TECHNICAL NOTES

The effect of pressure on the isomer shift of ^{57}Fe(^{57}Co) as an impurity in ZnSe, ZnTe and CdTe*

MÖSSBAUER resonance in ^{57}Fe has proved to be a useful tool for studying the effect of pressure on chemical bonding in insulators [1–3] and on the band structure of transition metals [4, 5]. The isomer shift measures the s electron density at the nucleus; however, since the $3s$ orbitals are significantly shielded from the nucleus by the $3d$ electrons, one can infer changes in energy or radial distribution of the $3d$ orbitals from changes in the isomer shift with pressure.

In this paper we show the effect of pressure on the isomer shift for ^{57}Fe (introduced as ^{57}Co) as an impurity in ZnSe, ZnTe, and CdTe. All three compounds have the zinc-blende structure at one atmosphere. Previous high pressure studies [6] have shown that ZnSe and ZnTe have first order phase transitions at about 165 and 135 kbar. The high pressure phase apparently has the NaCl structure [7] and is metallic or semimetallic [8]. CdTe has first order phase transitions at about 30 kbar and 100 kbar [6]. The phase at 30 kbar is NaCl [9, 10] and is semiconducting, while the high pressure phase is the diatomic analog of white tin [11] and is metallic [7].

The materials used in this work were those used in the electrical work [6, 7] or were reagent grade obtained from Pfaltz and Bauer. CoCl$_2$ was thermally diffused into the lattices at a temperature of 800°C. The maximum

concentration was 10^{-5}, and, in the case of CdTe it was very considerably less. The high pressure Mössbauer resonance techniques have been described elsewhere [12]. Figure 1 shows a typical spectrum for ZnTe at 90 kbar. The spectra were computer fit with Lorentzian peaks.
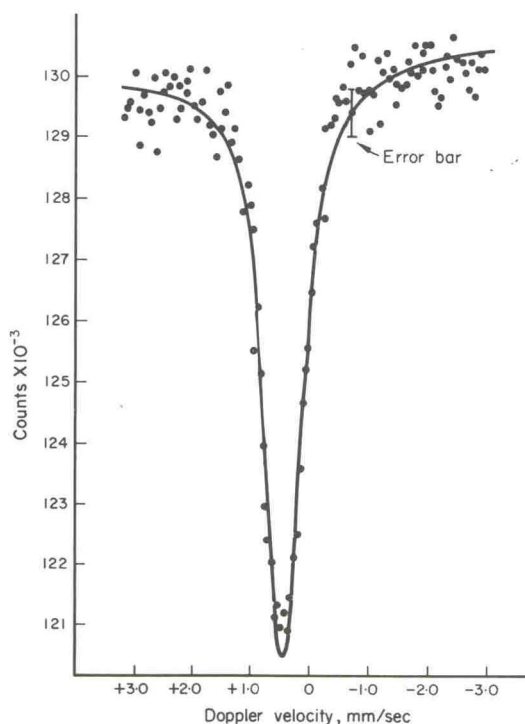

Fig. 1. Mössbauer spectrum of ZnTe at 90 kbar.

The results are shown in Fig. 2. The arrows represent the locations of the first order phase transitions observed electrically. (All isomer shifts are shown relative to metallic iron at one atmosphere.) The first point to be noted is that the atmospheric pressure isomer shifts are in the range 0·6–0·8 mm/sec. These are very close to the values observed for FeSe
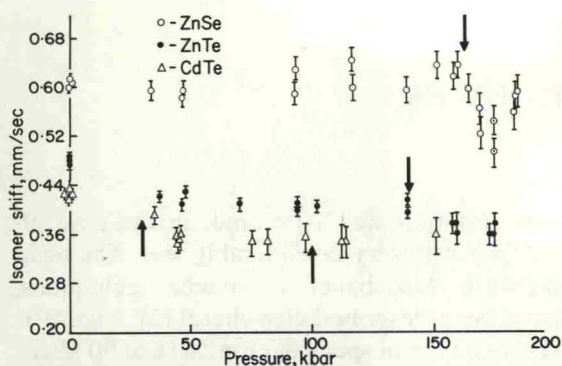
Fig. 2. Isomer shift vs. pressure—ZnSe, ZnTe and CdTe.

and FeTe[13], rather than near the typical ionic ferrous $(1\cdot2-1\cdot4 \text{ mm/sec})$ or ferric $(0\cdot3-0\cdot4 \text{ mm/sec})$ values. In the tellurides there was no sign of quadrupole splitting, but in ZnSe the peak was broadened sufficiently to imply a quadrupole splitting of about $0\cdot75$ mm/sec, which did not change significantly with pressure.

For ZnSe there is perhaps a slight increase in isomer shift (decrease in electron density at the nucleus) with increasing pressure in the zincblende phase. At the transition (165 kbar) there is a modest but distinct decrease in isomer shift, followed by a rise in the high pressure phase. ZnTe shows a small decrease in isomer shift with increasing pressure in the zincblende phase, and a small but measurable decrease at the transition (135 k/bar). The CdTe isomer shift exhibits a distinct decrease at low pressure, probably associated with the 30 kbar transition. There appeared to be no effect associated with the 100 kbar transition, but with the very high dilution of ^{57}Co and the intense scattering by the heavy nuclei, a small change could easily be missed.

The most important feature of the results is the relatively small change in isomer shift at the phase transitions. Since the transitions in ZnSe and ZnTe and the 100 kbar transition in CdTe involve not only a change in symmetry and coordination number, but also a semi-conductor-to-metal transition with a change of resistivity of several orders of magnitude, there must be drastic modifications of band structure in the host. Yet the change electron density at the ^{57}Fe nucleus at the transition is much smaller than the change in electron density with compression observed in a typical ionic compound over a 50 kbar range[2]. The ^{57}Fe orbitals must be strictly localized so that there is little change in $4s$ occupation or in radial extent of the $3d$ orbitals, even though the surrounding atoms undergo a drastic rearrangement.

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