PHYSICAL REVIEW B VOLUME 13, NUMBER 2 15 JANUARY 1976

Isotope shift at substitutional Cu in ZnO

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(Received 18 August 1975)

Heine and Henry have introduced a theory for the isotope shift for zero-phonon optical transition at defects in semiconductors. They remarked that substitutional Cu in ZnO was an anomalous case with an isotope shift opposite in sign to that expected for their model. Here the model is modified slightly to take account of the effect of the excess or deficit charge on the impurity nucleus, which is not discussed in the original. The first explicit calculation within their model is presented and it is shown that both the sign and the magnitude of the shift at Cu in ZnO agree with experiment within experimental accuracy. The point is that Cu is a very deep acceptor and not a shallow donor.

Heine and Henry (HH) have introduced[1] a theory of the isotope shift S of zero-phonon optical transitions at defects in semiconductors. In their model the shift in zero-point energy s of the local modes at the defect is related to the mode softening effect of electrons e and holes h on the modes of the perfect lattice. The latter effect is determined from the temperature dependence of the fundamental band gap ΔE_{cv} of the semiconductor.[2-4] Thus, the basis of the HH model is the assumption that the interatomic spring constant Λ is reduced to

$$\Lambda' = \Lambda[1 - \gamma_c P(c)] \qquad (1)$$

by the presence of a carrier c. In Eq. (1), $P(c)$ is the probability that the carrier be found on the bonds surrounding the defect atom (the atom for which isotopic substitution is to be made), and γ_c is the effect of the carrier.

The sum of the effects of a free e-h pair $\gamma_e + \gamma_h$ is given by[5]

$$\frac{\partial \Delta E_{cv}}{\partial T} = \tfrac{3}{4} k(\gamma_e + \gamma_h) \qquad (2)$$

at temperatures well above the Debye temperature. In Eq. (2), T denotes temperature and k is Boltzmann's constant. From analysis of data for several defects, HH concluded

$$\gamma_h = (3.6 \pm 1.0)\gamma_e . \qquad (3)$$

That is, the presence of either a hole or an extra electron will soften lattice modes, but the effect of h is about 3.6 times as great as that of e.

In order to calculate $P(c)$, one must determine the wave function of the carrier bound to the defect center in either the initial or the final state (or both). There is no known reliable general prescription for this,[6] but HH suggest a simple form[7]

$$\Psi(c) = [2^{2n}/2\pi a_c^{(2n+1)} \Gamma(2n+1)]^{1/2} r^{n-1} \times \exp(-r/a_c), \qquad (4)$$

where r is the distance from the defect atom nucleus, Γ is the gamma function, and n and a_c are parameters determined by the defect ionization enthalpy ΔH_I and the (single extremum, density of states) effective mass m_c^* of the appropriate band of the host semiconductor. The effective radius of the bound carrier a_c is defined by

$$a_c = (\hbar^2/2m_c^* \Delta H_I)^{1/2} . \qquad (5)$$

The exponential parameter n is defined by

$$n = (\Delta H_c^0/\Delta H_I)^{1/2} , \qquad (6)$$

where ΔH_c^0 is the hydrogenic or effective mass value for the binding enthalpy;

$$\Delta H_c^0 = 13.6 m_c^*/\epsilon^2 \text{ eV}, \qquad (7)$$

where ϵ is the optical dielectric constant. Finally, $P(c)$ should properly be defined as

$$P(c) = 4\pi \int_{R1}^{R2} |\Psi(c)|^2 r^2 dr, \qquad (8)$$

where R_1 and R_2 are the interior and exterior radii to the bonds from the center of the defect atom (see below).

HH gave explicit equations in terms of γ_c, $P(c)$, and Λ for S and for s, which they related by

$$s = (2M/\Delta M)(M/M_0)^{1/2} S. \qquad (9)$$

In Eq. (9), M is the mass of a particular defect atom, ΔM is the mass difference between the isotopes of the defect atom, and M_0 is an effective atomic mass of the host AB semiconductor

$$M_0 = 2M_A M_B/(M_A + M_B). \qquad (10)$$

The HH expressions for S will be modified slightly here in order to take account of the effect of the excess or deficit nuclear charge of the defect atom with respect to the host. HH did not discuss this effect.

Although they treated the variation of s and S with ΔH_I according to their theory and compared this variation with available data, they did not

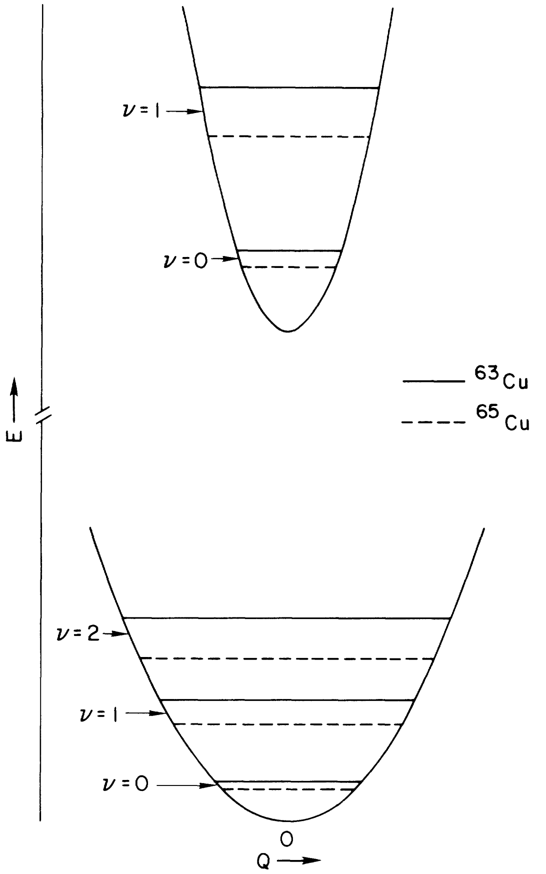

FIG. 1. Vibronic levels of the ground and excited electronic states for the case of substitutional Cu in ZnO. The separation between isotopes has been exaggerated for clarity. In this case the lattice around the defect is stiffer in the excited state than in the ground state because the hole is displaced from the defect center (see text). In such cases the zero-phonon transition energy is greater for the lighter isotope.

work out any case explicitly by evaluating the relevant Λ's, γ_c's, and $P(c)$'s. That is done here for the case of substitutional Cu on the Zn site in ZnO. This exercise serves to clarify several points in the HH theory.

The isotope shift at substitutional Cu in ZnO was first measured by Dingle.[8] He observed the characteristic green luminescent transition between the ground state and the first excited state of the neutral charge state of this very deep acceptor. Let us denote these states as $(\text{Cu}_{\text{Zn}}^- h^+)^0$ and $(\text{Cu}_{\text{Zn}}^- h^+)^*$ respectively to remind us that the hole is bound to the acceptor impurity, Cu_{Zn}^-, in both the initial and final states.

At 1.6 K, Dingle observed that this transition at a ^{63}Cu isotope has an energy, 2.85908 eV, 0.11 meV greater than at a ^{65}Cu isotope. Thus

$$S(^{63}\text{Cu}, {}^{65}\text{Cu}, \text{ZnO}) = 0.11 \text{ meV}. \tag{11}$$

This sign of S implies that the zero-point energy of the excited state, $(\text{Cu}_{\text{Zn}}^- h^+)^*$ is greater than that of the ground state, $(\text{Cu}_{\text{Zn}}^- h^+)^0$. (See Fig. 1.) According to Eq. (9), this difference in zero-point energy is

$$s = 11 \text{ meV}. \tag{12}$$

Dingle also noted that the ionization energy of the Cu_{Zn}^- acceptor ground state is

$$\Delta H_I^0(\text{Cu}_{\text{Zn}}^-, \text{ZnO}) \gtrsim 3.3 \text{ eV} . \tag{13}$$

Note that ΔH_I refers to the reaction

$$(\text{Cu}_{\text{Zn}}^- h^+) \rightarrow \text{Cu}_{\text{Zn}}^- + h^+ , \tag{14}$$

where h^+ denotes a free hole in the thermal distribution at the valence band edge. Therefore, the excited state has an ionization enthalpy

$$\Delta H_I^*(\text{Cu}_{\text{Zn}}^-, \text{ZnO}) \approx 0.45 \text{ eV} \tag{15}$$

referring to the corresponding reaction of $(\text{Cu}_{\text{Zn}}^- h^+)^*$.

Now, the orientationally averaged optical dielectric constant of ZnO is[9]

$$\epsilon(\text{ZnO}) = 3.72 \tag{16}$$

and the valence-band density of states mass is[10]

$$m_h^*(\text{ZnO}) = 1.8 m_0 , \tag{17}$$

where m_0 is the free electron mass. Therefore, from Eq. (7),

$$\Delta H_h^0(\text{ZnO}) = 1.8 \text{ eV} \tag{18}$$

and the effective radius of the ground state is, from Eq. (5),

$$a_h = 0.80 \text{ Å} . \tag{19}$$

We see that ΔH_I^0 is greater than ΔH_h^0 by a factor of about 1.8, which is not an unusual factor for a central-cell correction. The parameter n for the ground state is, from Eq. (6),

$$n \simeq 0.75. \tag{20}$$

For the excited state, we observe that ΔH_I^* is just the hydrogenic value for the second principal quantum state

$$\Delta H_I^* = \Delta H_h^0/(2)^2 = 0.45 \text{ eV}, \tag{21}$$

with no detectable central cell correction. Consequently, one may take the wave function for the bound h in the excited state Ψ_h' to be just the analog of the $2p$ hydrogen wave function. The radial part is

$$\Psi_h' = (3\pi a_2^3)^{-1/2} r/a_2 \, e^{-r/a_2} , \tag{22}$$

where a_2, which corresponds to twice the Bohr radius, is

$$a_2 = (\hbar^2/2m_h^* \Delta H_I^*)^{1/2} = 2.17 \text{ Å}. \tag{23}$$

From Eq. (4), the bound-hole wave function for the ground state is

$$\Psi_h^0 = [2^{3/2}/2a_h^{2.5}\,\pi\Gamma(2.5)]^{1/2} r^{-1/4} \exp(-r/a_h)\,. \quad (24)$$

Consider now the question of the proper values for R_1 and R_2 in Eq. (8). It seems reasonable to take R_1 equal to the radius of the Cu $3d$ core in the $3d^9 4(s\text{-}p)^2$ atomic configuration corresponding to the tetrahedrally coordinated Cu in ZnO. If the hole is found within the $3d$ core, it is not interacting with the s-p hybridized bonding electrons which are localized near the O atoms.[11] Moreover, its charge compensates that of the deficit proton in the Cu nucleus with respect to Zn. Thus, when h is within the radius, there appears to be no source for a perturbation of the lattice modes.[12] Therefore, we have

$$R_1 = R(\text{Cu } 3d) = 0.638\ \text{Å}\ , \quad (25)$$

where we have used the Slater effective charge[13] and rationalized covalent radii[14] models to determine R(Cu $3d$).

It seems reasonable to take R_2 equal to the nearest-neighbor distance minus the oxygen-core radius[14]

$$R_2 = 1.973\ \text{Å} - 0.275\ \text{Å} = 1.698\ \text{Å}. \quad (26)$$

If h is found outside this radius it will not overlap any of the bonds attached to the defect atom. Although it will have its full effect wherever it is found, it will not affect the local modes of the Cu atoms where the isotopic substitution occurs. Also, h will not screen the bonds to the Cu atom from the perturbing field of the Cu_{Zn}^- nucleus at all when it is found outside R_2.

Evaluating the relevant integrals, one finds

$$4\pi\int_0^{R_1} (\psi_h^0)^2 r^2\, dr = 0.338, \quad 4\pi\int_0^{R_2} (\psi_h^0)^2 r^2\, dr = 0.873;$$
$$4\pi\int_0^{R_1} \psi_h'^2 r^2\, dr = 0.0004, \quad 4\pi\int_0^{R_2} \psi_h'^2 r^2\, dr = 0.0230. \quad (27)$$

Therefore, the mode softening effects in the ground $(\text{Cu}_{\text{Zn}}^- h^+)$ state are

$$(0.873 - 0.338)\gamma_h + (1.0 - 0.338)\gamma_{\text{Cu}^-} = 0.535\gamma_h + 0.662\gamma_{\text{Cu}^-}\ , \quad (28)$$

where γ_{Cu^-} represents the mode softening effect of the deficit of one proton in the Cu nucleus with respect to Zn. Furthermore, the mode-softening effects in the excited $(\text{Cu}_{\text{Zn}}^- h^+)^*$ state are

$$(0.0230 - 0.0004)\gamma_h + (1.0 - 0.0004)\gamma_{\text{Cu}^-} = 0.0296\gamma_h + 0.9996\gamma_{\text{Cu}^-}\ . \quad (29)$$

What is the magnitude of γ_{Cu^-}? In previous work[15] the author has used the assumption

$$\gamma_{A^-} = \gamma_e\ , \quad (30)$$

where A^- denotes any acceptor impurity (such as Cu_{Zn}^-), to calculate the distribution coefficients of impurities in liquid-solid equilibrium. The general success of that calculation lends support to this assumption. Further evidence and argument in support of the accuracy of this approximation will be presented elsewhere.[16]

If we accept Eq. (30), we obtain from Eqs. (3) and (27) the estimate that the total mode softening effect in the ground state is (0.563 ± 0.007) $(\gamma_e + \gamma_h)$, and is (0.240 ± 0.06) $(\gamma_e + \gamma_h)$ in the excited state. Thus the excited state is stiffer (i.e., has a higher zero-point energy) by a term of (0.323 ± 0.05) $(\gamma_e + \gamma_h)$.

Note that the sign of this difference is in agreement with experiment,[8] Eqs. (11) and (12), and that this result follows from the fact that h, which has the dominant effect, is displaced from the central cell in the excited state. The unfortunate remark to the contrary by HH resulted from their error in regarding Cu_{Zn} as a shallow-donor electron trap, rather than as a deep-acceptor hole trap.

In order to determine the magnitude of s predicted by the (slightly modified) HH theory, we may note that[17]

$$\frac{\partial \Delta E_{cv}}{\partial T} = 0.8\ \text{meV/K} = 9.3k \quad (31)$$

in ZnO at high temperatures. Thus, by Eq. (2) we have

$$\gamma_e + \gamma_h = 12.4. \quad (32)$$

The implication of Eq. (32) is that the thermal excitation of one free e-h pair across ΔE_{cv} softens the lattice by the equivalent of 12.4 bonds or interatomic spring constants. (Of course, this mode softening effect is always spread over a very large number of atoms in the host crystal.) The magnitude of this effect, which may seem startling on first consideration, is explained in Refs. 3 and 4. For the present discussion one need only note that only the transverse acoustic, TA, lattice modes are appreciably softened by the creation of the e-h pair and that the TA modes are greatly affected because they are very sensitive to the magnitude of the bond charges between atoms. The creation of the e-h pair removes one full electron charge from the bonding valence band and this is sufficient to reduce several bond charges below the critical value needed to stabilize the TA of the tetrahedral structure.[3,4]

From Eq. (32) we find that the difference in lattice stiffness between the two states of $\text{Cu}_{\text{Zn}}^- h^+$ is about

$$(0.323 \pm 0.05)(\gamma_e + \gamma_h) = 4.01 \pm 0.6 \quad (33)$$

TA spring constants. In the HH model the TA phonon spectrum of the host is represented by an average frequency ω_0. Investigation of the TA phonon branch in ZnO shows[18,19]

$$\hbar\omega_0 = 8 \pm 2 \text{ meV}. \qquad (34)$$

Finally, the difference in zero-point energy between the two states of $\mathrm{Cu}^-_{\mathrm{Zn}}h^+$ is calculated to be

$$s = (4.0 \pm 0.6)(\tfrac{1}{2}\hbar\omega_0) = 16 \pm 6 \text{ meV} \qquad (35)$$

in good agreement with the empirical value of 11 meV, Eq. (12).

It should be remarked that the magnitude of the mode softening found in this case calls into question the simple assumptions of the HH model. The softening of the ground state by $0.563(\gamma_e + \gamma_h)$ corresponds to destroying 7.0 bonds at the Cu site that has only four nearest neighbors. This observation might be taken as support for the contention that the ground state experiences a large Jahn-Teller distortion.[19] On the other hand, this is the most extreme case, i.e., the largest s, known so that the HH model would be easier to justify in all other cases. The close agreement between calculation and experiment even in this limit suggests that the HH model could be better justified by a more realistic analysis of the defect modes.

ACKNOWLEDGMENTS

The author is indebted to T. N. Morgan and S. T. Pantelides for several helpful discussions.

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[1] V. Heine and C. H. Henry, Phys. Rev. B 11, 3795 (1975).

[2] H. Brooks, Adv. Electron. 7, 121 (1955).

[3] J. A. Van Vechten, in *Lattice Defects in Semiconductors* 1974 (Institute of Physics, London, 1975), p. 212.

[4] V. Heine and J. A. Van Vechten, Phys. Rev. B 13, (to be published).

[5] Note the factor of 2 discrepancy between this and Eq. (10) of Ref. 1. This results from the hypothesis made here and in Refs. 3 and 4 that the carriers act upon the $2N_a$ bonds, rather than upon the N_a atoms, in the crystal. See Ref. 4.

[6] Confer S. T. Pantelides, Phys. Rev. B 12, 2543 (1975).

[7] Note the error in the normalization constant in Eq. (51) of Ref. 1.

[8] R. Dingle, Phys. Rev. Lett. 23, 579 (1969).

[9] E. C. Heltemes and H. L. Swinney, J. Appl. Phys. 38, 2387 (1967).

[10] R. E. Dietz, J. J. Hopfield, and D. G. Thomas, J. Appl. Phys. Suppl. 32, 2282 (1961).

[11] Confer, e.g., M. L. Cohen, Science 179, 1189 (1973).

[12] Of course, there is the mass difference between Cu and Zn, but this effect does not change in the optical transition and so is irrelevant to the present discussion.

[13] J. C. Slater, Phys. Rev. 36, 57 (1930).

[14] J. A. Van Vechten and J. C. Phillips, Phys. Rev. B 2, 2160 (1970).

[15] J. A. Van Vechten, Phys. Rev. B 7, 1479 (1973).

[16] J. A. Van Vechten and C. D. Thurmond (unpublished).

[17] H. Watanabe and M. Wada, Jpn. J. Appl. Phys. 3, 617 (1964).

[18] W. Wegener and S. Hautecler, Phys. Lett. A 31, 2 (1970).

[19] T. Yamaguchi and H. Kamimura, J. Phys. Soc. Jpn. 33, 953 (1972).