the Brillouin zone, we can point out the following unrealistic features of the lattice-dynamical model. The γ's of all modes are rather closely spaced, and the solid tends towards the limit of a pure Grüneisen solid (i.e., one for which all the γ_i are equal). This explains, of course, the negligible temperature dependence of the calculated Grüneisen parameter. The mode γ's which are most severely distorted in this model are those corresponding to longitudinal modes. Thus, for long-wave LA phonons propagating in the [100] direction, the model gives

$$\gamma_l = -\tfrac{1}{6} + B_T (C'_{11} - C'_{12} + C'_{44})/2(C_{11} - C_{12} + C_{44}) \ , \tag{4}$$

whereas the correct value (derived from acoustic-continuum theory) is $-\frac{1}{6} + B_T C'_{11}/2C_{11}$, which in general is significantly different from (4). For potassium, for example, γ_l, as calculated from (4), is equal to 1.11, and the correct value of the γ of these longitudinal modes is 1.59.

For the corresponding [100] transverse modes the model yields the correct γ,

$$\gamma_t = -\tfrac{1}{6} + B_T C'_{44}/2C_{44} \, . \tag{5}$$

We note, finally, that because of the extremely small amount of dispersion and anisotropy which the γ's of this model exhibit, a simple expression of the form

$$\bar{\gamma} = \tfrac{1}{3}(\gamma_l + 2\gamma_t) \tag{6}$$

already gives a very good estimate of the Grüneisen parameter (as shown in the last column of Table I).

---

*Work supported by the Advanced Research Projects Agency through Contract No. SD-100 with the University of North Carolina Materials Research Center.

†On leave from the Soreq Nuclear Research Centre, Yavne, Israel.

[1] J. N. Shapiro and L. Knopoff, Phys. Rev. B 1, 3990 1970.

[2] G. R. Barsch and Z. P. Chang, Phys. Status Solidi 19, 139 (1967).

[3] R. A. Miller and D. E. Schuele, J. Phys. Chem. Solids 30, 589 (1969).

PHYSICAL REVIEW B VOLUME 3, NUMBER 4 15 FEBRUARY 1971

Valley-Orbit Splitting of Excitons – A Comment*

G. Ascarelli
Physics Department, Purdue University, Lafayette, Indiana 47907

(Received 1 June 1970)

It is shown that when an indirect exciton is created during an optical absorption, the matrix elements of the exciton Hamiltonian calculated between different degenerate final states of the system are not necessarily zero. This implies that valley-orbit splitting of the states assigned to the indirect exciton creation may exist.

In a recent paper Shaklee and Nahory[1] point out that on the basis of the translational invariance of the exciton wave function there is no possibility of any valley-orbit splitting of the exciton in the way proposed by Ascarelli.[2] They correctly point out that the existence of a mixing of excitons related to each one of the valleys of a multivalley insulator requires some mechanism to provide the necessary crystal momenta in order to compensate for the different crystal momenta of the individual excitons.

A mechanism that provides the crystal momentum exists in the indirect optical absorption, since not only is an exciton created, but a phonon of the appropriate wave vector is exchanged as well. The wave function describing the system therefore has zero wave vector for the creation of an exciton with zero kinetic energy.

Following Ref. 1, H_1 is defined as the perturbation Hamiltonian describing both the electron-hole interaction and the interaction of the exciton with the appropriate phonon. Then $H_{ij} = \langle \psi_i^* | H_1 | \psi_j \rangle$, where ψ_i and ψ_j are wave functions describing the existence of an exciton and a phonon, respectively, with momenta $(\vec{k}_i, -\vec{k}_i)$ and $(\vec{k}_j, -\vec{k}_j)$. Applying the translation operator T to H_1, we obtain

$$H_{ij} = \langle \psi_i^* | \ T^{-1} T H_1 | \psi_j \rangle = e^{i(\vec{K}_i - \vec{K}_j)\cdot\vec{a}} H_{ij} \, .$$

H_{ij} is therefore not necessarily zero, since the wave vectors $\vec{K}_i$ and $\vec{K}_j$ of both ψ_i and ψ_j are zero.

The emission of electromagnetic radiation during the annihilation of an exciton may give rise to valley-orbit splitting in the same way as absorption does, since the same arguments used above remain valid.

The magnitude of the valley-orbit splitting will depend on the distortion of the lattice in the vicinity of the exciton (providing a sort of central-cell correction) that arises from the interaction of the carriers with their polarization. One therefore expects that the splitting will be larger in ionic crystals that have a strong polaron interaction than in covalent semiconductors, where the electron-phonon interaction is provided by means of the deformation potential.

Indeed, while the stress-induced splitting of the different exciton peaks is the same in Si,[1] it is different in the peaks assigned to the valley-orbit-split exciton in AgBr.[2]

In conclusion, it is pointed out that although there is no valley-orbit splitting of related indirect exciton states in the absence of the electron-phonon interaction,[3] the neglect of the latter is not, in principle, justified in the description of the creation of excitons by means of indirect optical transitions.

The author is grateful to Professor P. Fisher and Professor S. Rodriguez for many fruitful discussions.

---

*Work supported in part by the National Science Foundation.

[1] K. L. Shaklee and R. E. Nahory, Phys. Rev. Letters 24, 942 (1970).

[2] G. Ascarelli, Phys. Rev. Letters 20, 44 (1968); Phys. Rev. 179, 797 (1969).

[3] P. J. Dean, Y. Yafet, and J. R. Haynes, Phys. Rev B 1, 4193(E) (1970); Y. Yafet (private communication).

PHYSICAL REVIEW B VOLUME 3, NUMBER 4 15 FEBRUARY 1971

Thermoelectric Power of Cu_3Au as a Function of Short-Range Order*

Kang-Pei Wang† and H. Amar
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122

(Received 20 May 1970)

A theoretical study of the diffusion thermoelectric power of Cu_3Au as a function of order above the critical temperature is made. This work is based on, and completes, our investigation on the residual resistivity of Cu-Au alloys above the critical temperature.

The diffusion thermoelectric power Q_D has been a subject of both experimental and theoretical investigation for a long time. Nevertheless, there has been practically no theoretical work done towards the study of the order dependence of Q_D of alloys. In this paper, we propose a pseudopotential theory of Q_D of binary alloys as a function of short-range order (SRO) and apply our formulation to Cu_3Au for which the reliable SRO parameters are available.[1]

Consider a disordered binary alloy with a total of N atoms of which N_A and N_B are of types A and B, respectively. Assume that these atoms are placed on a rigid Bravais lattice consisting of N sites. Further, postulate that the (pseudo)potential of the system can be written as a sum of the screened ionic pseudopotentials of types A and B, i.e.,

$$W(\vec{r}) = \sum_i \partial_i^A w_A(\vec{r} - \vec{r}_i) + \sum_i \partial_i^B w_B(\vec{r} - \vec{r}_i) , \qquad (1)$$

where the occupation operators[2] ∂_i^λ are defined as follows:

$\partial_i^\lambda = 1$ if the ith lattice site is occupied by an atom of type λ

$= 0$ otherwise

and ω_λ is the screened ionic pseudopotential of type λ.

For such a system, we have in a previous paper[3] been able to express the resistivity as a function of SRO as follows:

$$\rho(E) = \frac{3\pi m \Omega_0}{8\hbar e^2 E} \int_0^2 \left| \frac{q}{K} \langle \vec{k} + \vec{q} | w_A - w_B | \vec{k} \rangle \right|^2 \times m_A m_B \frac{q}{K} \sum_i \alpha_i C_i j(n_i q) d\left(\frac{q}{K}\right) , \qquad (2)$$

where Ω_0 is the atomic volume per ion, $m_\lambda = N_\lambda / N$, and E is the energy of an electron in the plane-wave state $|K\rangle$. The integrand appearing in Eq. (2) consists of two factors: the "atomic part," which is proportional to the square of the difference of the form factors of A and B atoms, i.e., $|\langle \vec{k} + \vec{q} | w_A | \vec{k} \rangle - \langle \vec{k} + \vec{q} | w_B | \vec{k} \rangle|^2$, and the "structural part," which is a function of short-range order parameters α_i, the coordination number of the ith shell c_i, and the vectors n_i locating the atoms in the ith shell.

The diffusion thermoelectric power in units of $\pi^2 k_B^2 T / 3eE$ can be written as[4]

$$Q_D = -E_F \left(\frac{\partial \ln \rho(E)}{\partial E} \right)_{E = E_F} . \qquad (3)$$