the observed phenomena. It should be clear, however, that detailed descriptions of the influence of screening must await a more thorough treatment of the Coulomb interaction, notably inclusion of higher lying bound states and the quasicontinuum as they might be influenced by screening.

Several valuable consultations with Dr. C. E. Bleil, Dr. E. Y. Wang, and Dr. L. T. Klauder, Jr. are gratefully acknowledged. I am especially grateful to Dr. J. G. Gay for many valuable comments on both the subject matter and preparation of the manuscript.

---

[1] B. O. Seraphin and R. B. Hess, Phys. Rev. Letters 14, 138 (1965); B. O. Seraphin and N. Bottka, Phys. Rev. 139, A560 (1965).

[2] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[3] Y. Hamakawa, P. Handler, and F. Germano, Phys. Rev. 167, 703, 709 (1968.

[4] E. Y. Wang, W. A. Albers, Jr., and C. E. Bleil, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Brown University, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 136.

[5] J. C. Phillips and B. O. Seraphin, Phys. Rev. Letters 15, 107 (1965).

[6] D. E. Aspnes, Phys. Rev. 147, 554 (1966), and 153, 972 (1967).

[7] C. B. Duke and M. E. Alferieff, Phys. Rev. 145, 583 (1966).

[8] R. Enderlein, Phys. Status Solidi 26, 509 (1968).

[9] H. I. Ralph, J. Phys. Chem. 1, 378 (1968).

[10] A. Many, T. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland Publishing Company, Amsterdam, The Netherlands, 1965).

[11] D. R. Frankl, *Electrical Properties of Semiconductor Surfaces* (Pergamon Press, Inc., New York, 1967).

[12] E. Y. Wang and W. A. Albers, Jr., Phys. Letters 27A, 347 (1968).

[13] R. E. Nahory and J. L. Shay, Phys. Rev. Letters 21, 1569 (1968).

[14] J. G. Gay and L. T. Klauder, Jr., Phys. Rev. 172, 811 (1968).

[15] G. B. Wright, in Proceedings of the International Conference on Luminescence, Budapest, Hungary, 1966 (unpublished), p. 1514.

[16] J. B. Krieger, Phys. Rev. 178, 1337 (1969).

[17] R. J. Elliott, Phys. Rev. 108, 1384 (1957), and in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd Publishers, London, England, 1963).

[18] The limitations of Eq. (6) as an approximation are discussed in Ref. 15.

[19] L. Hulthén and K. V. Laurikainen, Rev. Mod. 23, 1 (1951).

[20] J. G. Gay and W. A. Albers, Jr., to be published.

[21] R. C. Casella, J. Appl. Phys. 34, 1703 (1963).

[22] C. E. Bleil, E. Y. Wang, and W. A. Albers, Jr., Bull. Am. Phys. Soc. 14, 416 (1969).

[23] E. Y. Wang, W. A. Albers, Jr., and C. E. Bleil, Bull. Am. Phys. Soc. 14, 416 (1969).

PIEZO SOFT-X-RAY EFFECT

R. H. Willens, H. Schreiber, E. Buehler, and D. Brasen
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 2 June 1969)

The modulation of the L_{III} x-ray emission band of copper due to an alternating elastic strain is reported for the first time. The technique is useful for the determination of deformation potentials and for the locations of critical points and the Fermi energy in the electronic band structure.

We report here for the first time the modulation of the soft-x-ray emission spectrum due to an applied stress. Although the experiments reported here were done on polycrystalline material, this technique shows promise for determining deformation potentials and the energy location within a band of the points of high symmetry, i.e., degeneracy, in the electronic structure.

The soft-x-ray emission of a material has usually been interpreted as proportional to the product of the density of states $N(E)$ and the transition probability $P(E)$. The near impossibility of determining the density of states from an analysis of the soft-x-ray spectrum has been previously discussed by Rooke.[1] The Van Hove singularities, in many instances, are unresolved due to effects such as instrumental, lifetime, and Auger broadening. The one-dimensional representation of the transition probability is oversimplified. The emission intensity is the resultant of integrating over a surface of constant energy in k space, i.e.,

$$I(E) \sim \nu^3 \int_S P(\bar{k}) dS / \nabla_k E,$$

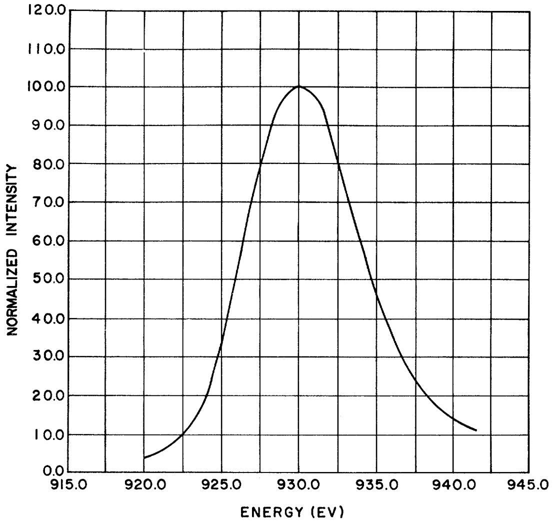

FIG. 1. The $L_{\rm III}$-emission spectrum of copper measured by a spectrometer using a crystal of potassium acid phthalate ($2d = 26.8$ Å).

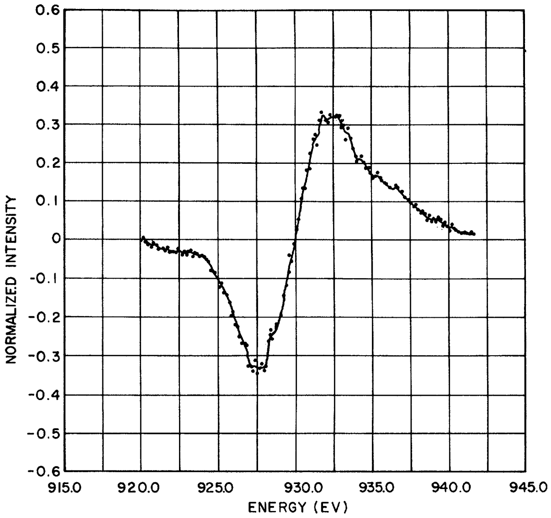

FIG. 2. The change of emission intensity, I(load) $-I$(unload), as a result of loading a copper specimen in uniaxial tension to a stress of 12 000 lb/in.^{2}.

where $P(\bar{k})$ is the probability of the transition and should be dependent on $\bar{k}$ especially at locations where there is a mixing of wave functions of different symmetry.

The soft-x-ray emission spectrum of a band should be affected in two ways due to an application of a mechanical strain. First, there should be a shift in energy of the emission band as a consequence of the deformation potentials. This shift does not necessarily have to be uniform as different subbands can shift varying degrees. Second, the strain alters the symmetry of the lattice and this may split formerly degenerate levels. This could be in the form of either $\bar{k}$-space or orbital degeneracy. For either case the change of emission would be affected mostly at locations of Van Hove singularities or critical points where degeneracy is prevalent.

The first material examined for the piezo soft-x-ray effect was polycrystalline copper. The specimen surface was prepared by mechanical polishing, electropolishing off the mechanically worked layer, and then finally cathodically etching by ion bombardment. Because the generation of x rays occurs appreciably below the surface (the active volume extends down to depths of several microns), preparation of the surface was not critical for observing the effect. However, the worked layer, which has crystallographic texture that may differ from the bulk, must be removed to obtain reproducibility. The $L_{\rm III}$ emission, which corresponds to transitions from the $3d$-$4s$ to the $2p_{3/2}$, has its maximum intensity at 13.330 Å (930.1 eV).[2] The spectrometer used for analyzing the spectrum is of similar construction to that described by Mattson and Ehlert.[3] For our experiments the sample chamber was redesigned to permit stressing the material under investigation in uniaxial tension or compression to levels of 40 000 lb/in.^{2}. The loading of the sample is done in a coaxial manner, so that negligible distortion strains which could affect the results are transmitted to the spectrometer. The crystal used to analyze the $L_{\rm III}$ spectrum of copper was singly bent potassium acid phthalate ($2d = 26.8$ Å). The spectrum was step scanned in wavelength increments of 0.002 Å. At each step position the specimen was alternately loaded and unloaded 100 times at 10-sec intervals. The load level corresponded to a stress of 12 000 lb/in.^{2} in tension. The magnitude of the piezo soft-x-ray effect required between 10^7 and 10^8 counts total to be accumulated at each step position to assure statistical significance.

Figure 1 shows the observed emission spectrum. This represents the data as recorded with no corrections applied. The data have been normalized to give the peak a value of 100. Figure 2 shows the change of the emission intensity, I(load)$-I$(unload), which results when the copper specimen is stressed. The curve drawn through the experimental points is computed on the basis of averaging adjacent readings, weighted at one-half, with the reading at the location in question. From the gross shape of this curve, it is evident that to the first approximation it represents the derivative. Superimposed on this curve there also appears to be a fine structure. This point will be discussed later. To check whether the results were reproducible, the specimen was removed from the sample chamber, the surface cathodically etched by ion bombardment, and the specimen replaced. Repeating the identical experiment produced the same results, even duplicating the positions of the fine structure. To check whether the effect was real and not associated with some spurious instrumental effect, a copper foil was attached at one point to the top of the specimen where the x rays were being generated. The experiment was then repeated. It is important to note for this experiment that all the misalignment strains transmitted to the spectrometer would be identical but the x-ray emission could only be from unstrained copper. In this case no emission change was observed between loaded and unloaded conditions, indicating that the piezo soft-x-ray effect is real.

If another specimen of polycrystalline copper is examined, identical to the first except possessing a different crystallographic texture (preferred orientation), the effect is appreciably modified. The gross derivative curve is similar, but the fine structure is altered. The curve presented in this Letter shows that the intensity change is zero at the peak position. This is more the exception than the rule; for most of the samples investigated, the intensity change under load is appreciable at the peak position.

If the piezo soft-x-ray effect were entirely associated with a band shift then the subtraction of the product of the derivative of the emission curve (Fig. 1) and a suitable constant (the energy shift corresponding to the sample strain) from the intensity change (Fig. 2) should result in a null curve. Figure 3 shows the result of carrying out this procedure. Curve 1 is the original plot. Curves 2 and 3 are the resultants of subtracting the product of derivative of the emission curve multiplied by 0.010 and 0.015 eV, respectively, from Curve 1. It is apparent that a shift cannot totally account for the observed effect. The energy shift due to the applied stress, which reduces most of the effect to zero, is about 0.015 eV at the top of the band and about 0.010 eV at the bottom of the band. This is with respect to the $2p_{3/2}$ level which can fairly well be assumed not to vary significantly at this stress level. The band shift is not uniform as different electronic subbands can shift varying amounts. Because the sample is polycrystalline with preferred orientation and only strained in uniaxial tension it is difficult to separate the average deformation potentials associated with dilation or shear strains. If it is assumed that the polycrystalline copper is isotropic with a Young's modulus of 20×10^6 lb/in.^{2}, the average deformation potential is 25 eV at the top of the band and about 17 eV at the bottom of the band. These numbers can only be considered approximate since the exact microscopic strain conditions are not known and further experiments with single crystals will need to be performed.

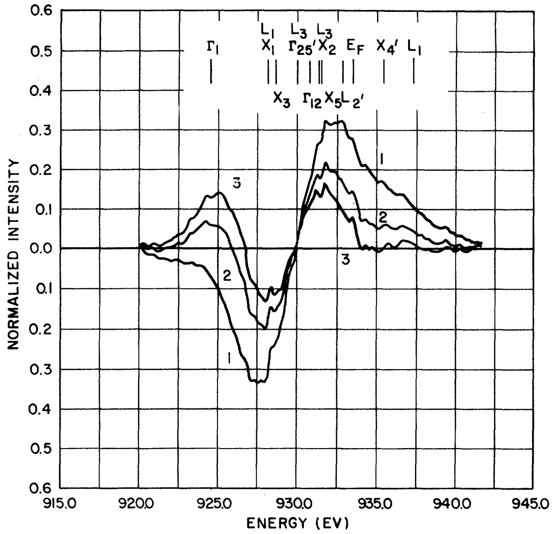

FIG. 3. Subtraction of the derivative of the emission spectrum from the intensity change due to stressing the copper specimen. Curve 1 is the original curve. Curves 2 and 3 are the results of the subtraction, assuming shifts of 0.010 and 0.015 eV, respectively. The energy location of the various high-symmetry points and the Fermi energy are those calculated by Burdick (see Ref. 5).

The remaining part of the effect, which cannot be subtracted away by a derivative technique, (e.g., curves 2 and 3 of Fig. 3 or perhaps a curve which would be intermediate to them in the midregion due to a continuous variation of the deformation potential through the band) must be associated with locations in the band which are extra sensitive to strain as regards altering the x-ray emission. This could be at the Fermi surface and Van Hove singularities or critical points.

The band structure of copper has been calculated by several investigators.[4-6] There is some arbitrariness in the correlation between the positions of the energy scales corresponding to the calculations and the soft-x-ray emission spectrum. However, Burdick[5] has attempted to correlate his energy scale with the soft-x-ray emission scale. The peak of the calculated density of states corresponds to the peak in the emission spectrum, which is probably quite reasonable. Burdick's calculated values for the Fermi energy and the energy of some of the high-summetry points are shown in Fig. 3. It would not be reasonable, at the present time, to assign any of the structure to definite critical points. Single-crystal data should hopefully elucidate this information. However, it is of interest to note that on the high-energy side of curve 3, Fig. 3, there is an abrupt increase of intensity at 933.8 eV and a small peak at 933.5 eV. This is the same as Burdick's calculated value of 933.5 eV for the Fermi energy.

The advantages of this technique over those which attempt to determine band structure, such as photoemission spectroscopy,[7] ion neutralization,[8] and optical and piezo-optical measurements,[9,10] are apparent in that the transitions are well defined (one of the states being an atomic level) and the specimen surface is no longer a critical consideration. Once the spectrum of the pure metal is understood, the application of this technique to the study of alloys will be useful in understanding their electronic structure.

We would like to thank A. G. Chynoweth and J. H. Wernick for the advice and encouragement given throughout this investigation, and Conyers Herring for his critical reading of the manuscript.

---

[1] G. A. Rooke, J. Phys. C: Phys. Soc. (London) Proc. 1, 767 (1968).

[2] A. E. Sandström, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1957), Vol. 30, pp. 186-187; D. W. Fisher, J. Appl. Phys. 36, 2048 (1965).

[3] R. A. Mattson and R. C. Ehlert, Advances in X-ray Analysis (Plenum Press, Inc., New York, 1966) Vol. 9, p. 456.

[4] B. Segall, Phys. Rev. 125, 109 (1962).

[5] G. A. Burdick, Phys. Rev. 129, 138 (1963).

[6] R. L. Jacobs, J. Phys. C: Phys. Soc. (London) Proc. 1, 1296 (1968).

[7] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1044 (1964).

[8] H. D. Hagstrum and G. E. Becker, Phys. Rev. Letters 16, 230 (1966).

[9] H. R. Philipp, W. C. Dash, and H. Ehrenreich, Phys. Rev. 127, 762 (1962).

[10] U. Gerhardt, Phys. Letters 9, 117 (1964).

PHONON FOCUSING IN SOLIDS*

B. Taylor, H. J. Maris, and C. Elbaum
Department of Physics, Brown University, Providence, Rhode Island 02912

(Received 27 June 1969)

In phonon-propagation studies using heat pulses it has been found that predominantly transverse phonons are observed for [100] propagation in LiF whereas mainly longitudinal phonons are observed for this direction in KCl. This result and similar effects previously reported on other crystals are explained in terms of a phonon-focusing effect that arises from elastic anisotropy.

The characteristics of phonon propagation in dielectric solids are conveniently studied by means of heat (phonon) pulses.[1-5] These pulses are produced by passing short-duration (typically 10^{-7}-sec) pulses of current through a resistive metal film (the "source") evaporated onto a selected area of the crystal under study. The phonon pulses are detected, after traveling through the crystal, at the face opposite the source. The detection of the arriving phonons is achieved by measuring the change in the electrical resistance of a superconducting film maintained very near its transition temperature. In the present investigation sources consisting of Constantan films, and detectors composed of an indium-tin alloy (94% In, 6% Sn), were used. The measurements were carried out in the temperature range $2°\mathrm{K} \lesssim T \lesssim 3.6°\mathrm{K}$ using a magnetic field to vary the transition temperature of the detector. The crystals were ultraviolet-grade LiF and optical-grade KCl supplied by the Harshaw Chemical Company.

In these experiments separate pulses are observed due to transverse and longitudinal phonons, these pulses arriving at different times because of the different velocities of the phonons. We have found that the relative amplitudes of these pulses depend very strongly on the propagation direction and that in the [100] direction the predominant mode differs in KCl and LiF. Figure 1 shows a pulse observed for propagation in the [100] direction in LiF. The velocity of the phonons associated with this pulse is that of