GaP (367.3 and 403.0 cm^{-1} , respectively). In order to identify this mode as being the SP, we determined its dispersion by varying the scattering angle, and compared it with the theoretical dispersion of SP at a single GaP-air interface.³ We then determined a set of selection rules for the scattering by varying the polarization of the incident light and the direction and polarization of the observed scattered light.

The GaP samples which we used in this study were prepared by cutting oriented rectangular parallelepipeds, $\approx 2.5 \times 2.5 \times 1 \text{ mm}^3$, from a single-crystal boule supplied by H. W. Verleur. These