TABLE V. Evaluation of the scattering integrals for
zero magnetic field.

β	0.01	0.03	0.10	0.30	
$K(\beta,0)$	0.98134	0.95779	0.90400	0.81345	
$L(\beta,0)$	0.92426	0.85843	0.73923	0.58260	
β	1.0	3.0	10	30	100
$K(\beta,0)$	0.65662	0.47220	0.27095	0.13407	0.05114
$L(\beta,0)$	0.37777	0.20344	0.07464	0.02108	0.00395

analysis are:

$$K(\beta,\gamma^s) \equiv \int_0^\infty \frac{x^3(x^2+\beta)e^{-x}}{(x^2+\beta)^2+\gamma^s x^3} dx, \quad (B1)$$

$$L(\beta,\gamma^s) \equiv \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{9/2}e^{-x}}{(x^2+\beta)^2+\gamma^s x^3} dx, \quad (B2)$$

where

$$\beta \equiv 6\mu_L{}^s/\mu_I{}^s, \quad (B3)$$

$$\gamma^s \equiv (9\pi/16)(\mu_L{}^s H/c)^2. \quad (B4)$$

These integrals have been numerically integrated and
tabulated by Beer, Armstrong, and Greenberg.[29] How-
ever, they do not include the case for zero magnetic
field, which is needed when evaluating R_0/R_∞ and the
experimental values of β_2.

The integrals $K(\beta,\gamma)$ and $L(\beta,\gamma)$ can be evaluated
for $\gamma=0$ by considering the Taylor-series expansions:

$$K(\beta,\gamma) \sim K(\beta,0)+(\partial K/\partial\gamma)_{\gamma=0}\gamma \quad (\gamma \ll 1), \quad (B5)$$

$$L(\beta,\gamma) \sim L(\beta,0)+(\partial L/\partial\gamma)_{\gamma=0}\gamma \quad (\gamma \ll 1). \quad (B6)$$

Table V can now be constructed.

Indirect Optical Absorption of AgCl-AgBr Alloys*

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(Received 21 March 1966)

High-resolution measurements of the optical absorption edge of pure crystals of AgBr and AgCl are in good
agreement with the theory of phonon-assisted indirect transitions. The indirect optical absorption of
AgCl-AgBr mixed crystals has been studied between 4.2 and 77°K. At 4.2°K, the addition of AgBr to AgCl
causes the absorption edge to shift continuously from the pure AgCl threshold at 3.252 eV to the pure AgBr
threshold at 2.691 eV. Above 5.7 mole % AgBr in AgCl, the absorption coefficient increases steeply to values
considerably greater than that of pure AgBr at the same wavelength. The effect of the alloying on the pure-
crystal absorption spectra is somewhat different for the two extremes of mixing. In AgBr-rich mixed crystals
(>90 mole % AgBr in AgCl), a temperature-independent component with a sharp threshold is observed at
an energy precisely halfway between the indirect phonon-emission and phonon-absorption thresholds (which
still appear with phonon energy 0.0082 eV as in pure AgBr). This suggests that nonvertical transitions can
occur in the alloy without the aid of phonons to conserve crystal momentum. The zero-phonon threshold is
not so evident for dilute concentrations of AgBr in AgCl, where a weak shoulder and tail extends approxi-
mately 0.07 eV to longer wavelengths. Some comparison with theory is given, but present understanding of
the band structure of alloys is rather incomplete.

I. INTRODUCTION

THE optical-absorption spectra of AgCl and AgBr
differ in a fundamental way from those of the
alkali halides. The alkali halides are strongly ionic ma-
terials which are transparent throughout the visible and
near-ultraviolet regions of the spectrum when suffici-
ently free of F centers and other imperfections. In the
vicinity of 2000 Å the fundamental absorption edge
rises steeply to above 10^5 cm^{-1} because of excitation
from the ground state of the crystal to exciton states.[1]

Moreover, the first peak of the absorption spectra is a
doublet due to the spin-orbit coupling of the hole on
the halogen ion. Although AgCl and AgBr are less ionic
compounds with considerable covalent bonding, they
also have strong, direct exciton spectra showing the
influence of the spin-orbit doublet of the halogen ion.[2,3]
However, in contrast to the alkali halides, AgCl and
AgBr have optical absorption tails which extend to-
wards longer wavelengths, approximately 2 eV from the
direct exciton spectra.[4] The origin of these long wave-
length absorption tails has been a matter of speculation
for many years.

[1] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev.
116, 1099 (1959).

[2] Y. Okamoto, Nachr. Akad. Wiss. Goettingen, Math.-Physik.
Kl., IIa No. 14, 275 (1956).
[3] S. Tutihasi, Phys. Rev. **105**, 882 (1957).
[4] F. Seitz, Rev. Mod. Phys. **23**, 328 (1951).

Experimental and theoretical work now indicate that the long-wavelength absorption tails arise from phonon-assisted indirect transitions. Band-structure calculations by Bassani, Knox, and Fowler[5] and Scop[6] show that the valence bands of both AgCl and AgBr have at least one maximum away from the center of the Brillouin zone. The conduction band on the other hand is of approximately standard form at the center of the zone. The temperature dependence of the absorption of AgBr and AgCl near 4.2°K,[7] has been shown to be characteristic of indirect transitions. Analysis of the absorption spectra shows that phonons near 90°K are emitted or absorbed to conserve crystal momentum for the electronic transition. The energy corresponding to 90°K is very near the amximum phonon energy of the acoustic phonon reported for AgCl by Cole.[8]

This paper reports further attempts to clarify the origin of the structural details observed in the absorption spectra of AgCl and AgBr at 4.2°K. Both pure AgCl and AgBr and mixed AgCl and AgBr have been studied in this regard. A preliminary report of the data and structural details for pure crystals and dilute alloys of AgCl has been given elsewhere.[9] A comparison of the data on pure crystals with the theory of phonon-assisted, indirect transitions is given in the present paper. Also, the absorption spectra of mixed AgCl and AgBr between 4.2 and 77°K in the wavelength region corresponding to indirect transitions in the pure crystals are presented. The mixed-crystal results tend to agree with the theory of indirect transitions but interesting new features arise. For each of the extremes of mixing an additional absorption component is observed compared to the spectra of the pure crystals. The AgBr-rich mixed crystals reveal phonon absorption and emission thresholds just as pure AgBr does, but the characteristics of the additional component suggest that non-vertical transitions also take place *without* the aid of phonons to conserve crystal momentum. On the other hand, the AgCl-rich mixed crystals exhibit a shoulder and tail adjacent to the pure AgCl absorption edge which extends further toward longer wavelengths than the indirect-phonon-absorption component. The perturbing effect of the Br^- ion on the AgCl absorption spectrum is, therefore, considerably different from that of the Cl^- ion on AgBr.

II. EXPERIMENTAL METHOD

The pure and mixed crystals were either grown from the melt in an inert atmosphere by the Kyropoulos

technique or prepared as relatively thin samples (100 μ thick) by growing between quartz plates.[10,11] In either case high purity AgCl and AgBr was used as starting material. Although AgCl and AgBr are miscible in all relative concentrations,[12] most crystals for the present work were prepared with concentrations of the minority constituent less than 10%. AgBr-rich boules were grown with approximately 0.1, 1.0, 3.9, and 9.0 mole% AgCl added to the melt. For the AgCl-rich boules, AgBr in amounts of approximately 0.03, 0.08, 0.3, 0.7, and 1.4 mole% was added to the melt. The various crystals were found to be homogeneous and good back reflection x-ray patterns were obtained. Chemical analyses were later performed in order to determine the alloying concentrations. Because of segregation of the mixture between the liquid and solid phases, the analytical results differed by 20-50% from the initial concentration of the melt. The absorption curves shown later are all identified by the results of chemical analysis. Optical spectra obtained for samples prepared in different ways were identical and dependent only upon the alloying concentration.

The metal cryostat which was used for measuring the absorption spectra is shown in Fig. 1. The Dewar had a liquid-helium capacity of one-half liter and held liquid helium for up to three hours under operating conditions. The temperature could be controlled to within at least two to three degrees of any given temperature by first boiling the liquid helium from the center tube[13] and then regulating the current in the heater. The temperature of the sample was determined by measuring the resistance of a calibrated Ge thermometer which was in good contact with the copper sample holder in close proximity to the sample.

The optical-absorption measurements were carried out with a Cary model 14R recording spectrophotometer. The usual tungsten source was replaced with a 625-W quartz-iodine light source.[14] With the intensity provided by this source, it was possible to make measurements with spectral slit widths of 0.3 Å, and under these conditions the error in the absorption coefficients due to spectral bandwidth is neglibigle. The largest uncertainty in the absolute value of the absorption coefficient depended upon corrections for the absorption of multiply reflected radiation,[15] which were usually less

[5] F. Bassani, R. S. Knox, and W. Beall Fowler, Phys. Rev. **137**, A1217 (1965).

[6] Peter M. Scop, Phys. Rev. **139**, A934 (1965).

[7] F. C. Brown, T. Masumi, and H. H. Tippins, J, Phys. Chem. Solids **22**, 101 (1961).

[8] H. Cole, J. Appl. Phys. **24**, 482 (1953).

[9] B. L. Joesten and F. C. Brown, Phys. Letters **17**, 202 (1965); Bull. Am. Phys. Soc. **11**, 1086 (1965). See also F. C. Brown, B. L. Joesten, and W. B. Fowler, *International School of Physics, Enrico Fermi, Course XXXIV* (Academic Press Inc., New York, to be published).

[10] The methods for growing the plate crystals and also for purification are described in *The Art and Science of Growing Crystals*, edited by J. J. Gilman (John Wiley & Sons, Inc., New York, 1963), p. 214.

[11] The authors are indebted to W. West and F. Moser, Research Laboratories, Eastman Kodak Company, who kindly supplied several of the materials, especially the plate crystals and analysis. They are also grateful to Dr. J. Luvalle, Research Laboratory, Fairchild Space and Defense Systems for some zone-refined AgBr.

[12] R. B. Wilsey, J. Franklin Inst. **200**, 739 (1925).

[13] T. Timusk, J. Phys. Chem. Solids **26**, 849 (1965).

[14] Sun Gun, Sylvania Electric Products Corporation.

[15] J. Tauc, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (Heywood and Company Ltd,. London, 1965), Vol. 9.

than 10% for the present cases. These corrections were carefully computed when making comparisons between theory and experiment.

III. PURE AgCl AND AgBr

A. Theoretical Discussion

When the extrema of the valence band and conduction band of a perfect crystal do not have a common position in **k** space, direct optical transitions cannot take place, because the wave vector of the photon cannot make up for the change in the crystal momentum of the electronic state. When the electron-phonon interaction is included, however, phonons can be emitted or absorbed in the transition so as to conserve crystal momentum. The theory of these phonon-assisted indirect transitions with excition effects taken into account has been given by Elliott.[16] The effects of indirect transitions are most strikingly revealed in the temperature dependence of the optical-absorption spectrum. For a single phonon energy and for a given electronic transition, the absorption coefficient at a temperature T should consist of two components $K_e(h\nu,T)$ and $K_a(h\nu,T)$, due to phonon emission and phonon absorption, respectively. The process involving phonon absorption is proportional to the number of available phonons $N = (e^{\theta/T}-1)^{-1}$ and is given by

$$K_a(h\nu,T) = (a/h\nu)(e^{\theta/T}-1)^{-1}g(h\nu-E_g'+k\theta), \quad (1)$$

whereas the process involving phonon emission is proportional to $N+1 = (1-e^{-\theta/T})^{-1}$ and is given by

$$K_e(h\nu,T) = (b/h\nu)(1-e^{-\theta/T})^{-1}g(h\nu-E_g'-k\theta). \quad (2)$$

In these equations k is Boltzmann's constant with $k\theta$ giving the phonon energy. The function g represents a basic shape function which rises from a threshold, $h\nu_{th} = E_g' \pm k\theta$, with a characteristic shape depending on the type of transitions taking place. For allowed exciton states and standard electronic band shapes, the shape function is of the form

$$g(h\nu-E_g'\pm k\theta) = (h\nu-E_g'\pm k\theta)^{1/2}. \quad (3)$$

The energy E_g' is just the band gap energy less an exciton binding energy. It will vary with temperature because the band gap depends on temperature. However, the separation between the two thresholds remains constant and equal to $2k\theta$. The quantities a and b above involve the square of matrix elements for phonon emission and absorption and are almost but not quite equal. The phonon-absorption component, (Eq. 1), vanishes as the temperature goes to zero, and the phonon-emission component approaches a basic shape spectrum. The experimental low-temperature spectrum represents the basic shape function for at least one phonon and one exciton state. In general, it will be the superposition of basic

16 R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
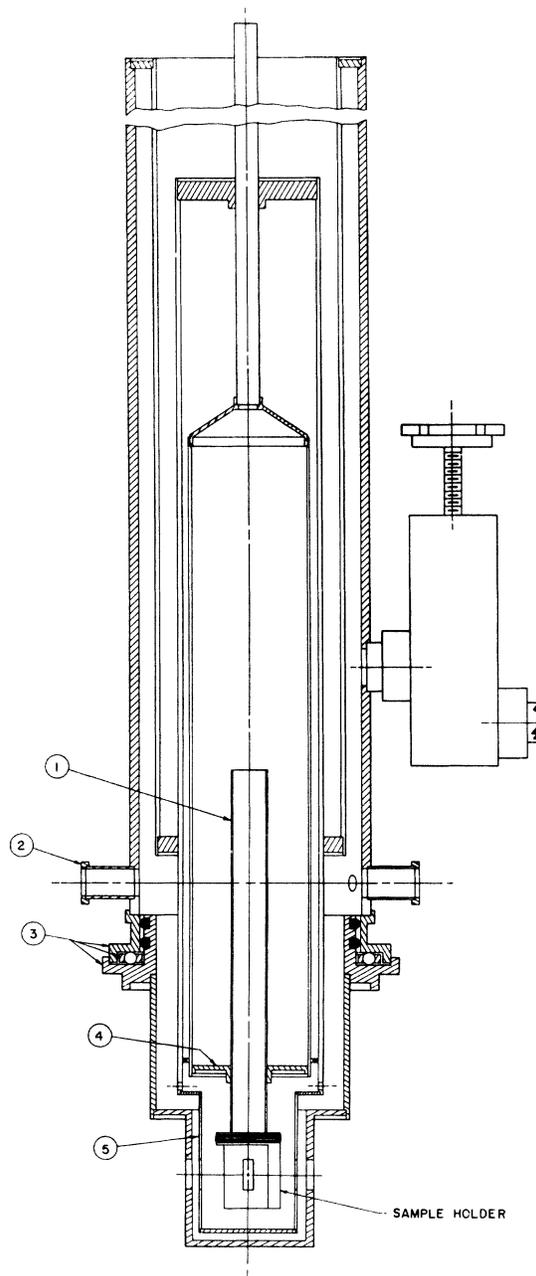
FIG. 1. Drawing of liquid-helium-temperature cryostat suitable for optical measurements in the cell compartment of a Cary spectrophotometer. Silica windows are waxed onto the rotating-window assembly and two sample positions are provided. (1) ½-in. o.d. wall Inconel tube. (2) Electrical lead ports. (3) Window rotating assembly. (4) Inconel bottom. (5) Liquid nitrogen shield.

shape spectra resulting from phonons of more than one energy as well as several electronic states.

B. Comparison of Theory and Experiment

The low-level absorption spectra at low temperatures have been reported for AgCl and AgBr elsewhere,[9] and
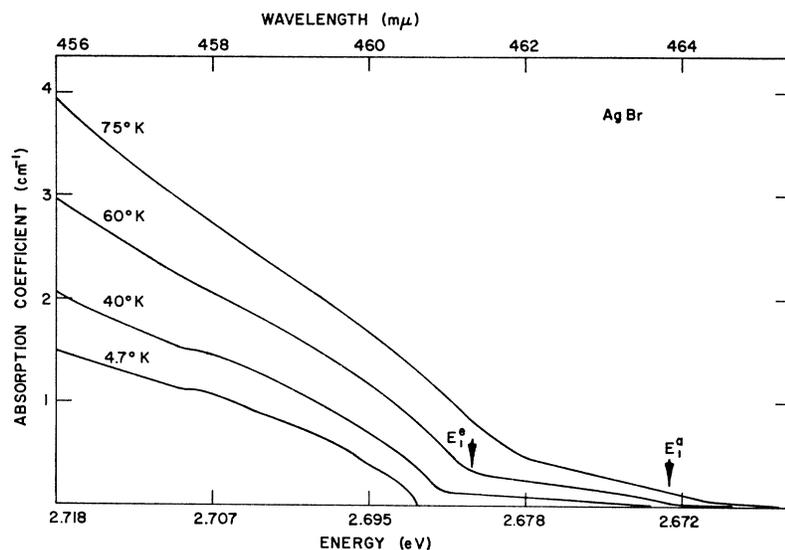
FIG. 2. The absorption edge for pure AgBr at several different temperatures. The spectra have been corrected for absorption of multiply reflected light. $E_1{}^e$ and $E_1{}^a$ denote the thresholds corresponding to emission and absorption of a 0.009-eV phonon.

it is the intent of this section to illustrate the internal consistency of interpreting these spectra in terms of phonon-assisted indirect transitions as discussed in the previous section. The absorption spectrum of AgBr is shown for several temperatures in Fig. 2. The energies E^a and E^e refer to the thresholds for structural components as defined in the 60°K spectrum. The strength of the component with threshold at E^a decreases with the temperature, and the component is not present at temperatures near 4.2°K. The difference between E^e and E^a is the same for each temperature within experimental uncertainty and has an average value determined from several spectra of

$$(E^e - E^a)_{av} = 0{,}0161 \pm 0.0003 \text{ eV}.$$

Thus, E^e and E^a can be related to the thresholds of indirect transitions with the emission or absorption of a phonon of 0.00805 eV or about 94±2°K.

This value of the phonon energy can be used in Eqs. (1) and (2) to compare the experimental absorption spectrum at temperature T with what is obtained by using the 4.2°K spectrum as the basic shape and the theoretical temperature dependence. The results of such a comparison are shown in Fig. 3 for 50°K. So by considering only one phonon energy rather good agreement between the experimental spectrum and the constructed spectrum is obtained. Similar comparisons have been made for AgCl also. The agreement in this case is not quite as good as regards the shape, suggesting, perhaps, that more than one phonon energy should be considered. It is difficult, of course, to include more than one phonon energy in the comparison, since the 4.2°K spectrum must be decomposed into the various basic shapes to be used with each of the chosen phonon energies. The low temperature spectra are quite complex for both AgCl and AgBr (see, for example, a figure for AgCl, Ref. 9) making the decomposition all the more difficult.

IV. MIXED AgCl AND AgBr

A. Theoretical Discussion

Turning now to mixed crystals, the problem of optical transitions is not so straightforward. The term "mixed crystal" in its present context refers to a miscible chemical system AgCl-AgBr presumably with a random arrangement of alloying constituent. There are two examples of mixed-crystal systems which represent what might be called the extremes of possibilities for optical transitions in mixed crystals. In the Ge-Si system[17] the optical absorption changes gradually from that of pure silicon to that of pure germanium as a function of concentration. The absorption seems to be more characteristic of the mixed crystal than that of the individual components. The KCl-KBr system,[18] on the other hand, is an example of a case where the individual components keep their identity in the mixed crystal.

The theoretical problem concerning the band structure of mixed crystals is very difficult. Parmenter[19] has developed the theory of the virtual crystal model of a mixed crystal and the results have been used successfully[20] in explaining experimental work on Ge-Si mixed crystals. Recently des Cloizeaux[21] presented a theory of impurity bands in the context of random processes. This theory when more fully developed may be useful in understanding optical processes in mixed crystals. In general, however, it appears that our understanding of the band structure of alloys leaves much to be desired.

The framework within which the optical absorption of mixed AgCl and AgBr may be discussed can be stated

[17] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. **109**, 695 (1958).

[18] H. Mahr, Phys. Rev. **122**, 1464 (1961).

[19] R. Parmenter, Phys. Rev. **97**, 587 (1955).

[20] F. Bassani and D. Brust, Phys. Rev. **131**, 1524 (1963).

[21] J. des Cloizeaux, Phys. Rev. **139**, A1531 (1965).

FIG. 3. Comparison of theory and experiment for the indirect absorption edge of pure AgBr at 50°K. The solid line is taken from the spectrophotometer tracing (corrected for the absorption of multiply reflected light) for a crystal 0.284 cm thick at 50°K. The basic shape was determined from the phonon-emission curve observed at 4.2°K; then the components K_e and K_a were constructed according to theory for 50°K assuming a single phonon of 0.008-eV energy. The dots are the sum of K_e and K_a and it can be seen that they agree quite well with experimental tracing.
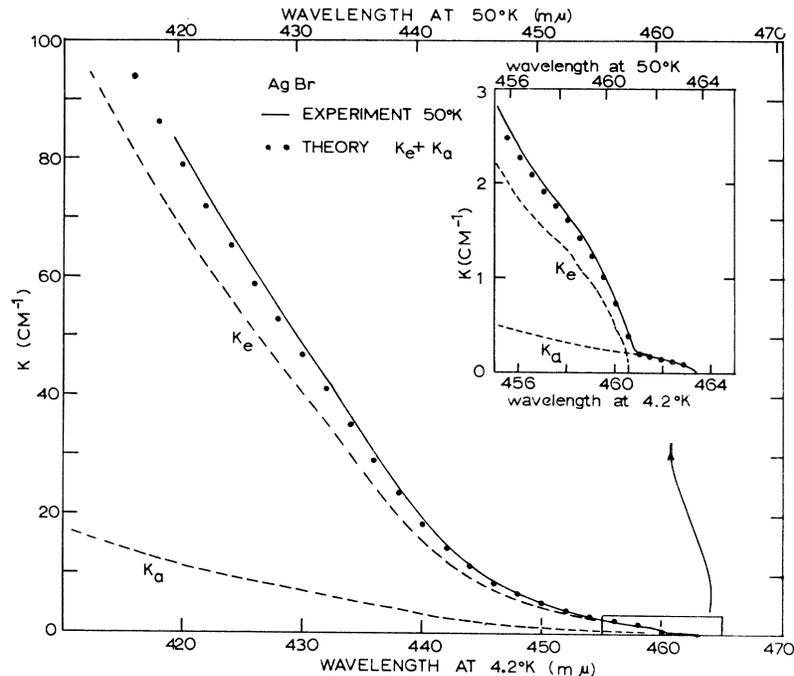
as follows[22]: The basic question to consider when an impurity is placed in a solid is whether or not there are localized energy states associated with the impurity. A localized energy state is not degenerate with the band states of the pure material and can be thought of separately from the usual electronic band structure. A localized energy state may give rise to an optical absorption, and in this case it is useful to consider the degree of localization by estimating an oscillator strength for the absorption band. The oscillator strength of an absorption band is strictly defined in terms of a dipole matrix element between two states of the impurity but in practice can be estimated from the integrated absorption with the help of Smakula's formula.[23]

On the other hand, the energy states of the impurity may mix so thoroughly with those of the host that a band structure can still be calculated for the mixed crystal. Such a calculation can be made using the virtual-crystal model.[19] In this model the potential at each lattice site of the actual crystal is replaced with an average potential taking into account the relative concentration of the constituents of the real crystal. The one-electron energy eigenvalues are then calculated using the average potential. Of the two systems originally cited, the Ge-Si mixed crystals can evidently be understood on the basis of the virtual-crystal model. But the results of the KCl-KBr system cannot be explained using the virtual crystal model.

Materials in which indirect transitions are observed

should provide a sensitive test for the validity of the virtual-crystal model. In a pure crystal indirect transitions may occur with the emission or absorption of phonons to conserve crystal momentum. The requirement that crystal momentum be conserved is a result of the periodicity of the lattice. On the basis of the virtual-crystal model, a nonvertical transition still requires a phonon to conserve crystal momentum since the virtual crystal is periodic. But a mixed crystal does not, in general, have translational symmetry since, for example, a translation may put a Cl^- ion at the site of a Br^- ion. The disorder in the mixed crystal can thus conceivably make previously forbidden transitions possible, assuming that the disorder is not so great as to completely destroy the concept of a band structure. The result of such relaxation of the conservation of crystal momentum would be nonvertical transitions without the emission or absorption of a phonon. The addition of such a component to the regular absorption spectrum should be easily observed since it would be independent of temperature, except for the usual shift due to the temperature dependence of the energy gap, and it should have a threshold E_g' exactly halfway between the indirect phonon-emission and phonon-absorption thresholds.

The shape of the disorder-induced nonvertical absorption can be indicated in the following way: Suppose an optical matrix element can be calculated which connects two points of **k** space for a mixed crystal without the aid of the electron-phonon interaction. Call this matrix element $H(\mathbf{k}', \mathbf{k}'')$ where $\mathbf{k}'$ and $\mathbf{k}''$ represent the points of **k** space connected by the interaction. The

[22] W. Beall Fowler (private communication).
[23] A. Smakula, Z. Physik **59**, 603 (1940).

QUANTUM ENERGY (eV)
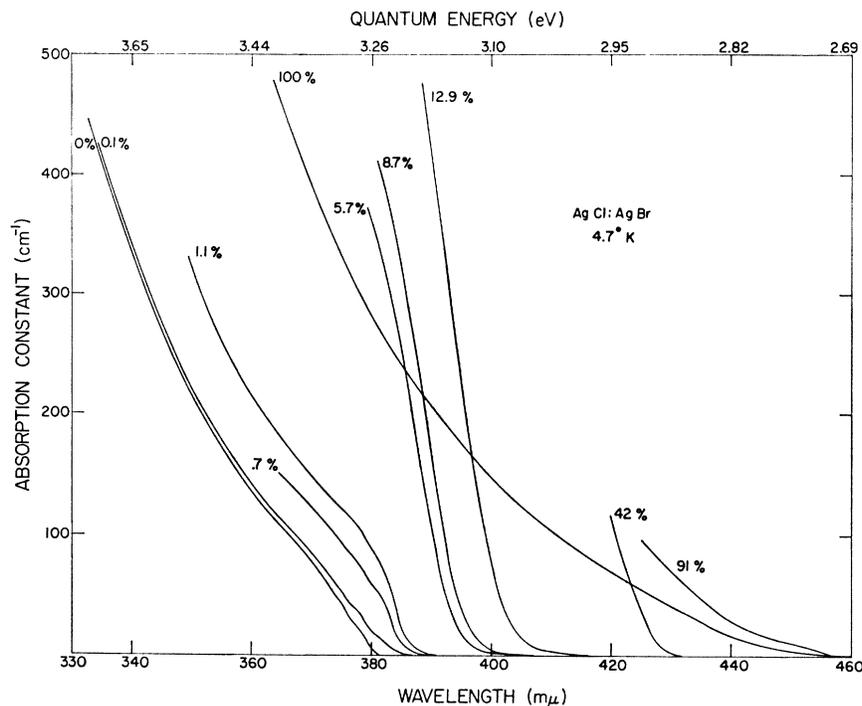
FIG. 4. Absorption coefficient (approximate values) versus photon energy or wavelength for pure crystals and alloys at 4.7°K. The amount of AgBr in AgCl was determined by chemical analysis and is indicated in mole percent.

WAVELENGTH (mμ)

method of calculating such a matrix element has been discussed by Braunstein, Moore, and Herman.[17] The interaction which brings about the connection between the different points of **k** space is related to the disorder of the mixed crystal and certainly is independent of temperature. Once the states at different points of **k** space can be connected by the matrix element $H(\mathbf{k}',\mathbf{k}'')$ the absorption coefficient can be derived in the usual way. For the formation of an allowed exciton with the same electronic states as were used for the phonon-assisted indirect absorption, this amounts to removing the phonon population from Eq. (1) or (2), and changing the threshold to E_g'. That is, the shape of such a disorder component might be expected to be the same as for the pure crystal and should be independent of temperature but dependent on the amount of mixing.

B. Experimental Results

The general features of the mixed-crystal absorption spectra at 4.7°K are shown in Fig. 4. The percentages are the result of chemical analyses and indicate the mole% AgBr in AgCl. The absorption edge appears to shift continuously from that of pure AgCl to that of pure AgBr. Notice that the absorption coefficients of the mixed crystals become larger than that of pure AgBr at the same wavelength for concentrations about 5.7 mole% AgBr in AgCl. A more detailed look at the spectra reveals that the modification of the pure-crystal absorption is quite different for the two extremes of mixing.

The absorption coefficients representative of the AgBr rich mixed crystals are shown for 1% in Fig. 5. These spectra are to be compared with those of Fig. 2. The striking feature of Fig. 5 is the additional component which appears in the mixed-crystal absorption spectra compared to the pure-crystal spectra. The additional component has a sharp threshold precisely halfway between the phonon-emission and phonon-absorption thresholds associated with the pure-crystal absorption. Figure 6 shows the additional component at 4.7°K for three concentrations where the spectrum for pure AgBr was subtracted from each of the mixed crystal spectra. There is a shift of the regular phonon emission threshold towards shorter wavelengths with increased mixing; so the pure-crystal spectrum was translated to make the phonon-emission threshold of the pure crystal coincide with that of the mixed crystal. Figure 6 also illustrates that the strength of the additional component increases with mixing. The results of treating the spectra of a given crystal for several temperatures in the same way as for Fig. 6 are shown in Fig. 7. The additional component is essentially independent of temperature. Finally, Fig. 8 illustrates that the curvature of the additional component follows a $(\hbar\omega - E_g')^{1/2}$ dependence. From Eq. (3) this is the energy behavior which is expected for an indirect allowed exciton transition with a threshold at E_g' rather than $E_g' \pm k\theta$. All of the characteristics of the additional component, in particular its threshold halfway between E^e and E^a, are consistent with the interpretation that nonvertical optical tran-

WAVELENGTH (mμ)
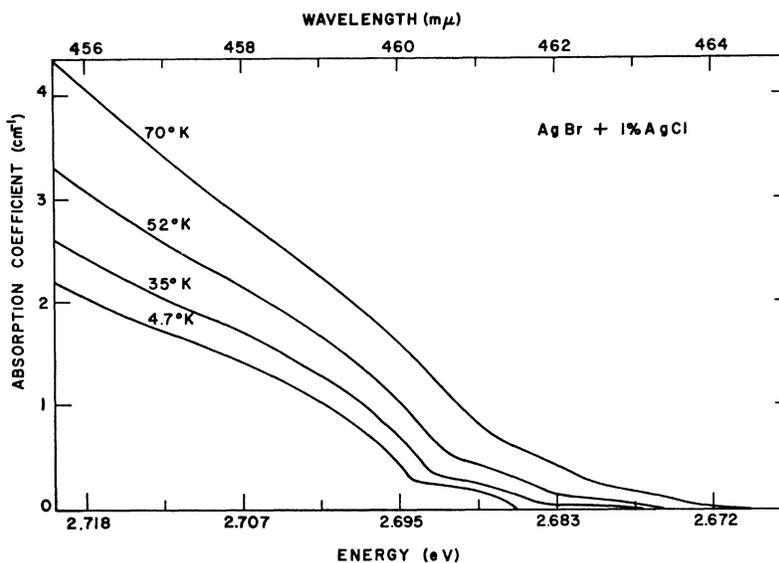
FIG. 5. The absorption spectra at different temperatures for AgBr containing 1 mole % AgCl. Comparison of this figure with Fig. 2 shows that a disorder-induced component sets in exactly halfway between the edges associated with phonon emission and phonon absorption.

sition takes place without the emission or absorption of a phonon.

The AgCl edge is affected by alloying differently than the AgBr absorption. For example, the spectrum of AgCl+0.1 mole% AgBr at 30°K is shown in Fig. 9. The 30°K spectrum for pure AgCl is also shown in Fig. 9 for comparison. A distinct shoulder and tail are observed adjacent to the threshold associated with pure AgCl. The absorption tail in the mixed crystal extends about 0.05 eV to higher wavelength, several times the energy of the phonon important for indirect transitions in the pure crystal. Furthermore, this absorption in dilute AgCl:AgBr is much more sensitive to the mixing than at the other extreme. A significant change is detected in the AgCl spectrum for an addition of 0.1 mole% AgBr, whereas for the same concentration of AgCl in AgBr, no change could be detected. The strength of the shoulder and tail in the AgCl-rich samples increases with mixing, and at 5.7% the absorption rises steeply to values which exceed the absorption coefficient of pure AgBr at the same wavelength. The shoulder seems to have a flat portion which ends approximately halfway between the energies corresponding to the phonon-emission and absorption thresholds. Therefore, some disorder-induced indirect transitions may be taking place in the AgCl-rich mixed crystals also. However, most of the absorption produced by mixing appears to be dominated by the mechanism which gives rise to the extended tail.

The exact origin of the shoulder and tail in the AgCl-rich system is difficult to determine without the information provided by additional experiments such as photoconductivity. There would seem to be at least two possible alternatives, however, The first alternative treats the shoulder and tail as part of an absorption band such as might result from a localized state of the

Br⁻ ion. The second alternative considers the possible perturbations of the Br⁻ ion on the band states of the pure crystal.

The possibility of a localized state can be discussed with respect to the oscillator strength of the shoulder and tail. The position of the peak of the band in the present case is rather arbitrary, but when a pure crystal spectrum is subtracted from a mixed crystal spectrum for the same temperature, the shoulder bends over slightly, but definitely, at the position of the absorption edge of the pure crystal. Although this additional component does not fall to zero on the high-energy side the spectrum in Fig. 9 suggests a band with a peak absorption coefficient of 6 cm⁻¹ and a width at half-maximum of 0.026 eV. The oscillator strength for such a band is 0.5×10^{-4}. using an index of refraction of 2 for AgCl and an impurity concentration of 2.3×10^{19}/cc in Smakula's formula.

PHOTON ENERGY (eV)
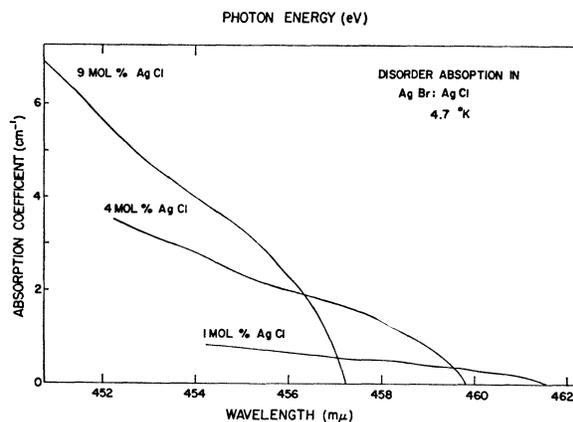
FIG. 6. The disorder-induced component of the AgBr-rich alloy at 4.7°K for three different concentrations.
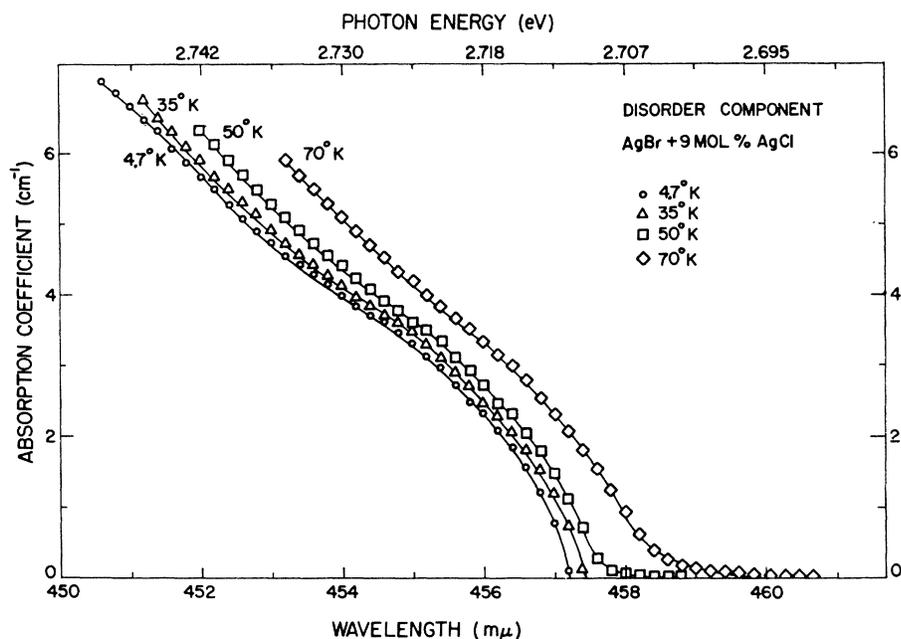
FIG. 7. Showing the temperature dependence of the disorder-induced component for AgBr containing 9 mole % AgCl. Notice that the strength of the disorder-induced absorption is independent of temperature.

There are several reasons why this shoulder and tail are unlike a typical absorption band. First, the width at half-maximum is an order of magnitude smaller than the width of a typical lattice broadened absorption band such as an F center. For example, AgI added to AgCl

FIG. 8. $(K\hbar\omega)^2$ versus $\hbar\nu$ for AgBr containing 1, 4, and 9 mole % AgCl.

in the concentrations we are considering here[24] gives a resolvable absorption band near 77°K which has a width of 0.2 eV quite comparable to the typical width of an F center in the alkali halides. Secondly, the oscillator strength as caluclated above is quite small to be associated with a localized excitation on the Br⁻ ion. It can also be seen that additional absorption prevails to higher energy and appears more like a shoulder than a band. This absorption rises quite steeply as the mixing is increased. Part of it at least may be brought about by a breakdown of selection rules as discussed above.

Another possible explanation relates the effects of the Br⁻ ion more directly to the band states of the pure crystal. Since the ground state of the Br⁻ ion is apparently degenerate with the valence band of AgCl and well below the top of the valence band,[22] the perturbing effects of the Br⁻ ion on the uppermost edge of the valence band may be expected to be small. This, by the way, is another reason for not interpreting the shoulder as due to a local excitation. However, it is quite possible that the conduction-band states are perturbed to some extent because of the deformation associated with the larger size of the Br⁻ ion. The Br⁻ ion radius is larger than the Cl⁻ ion by 10% (1.95 Å for Br⁻ compared to 1.81 Å for Cl⁻). Because of the hard-core repulsive forces this may represent quite an extended strain in the lattice. Further experimental information is required to determine which of these various possibilities is most nearly correct.

Little is known at present about the vibrational spectrum of the alloys. It is conceivable, for example, that some nonrandom arrangement of impurity occurs as

[24] F. Moser, Bull. Am. Phys. Soc. 9, 228 (1964) and private communication.
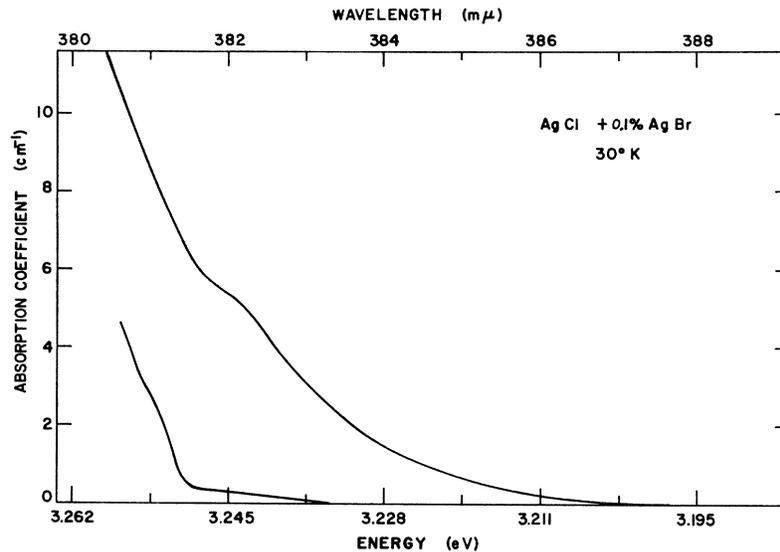
FIG. 9. Showing the tail which occurs for a AgCl-rich alloy. The lower curve is for pure AgCl; the upper for AgCl containing 0.1 mole % AgBr. Both curves are for a temperature of 30°K.

in the GaAs-GaP system.[25] No evidence for this has yet appeared, however.

V. SUMMARY

A disorder-induced optical-absorption component appears in AgBr-rich-mixed crystals of AgCl and AgBr. The additional component has characteristics which can be associated with the breakdown of the regular-crystal momentum selection rules for a periodic structure. The additional absorption can be described in terms of the pure-crystal band structure as arising from transitions which are nonvertical since different points of the Brillouin zone are involved. The disorder brought about by the presence of the Cl⁻ ion in the AgBr lattice seems to have the effect of relaxing the requirement that crystal momentum be conserved without destroying the other concepts associated with a periodic crystal. This disorder-induced absorption component is a new phenomenon and should be found in other alloy systems

where an indirect edge cocurs and where a lighter or smaller impurity ion is incorporated.

On the other hand, AgCl-rich mixed crystals of AgCl and AgBr have an optical absorption component which cannot be understood entirely in terms of the disorder of the mixed crystals. The perturbation of replacing Cl⁻ ion with the larger Br⁻ ion in small concentrations (as small as 0.03 mole%) is reflected by the appearance of a shoulder and tail adjacent to the regular pure AgCl optical absorption edge at 4.7°K. The characteristics of the shoulder and tail do not necessarily suggest that the Br⁻ ion has a localized state in AgCl.

ACKNOWLEDGMENTS

[25] Y. S. Chen and G. L. Pearson, Bull. Am. Phys. Soc. 10, 269 (1965); H. W. Verleur and A. S. Barker, ibid. 11, 73 (1966).