

Isoelectronic impurities in II-VI semiconductors: ZnTe doped with Ca, Sr, and Ba

M. J. Seong, I. Miotkowski, and A. K. Ramdas

Department of Physics, Purdue University, West Lafayette, Indiana 47907

(Received 7 December 1998)

Photoluminescence (PL) and absorption spectra of ZnTe doped with Ca, Sr, and Ba, substituting the cation Zn, exhibit features characteristic of excitons bound in a short-range potential generated by isoelectronic impurities. A no-phonon line (NPL) in both PL and absorption, phonon side bands as mirror images about the NPL, and a doublet splitting resulting from the exchange interaction between an electron and a hole characterize the spectra. Localized vibrational modes for ZnTe:Ca and ZnTe:Sr and a gap mode for ZnTe:Ba are observed in the phonon side bands and, more directly, in the Raman spectra. Ba centers show weaker phonon side bands than those of Ca and Sr. These spectra are compared with the case of the isoelectronic oxygen center in ZnTe, where the anion Te, rather than the cation, is replaced by oxygen. [S0163-1829(99)00220-9]

I. INTRODUCTION

As is well known, excitons in the tetrahedrally coordinated compound semiconductors can be trapped effectively by isoelectronic impurities.¹ The short-range potential due to the difference between the electronegativity of the impurity and that of the host atom it replaces; the additional contribution to this potential arising from the difference in their ionic radii; the strong exchange interaction between the spins of the electron and the hole—these are the unique aspects of the electronic system characterizing the excitons bound to isoelectronic impurities. We recently reported the occurrence of excitons bound to isoelectronic impurities in ZnTe consisting of OO pairs characterized by differing pair separations and compared their photoluminescence (PL) and absorption spectra with those of the isolated oxygen centers in the same host.^{2,3} Oxygen in ZnTe and nitrogen and bismuth in GaP are excellent illustrative examples of comprehensively studied isoelectronic traps in semiconductors.^{4,5} In both ZnTe:O and GaP:(N or Bi), it is the anion which is replaced with the impurity. It is noteworthy that while many examples⁶ of isoelectronic traps associated with an anion are known, none in which excitons bound to those in cation sites has been reported.¹ The corresponding case of isoelectronic impurities in the cation sites of the host offer a physically interesting situation in the context of the physics of such impurities. Motivated by such considerations, we have specially grown single crystals of ZnTe doped with Mg, Ca, Sr, Cd, or Ba and investigated their PL and absorption spectra, presented and discussed in this paper.

II. EXPERIMENTAL

Single crystals of ZnTe doped with Ca, Sr, or Ba were grown from melt using the Bridgman technique. In each case, doping was achieved with the addition of a small amount of the impurity element to the ZnTe source material inside a quartz ampoule. For absorption measurement both sides of platelets cut from the ingots were polished to a surface roughness of $\sim 0.5 \mu\text{m}$. For PL measurement, cleaved as well as polished specimens were used.

A SPEX (Model 14018) 0.85 m double grating mono-

chromator and an RCA (type C31034A) photomultiplier were used for PL measurement.⁷ The samples were excited with the 4420 Å line from a Omnicrome He-Cd laser⁸ or the 6471 Å, 5309 Å, or 5208 Å lines from a Spectra-Physics Kr⁺ laser.⁹ The sample temperature was controlled from 1.5 K to 300 K in a Janis 10 DT (Ref. 10) cryostat. Absorption measurements were carried out using a 650 W tungsten halogen lamp as well as an Xe arc lamp as a white light source, the sample being cooled in a Janis SuperTran¹⁰ cryostat. A SPEX (Model 1403) 0.85 m double grating monochromator and an RCA (type C31034A) photomultiplier were used to record the transmission spectra.

III. RESULTS AND DISCUSSION

The PL spectrum of the isolated oxygen center in ZnTe at 10 K is displayed in Fig. 1. The line labeled O(A):NPL is the no-phonon line (NPL) originating from the upper level, having a total spin of $J=1$ from the doublet associated with the exchange interaction between the electron and the hole bound to an isolated oxygen center. As the temperature is lowered below ~ 5 K, the electric dipole forbidden transition from the excitonic ground state ($J=2$ state), i.e., the B line appears at the energy 1.5 meV below the A line. The oxygen center shows a strong electron-phonon coupling which diverts most of the luminescence intensity into its phonon side band; its prominent TA, LA, TO, and LO phonon replicas as well as their multiples can be distinctly observed and accounted for on the basis of the *Franck-Condon principle*.¹¹ The corresponding PL spectra for ZnTe:Ca, Sr, or Ba, where the isoelectronic impurity replaces Zn, are also displayed in Fig. 1 along with the position of the free exciton. For Ca and Sr, the overall shape of the phonon side band shows a strong similarity to that of the oxygen center, although their phonon replicas do not manifest as distinctly resolved as in the case of oxygen. The PL spectrum of the Ba center shows phonon sidebands reminiscent of the corresponding features for nitrogen traps in GaP in that the NPL line is stronger than phonon side bands, in contrast to those of oxygen, Ca, and Sr. In the following subsections, we discuss in more detail the characteristics of each center.

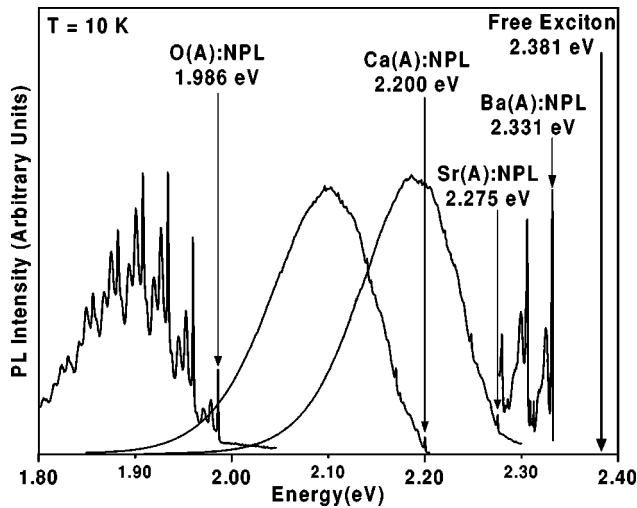


FIG. 1. Photoluminescence (PL) spectra of excitons bound to O, Ca, Sr, or Ba in ZnTe. Each spectrum was measured from the sample doped with the indicated isoelectronic impurity. All the measurements are made at 10 K. The 4420 Å line from a He-Cd laser was used for O, Ca, and Sr doped samples while the Ba doped sample was excited with the 5309 Å line from a Kr⁺ laser in order to remove some of the phonon replicas of excitons bound to residual acceptors. Different intensity scales are used for the different PL spectra. The energy position of the free exciton of ZnTe at 2.381 eV is indicated for comparison.

A. ZnTe:Ca

The temperature dependence of the PL spectrum of the Ca center in ZnTe is shown in Fig. 2 along with a portion of its phonon side band showing only the one-phonon replicas. The no-phonon *A* line is observed at 2.1997 eV and the *B* line at 2.1986 eV, yielding the *A* and *B* doublet splitting of 1.1 meV for the Ca center. The electric dipole forbidden *B* line completely dominates the dipole allowed *A* line at 1.5 K due to the thermal depopulation of the $J=1$ upper level of the doublet. As is the case for ZnTe:O, the phonon assisted mixing of the $J=2$ and $J=1$ states, as well as the residual strain around the isoelectronic center, presumably allows the *B* line to appear in spite of it being electric dipole forbidden.¹ All the phonon components are identified and labeled in Fig. 2. As the temperature is lowered from ~ 10 K, where only the *A* line is visible, to 1.5 K, where only the *B* line is observed, the same set of phonon replicas appears, but shifted to lower energies by 1.1 meV, the *A-B* doublet splitting. The energies of the phonon components are listed in Table I. We draw attention to a strong and sharp phonon replica labeled “LVM” (localized vibrational mode), characterized by an energy larger than that of the LO phonon. It can be interpreted as the phonon replica associated with the LVM around the isoelectronic Ca impurity since Ca is lighter than the host cation Zn it replaces; it is also interesting that its intensity is larger than that of the LO phonon replica. In Fig. 3, the Raman spectrum of the Ca doped ZnTe is displayed. TO, LO, and LVM features along with their overtones are observed with energy shifts consistent with the energies of the corresponding signatures in the side bands of Ca no-phonon lines.¹² In Fig. 4, absorption as well as PL spectra with their one phonon side band is displayed. The *A* line is observed at the same energy in both PL and absorp-

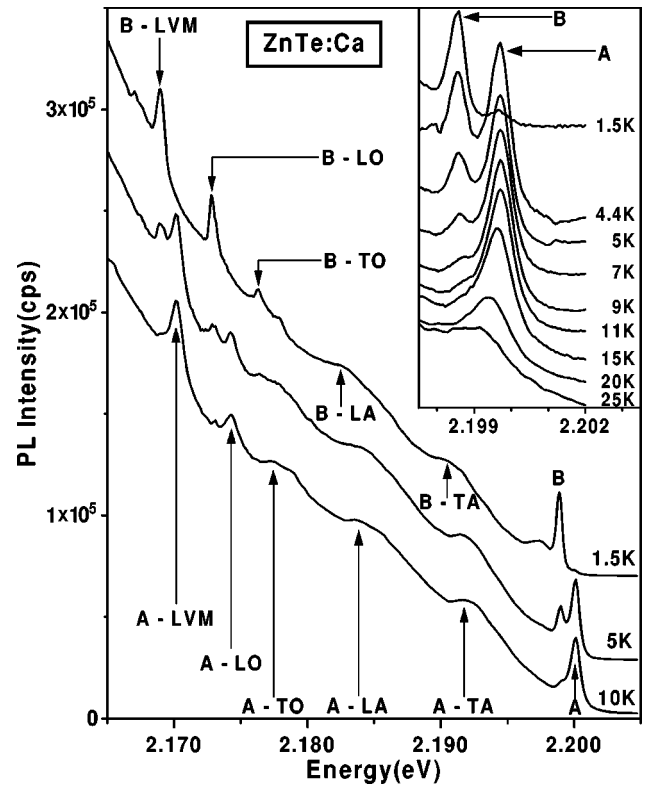


FIG. 2. The temperature dependence of the PL spectrum of a Ca center in ZnTe along with a portion of its phonon side band showing only the one-phonon replicas. The spectra at 5 K and 1.5 K are shifted for clarity. The inset shows the temperature dependence of the no-phonon *A* and *B* lines from 25 K to 1.5 K. The sample is excited with the 4420 Å line from a He-Cd laser. cps=counts per second.

tion spectra and the phonon side bands are mirror images of each other around the common no-phonon *A* line.

B. ZnTe:Sr

The temperature dependence of the PL spectrum of the Sr center in ZnTe is displayed in Fig. 5 in the spectral range including its one-phonon replicas. From its temperature dependence, the *A* line can be interpreted as electric dipole allowed while the *B* line, as in the case of the Ca center, is to be viewed as electric dipole forbidden. The no-phonon *A* and *B* lines are observed at 2.2749 and 2.2738 eV, respectively, with *A-B* exchange splitting of 1.1 meV for the isoelectronic Sr impurity. At 1.5 K only the *B* line and its phonon replicas, shifted to lower energies by 1.1 meV from the corresponding features of *A* line, are observed. While the overall shape of the phonon side bands of Ca and Sr shows a strong resemblance, as can be seen in Fig. 1, a comparison of the energies of the phonon features shows an observable difference in their LVM's, occurring at 29.9 and 27.3 meV, respectively. This LVM of Sr along with the TO and LO phonons in ZnTe is observed in the Raman spectrum shown in Fig. 6, with the same energy shifts as the energies of the corresponding features in the side bands of Sr no-phonon lines in luminescence. The no-phonon *A* line is observed in absorption at the same energy as that in luminescence but the phonon side bands in absorption are not resolved as distinctly as their

TABLE I. Measured energy positions of no-phonon lines of excitons bound to Ca, Sr, and Ba and their phonon replicas in ZnTe. ΔE_{JJ} , the electron-hole exchange splitting, is also listed for each center.

Center	Line	Energy (eV)	ΔE_{JJ} (meV)	Phonon energy (meV)
Ca	Ca(A)	2.1997 ± 0.0001	1.1 ± 0.1	TA = 8.5 ± 0.5
	Ca(B)	2.1986 ± 0.0001		LA = 16.5 ± 0.4
				TO = 22.7 ± 0.2
				LO = 25.9 ± 0.2
				LVM = 29.9 ± 0.1
Sr	Sr(A)	2.2749 ± 0.0001	1.1 ± 0.1	TA = 8.8 ± 0.3
	Sr(B)	2.2738 ± 0.0001		LA = 17.3 ± 0.4
				TO = 22.7 ± 0.2
				LO = 26.1 ± 0.1
				LVM = 27.3 ± 0.1
Ba	Ba(A)	2.3312 ± 0.0001	1.2 ± 0.1	TA = 6.6 ± 0.4
	Ba(B)	2.3300 ± 0.0001		Gap mode = 19.9 ± 0.1
				TO = 22.8 ± 0.2
				LO = 26.1 ± 0.1

counterparts in luminescence as displayed in Fig. 7. This seems to be due to the fact that the energies of the Sr no-phonon line and its phonon side bands in absorption are very close to the onset of the intrinsic absorption edge of ZnTe.

C. ZnTe:Ba

The temperature dependence of the PL spectrum of a Ba doped ZnTe sample is displayed in Fig. 8 along with a portion of its phonon side band showing the one-phonon replicas. The *A* and *B* lines for the Ba center are observed at 2.3312 and 2.3300 eV, respectively, and in turn, yield a doublet splitting of 1.2 meV for excitons bound to Ba. At 1.5 K only the *B* line is observed with the phonon replicas associated with it, shifted accordingly. The phonon side band occurring at 19.9 meV below the no-phonon lines can be interpreted as the gap mode resulting from Ba being heavier than

both Zn and Te. The phonon coupling of the Ba center is quite different from those for Ca and Sr in the following points of view: (i) In contrast to the case of Ca and Sr, the no-phonon lines are stronger than the phonon side band for the Ba center. (ii) The LO phonon shows the strongest coupling in luminescence from the Ba center while the LVM's are distinctly stronger than the LO-phonon assisted feature in

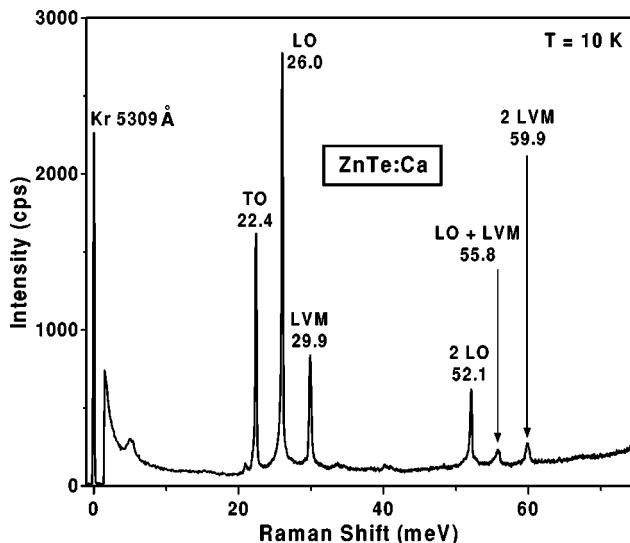


FIG. 3. The Raman spectrum of the Ca doped ZnTe excited with the 5309 Å line from a Kr^+ laser. A neutral density filter reducing the intensity by a factor of 6 enabled the laser line to be recorded.

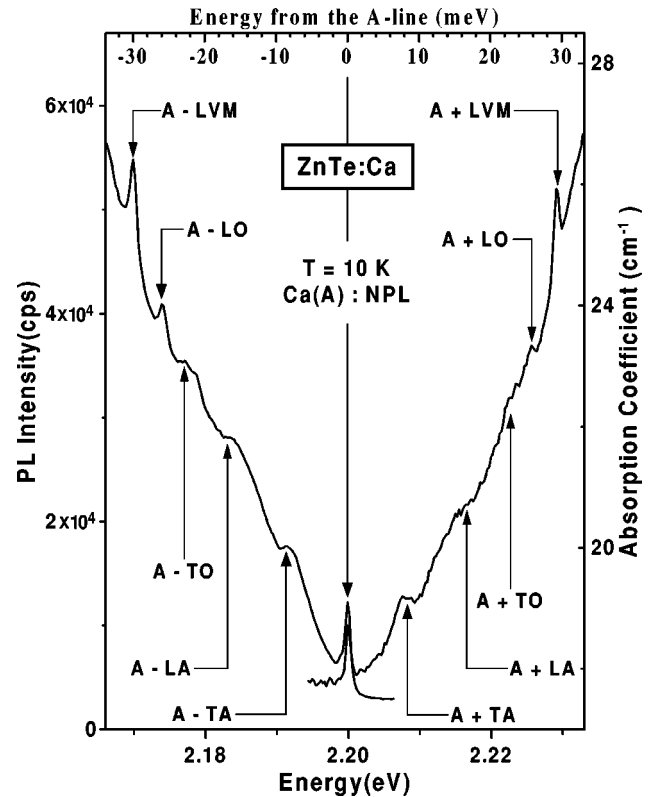


FIG. 4. The absorption and emission spectra of ZnTe:Ca. They are “mirror images” of each other about the common no-phonon *A* line. Both measurements are made at 10 K. The scale on the top of the figure emphasizes the energy separations of the phonon replicas with respect to the *A* line; plus in absorption and minus in emission.

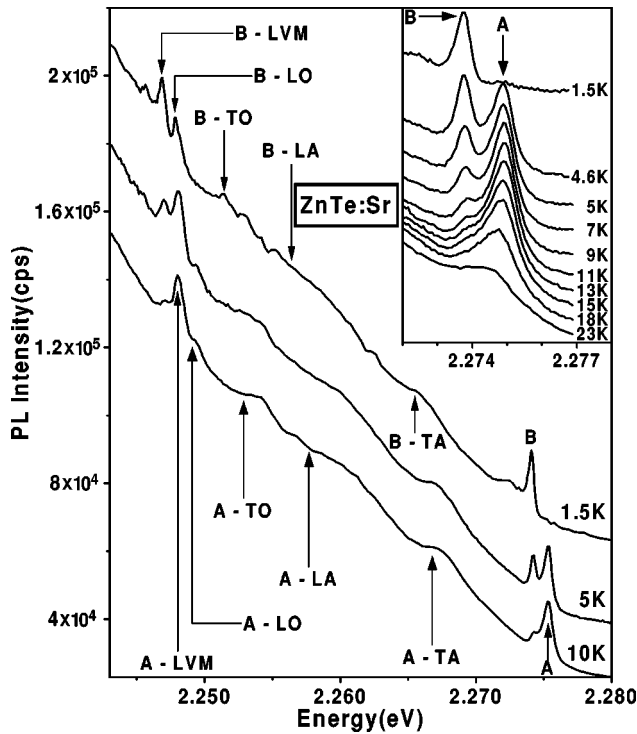


FIG. 5. The temperature dependence of the PL spectrum of ZnTe:Sr. The spectra at 5 K and 1.5 K are shifted for clarity. The detailed temperature dependence of the no-phonon *A* and *B* lines from 23 K to 1.5 K are shown in the inset. The sample is excited with the 4420 Å line from a He-Cd laser.

the PL spectra of Ca and Sr. The explanation for this difference in phonon coupling could be associated with much larger ionic radius of Ba than those of Ca and Sr with respect to that of Zn, thus producing a lattice distortion around the Ba impurity. In fact, in contrast to Ca and Sr cases, the *B* line is already stronger than the *A* line even at 5 K, presumably due to the relaxation of the forbidden nature of *B* line resulting from the lattice distortion around the Ba center.

The following arguments may be cited in support of our identification of the features discussed above as due to excitons bound to Ca, Sr, and Ba centers, respectively, in ZnTe: (i) As can be observed in Figs. 2, 5, and 8, they all show the temperature dependence of the electric dipole allowed and forbidden transitions, *A* and *B* lines, exhibiting a behavior characteristic of excitons bound to isoelectronic impurities in zinc-blende semiconductors. (ii) These features do not have any correlation with the oxygen luminescence since it can be observed with or without oxygen trap in ZnTe. Besides, they show an electron-hole exchange splitting different from that for excitons bound to oxygen centers in ZnTe, 1.5 meV for both the isolated oxygen and OO pairs, but 1.2 meV for Ba and 1.1 meV for Ca and Sr. (iii) The features shown in Figs. 2 and 5 are the strongest luminescence bands in the PL spectra whenever ZnTe is intentionally doped with Ca and Sr, respectively. In addition, the Ca “PL” in Fig. 2 shows no correlation with the Sr “PL” in the other. The PL spectrum in Fig. 8 is observed only with Ba doped ZnTe samples. In some of the ZnTe samples without intentional Ca doping, the same feature as that in Fig. 2 sometimes appears but only as a very small luminescence band, which is presumably due to

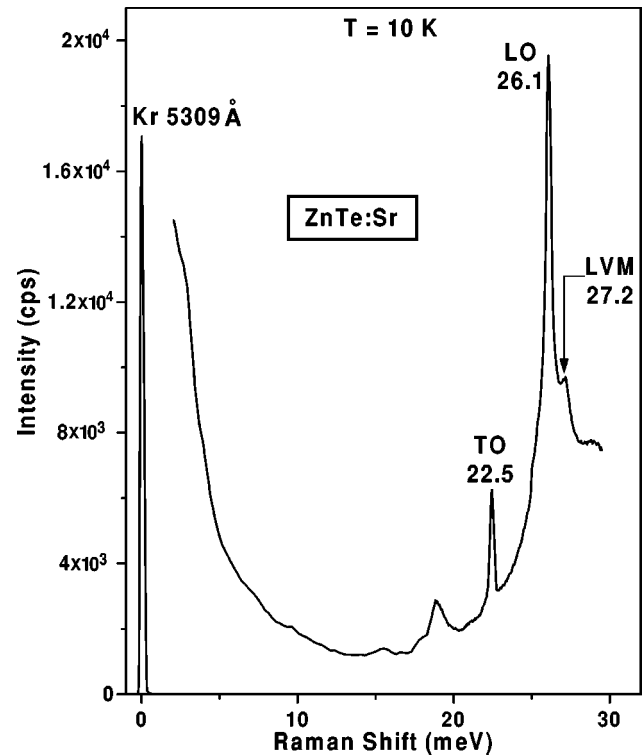


FIG. 6. The Raman spectrum of ZnTe:Sr excited with the 5309 Å line from a Kr⁺ laser. A neutral density filter is used around the laser line to reduce the intensity by a factor of 6.

the inadvertent introduction of a very small amount of residual Ca atoms from the host material.

We note here that Mg is a common residual impurity in Ca, Sr, and Ba. Hence one must rule it out as the isoelectronic impurity responsible for the signatures we identify with Ca, Sr, and Ba. In this context the LVM signatures at 29.9 meV for Ca and at 27.2 meV for Sr and the gap mode feature at 19.9 meV for Ba are significant in that they differ from the LVM frequency of ZnTe:²⁴Mg at 33.7 meV.¹³ This difference is yet another evidence supporting our attribution of the isoelectronic features of Figs. 2, 5, and 8 to Ca, Sr, and Ba, respectively.

Finally, in our experience the Sr feature is always observed in the PL spectra of Ba doped ZnTe samples along with excitons bound to Ba traps since Sr is extremely hard to remove from the source material of Ba and all the commercially available Ba inevitably comes with residual Sr in it. This is another strong evidence that the feature discussed in this subsection is due to excitons bound to Ba traps.

IV. CONCLUDING REMARKS

In the present study we have demonstrated the first successful observation of excitons bound to isoelectronic impurities replacing cation sites of the host semiconductor ZnTe. It is interesting to note that we have not observed any evidence of excitons bound to Mg and Cd centers in ZnTe: their solubility evidently enables the formation of solid solutions Mg_xZn_{1-x}Te (0 ≤ x ≤ 0.55) and Cd_xZn_{1-x}Te (0 ≤ x ≤ 1), respectively. On the one hand, to form an isoelectronic trap, the electronic states of the impurity atom must differ significantly from those of the atom it replaces in order to produce

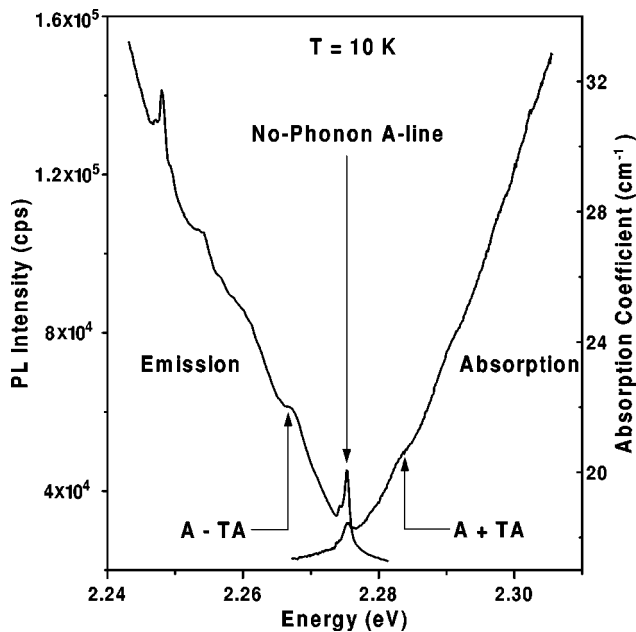


FIG. 7. Absorption and luminescence ‘‘mirror image’’ about the common no-phonon A line in ZnTe:Sr. The scale on the top of the figure emphasizes the energy separations of the phonon replicas with respect to the A line; plus in absorption and minus in emission.

a local potential capable of binding a hole or an electron, implying a low solubility limit for such impurities; on the other hand, isoelectronic substituents with very high solubility easily form an alloy with the host, where the electronic properties can be represented by the virtual crystal model.¹⁴ It is instructive to consider the situation in terms of the relative electronegativities of the host atom and the isoelectronic impurity. The electronegativities of Mg and Cd, 1.31 and 1.69, respectively, are closer to that of Zn, 1.65, in contrast to those of Ca, Sr, and Ba which are 1.00, 0.95, and 0.89, respectively.¹⁵ It appears that the occurrence of excitons bound to isoelectronic Ca, Sr, and Ba impurities when they replace Zn can be attributed to the significant difference in their electronegativities with respect to that of Zn.

The relative intensity of the B line to that of the A line of the Ba center is larger than that for Ca and Sr centers at a given temperature. As can be seen in Fig. 8, even at 5 K the B line is stronger than the A line for the Ba center, in contrast to their behavior in Ca and Sr centers (Figs. 2 and 5). It appears that one must seek the explanation for this difference in the nature of the potential in which the exciton is formed as influenced by the differences in the ionic radii of the isoelectronic impurities and the host atoms. The ionic radii of Ca and Sr, 1.06 Å and 1.27 Å, respectively, are closer to that of Zn, 0.83 Å, than that of Ba, 1.43 Å.¹⁵ A lattice

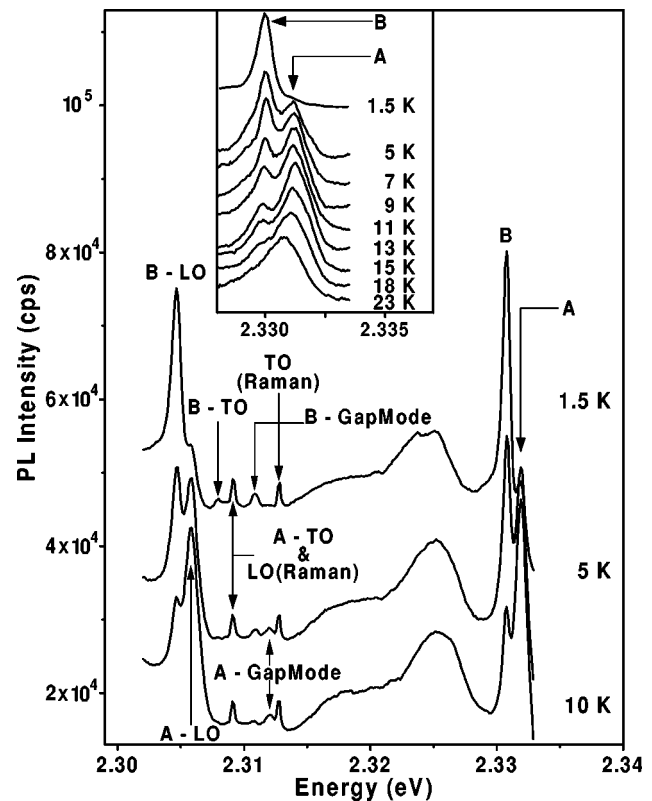


FIG. 8. The temperature dependence of the PL spectrum of ZnTe:Ba. The sample is selectively excited with 45 mW of the 5309 Å line from a Kr⁺ laser to prevent the occurrence of the phonon side bands from excitons bound to *some residual impurities* in the spectral range of the Raman lines. The high excitation power caused a local heating resulting in the appearance of the A line at 1.5 K. The spectra at 5 K and 1.5 K are shifted for clarity. The detailed temperature dependence of the no-phonon A and B lines, excited with 6 mW of the 4420 Å line from a He-Cd laser, from 23 K to 1.5 K are shown in the inset.

distortion and an associated residual strain may thus arise around the Ba center, in turn influencing the short-range potential binding the exciton. If such a distortion produces a lowering of the local symmetry of the isoelectronic center, studies under external magnetic field and uniaxial stress would be instructive in the context of lowering symmetry of the isoelectronic impurity T_d .

ACKNOWLEDGMENTS

The authors acknowledge support from the National Science Foundation Grant No. DMR 92-21390 (Materials Research Group) and Grant No. 94-00415 (Materials Research Science and Engineering Center).

¹W. Czaja, *Isoelectronic Impurities in Semiconductors* in *Festkörperprobleme XI*, edited by O. Madelung (Pergamon, Oxford, 1971), pp. 65–85.

²M. J. Seong, I. Miotkowski, and A. K. Ramdas, *Phys. Rev. B* **58**, 7734 (1998).

³Isolated oxygen isoelectronic centers in ZnTe were discovered by

R. E. Dietz, D. G. Thomas, and J. J. Hopfield, *Phys. Rev. Lett.* **8**, 391 (1962).

⁴D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **150**, 680 (1966).

⁵J. J. Hopfield, D. G. Thomas, and R. T. Lynch, *Phys. Rev. Lett.* **17**, 312 (1966).

⁶For example (i) AgBr:I, W. Czaja and A. Baldereschi, *J. Phys. C*

- 12**, 405 (1979); (ii) CdS:Te, J. D. Cuthbert and D. G. Thomas, *J. Appl. Phys.* **39**, 1573 (1968); (iii) ZnS:Te, T. Fukushima and S. Shionoya, *Jpn. J. Appl. Phys.* **12**, 549 (1973); (iv) InP:Bi, P. J. Dean, A. M. White, E. W. Williams, and M. G. Astles, *Solid State Commun.* **9**, 1555 (1971).
- ⁷SPEX Industries Inc., 3880 Park Ave., Metuchen, NJ 08840.
- ⁸Omnichrome, 13580 Fifth Street, Chino, CA 91710.
- ⁹Spectra-Physics Lasers, 1330 Terra Bella Avenue, P.O. Box 7013, Mountain View, CA 94039.
- ¹⁰Janis Research Inc., P.O. Box 696, 2 Jewel Dr., Wilmington, MA 01887-0696.
- ¹¹B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids* (Oxford University Press, Oxford, 1989).
- ¹²In addition to the 5309 Å line of a Kr⁺ laser used to excite the Raman spectrum shown in Fig. 3, we ensured that the Raman lines occur with the same shifts when excited with the 5208 Å and the 6471 Å lines of Kr⁺. We also confirmed that they are observed in ZnTe:Ca specimens from different ingots.
- ¹³M. Dean Sciacca, A. J. Mayur, N. Shin, I. Miotkowski, A. K. Ramdas, and S. Rodriguez, *Phys. Rev. B* **51**, 6971 (1995); see also R. Vogelgesang, A. J. Mayur, M. Dean Sciacca, Eunsoon Oh, I. Miotkowski, A. K. Ramdas, and S. Rodriguez, *J. Raman Spectrosc.* **27**, 239 (1996).
- ¹⁴P. J. Dean and D. C. Herbert, *Bound Excitons in Semiconductors in Excitons*, edited by K. Cho (Springer, Berlin, 1979), pp. 55–182.
- ¹⁵Pauling's electronegativity values quoted from J. Emsley, *The Elements*, 3rd ed. (Oxford University Press, Oxford, 1998).