

## $^{55}\text{Mn}$ , $^{125}\text{Te}$ , and $^{113}\text{Cd}$ NMR studies of the diluted magnetic semiconductor $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ in the range $x = 0.01-0.6$

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$^{55}\text{Mn}$ ,  $^{125}\text{Te}$ , and  $^{113}\text{Cd}$  NMR has been used in the diluted magnetic semiconductor  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  ( $x = 0.01-0.6$ ) for probing into local electronic structure. The detection of  $^{55}\text{Mn}$  nuclei in the magnetically ( $3d^5$ ) and quadrupolar ( $I = \frac{5}{2}$ ) broadened NMR spectra has been possible only at low frequency because of the  $\text{Mn}^{2+}-\text{Mn}^{2+}$  exchange interaction, particularly in the antiferromagnetic clusters for high values of  $x$  (0.125-0.6).  $^{125}\text{Te}$ , which undergoes transferred hyperfine interaction from  $\text{Mn}^{2+}$ , could, however, be detected at high frequencies (94.88 MHz) for  $x = 0.6$  and 0.3. At these high  $x$  values, exchange within the clusters reduces the effective magnetic moment  $\langle S_z \rangle$  experienced by Te and consequently the broadening is within limits. The situation is quite different in  $^{113}\text{Cd}$ , as  $\text{Mn}^{2+}$  is not the nearest neighbor nor is it bonded to Mn directly. However, it does undergo dipolar interaction with the  $\text{Mn}^{2+}$  spin and is also affected by the spin polarization of the  $sp$  band of CdTe by  $\text{Mn}^{2+}$ . Thus  $^{113}\text{Cd}$  NMR has been detected for all  $x$  values. The shift changes sign between  $x = 0.6$  and  $x = 0.3$  in both Mn and Te, from positive to negative in Mn and negative to positive in Te as expected for direct versus transferred hyperfine interaction. The shift also changes sign in  $^{113}\text{Cd}$ ; as expected it parallels the Mn shift.

The II-VI semiconductor CdTe has been under investigation for quite some time, because of its great technological and scientific interest. During the last decade, doping of CdTe, or for that matter other II-VI semiconductors having the zinc blende or wurtzite structure, with the  $3d$  magnetic ion  $\text{Mn}^{2+}$ , has resulted in the diluted magnetic semiconductors (DMS).  $\text{Mn}^{2+}$  doping (more than 70% of Cd can be replaced by Mn) drastically affected the electronic, optical, and magnetic properties of the host CdTe and has been well documented.<sup>1,2</sup> However, the  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  DMS system has basically attracted great interest as a random magnetic spin system,<sup>2</sup> wherein  $\text{Mn}^{2+}$  substitutes for Cd sites in a random fashion. However, as the Mn-Te distance is less than the Cd-Te distance, Te shifts towards  $\text{Mn}^{2+}$  (Fig. 1) and the lattice dis-

torts. Thus extensive magnetic and magneto-optic studies<sup>1</sup> of the  $\text{Mn}^{2+}$ -based DMS system have been carried out. Comparatively little attention has been paid to ascertaining how the CdTe and/or CdSe lattice and band structure are affected by  $\text{Mn}^{2+}$  substitution.

Recent photoemission experiments<sup>3</sup> in II-VI semiconductors including  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  exhibit a moderately narrow metal  $d$  subband ( $3d^{10}$ ) inside the main valence band, which strongly influences the electronic properties through  $p-d$  repulsion and hybridization. Further, the 10  $d$  electrons are unable to compensate in full electrostatically for the 10 added protons, as  $d$  orbitals with their vanishing amplitudes at the nucleus are not corelike charges. Thus they do not completely screen the 10 added protons. This leaves a net attractive electron-ion potential. Consequently the valence  $s$  electrons of Group IIB elements are more strongly bound to the nucleus than the core  $s$  orbitals in Group IIA. This imperfect  $d$ -orbital screening in Group IIB makes the atomic sizes and lattice parameters of those atoms smaller than those of Group IIA, despite the added orbital shell. Thus compared to Group IIA (ionic compounds), the more tightly bound valence  $s$  electrons in Group IIB elements force them to form electron-sharing bonds. Smaller band gaps, lattice constants, and cohesive energies, and large bulk moduli are then direct manifestations of their reduced ionicities—a consequence of incomplete  $d$ -orbital screening effects. Thus the ionicity of the chemical bond in CdTe is only 0.717. Hence there is considerable covalent admixture in the tetrahedral  $sp^3$  bond.

Early crystal-structure studies of different DMS alloys indicate that their lattice parameters obey Vegard's law very closely<sup>1,2</sup> and the lattice constant  $a$  for the cubic crystal decreases linearly with  $x$ . However, recent extended x-ray-absorption fine-structure<sup>4</sup> (EXAFS) studies on  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  indicate that Zn-Se and Mn-Se bond

DISTORTION IN  $\text{Cd}_{1-x}\text{Mn}_x\text{X}$

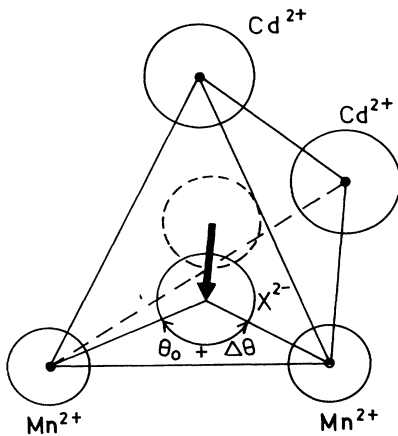


FIG. 1. Random substitution of Mn in Cd tetrahedra.

lengths remain practically constant throughout the entire range of  $x$ . It may be pointed out that EXAFS provides detailed information on the immediate atomic environment of a given lattice. In DMS ( $A^{II}MnB^{VI}$ ), it is sensitive to the local spatial distribution of the four cations tetrahedrally bound to the anion, whereas x-ray diffraction determines the lattice parameter averaged over many cation and anion sites. EXAFS and x-ray results thus do not contradict each other, but imply that the two sublattices distort to keep Zn-Se and Mn-Se bond lengths constant throughout the range. Thus in Mn-substituted CdTe, the sublattices are not strictly cubic, permitting many forbidden optical transitions involving local mode excitations of  $Mn^{2+}$ . This lattice distortion directly affects the  $Mn^{2+}$ - $Mn^{2+}$  superexchange which is mediated through the intervening  $p$  orbital of the Te anion and the Mn-Te-Mn angle is also directly affected (Fig. 1). Further, the localized  $3d$  electrons on  $Mn^{2+}$ , polarize the  $sp$  conduction band of the parent CdTe lattice. The present paper is an attempt at a detailed study of the effect of Mn on the local properties of Cd and Te lattices. As NMR is a very good probe of local structure and bonding and all three nuclei in the ternary alloy  $Cd_{1-x}Mn_xTe$  are magnetic ones, attempts have been made to throw light on this aspect of DMS with NMR.

It was realized at the outset that NMR studies of DMS would be a formidable task. First,  $^{111}Cd$  and  $^{113}Cd$ , as well as  $^{125}Te$ , are not abundant nuclei, thus requiring high-sensitivity Fourier-transform-NMR techniques for detection.  $^{55}Mn$  NMR in this sample is particularly difficult, as it is a quadrupolar nucleus ( $I = \frac{5}{2}$ ) with five unpaired  $d$  electrons, leading to quadrupolar as well as magnetic broadening of the signal. This broadening would also affect the Cd and Te signals. However, the exchange interaction in  $Mn^{2+}$  ( $J$  is known to increase with  $x$ ) is expected to narrow the otherwise very broad signals. Considerable effort was spent on searching the NMR signals under diverse experimental conditions, and I detected  $^{55}Mn$  NMR signals for  $x = 0.125, 0.3, \text{ and } 0.6$ ,  $^{125}Te$  signals for  $x = 0.3 \text{ and } 0.6$ , and  $^{113}Cd$  signals for  $x = 0.01, 0.125, 0.3, \text{ and } 0.6$  (Table I).

The  $Cd_{1-x}Mn_xTe$  single crystals studied were grown at Purdue University using a modified Bridgman technique<sup>5</sup>

TABLE I. Shifts in  $Cd_{1-x}Mn_xTe$  (ppm).  $^{113}Cd$  and  $^{125}Te$  shifts measured with respect to single-crystal CdTe as a reference.  $^{55}Mn$  shifts measured with respect to aqueous  $KMnO_4$  solution.

$x$	$^{113}Cd$	$^{125}Te$	$^{55}Mn$
0.01	117	...	...
0.125	1140 297	...	1637 1659
0.30	-824 -573	4343	-1583 -1606
0.6	1381	-919	1848 257

and were obtained through the courtesy of J. K. Furdyna. NMR detection could be made on the CXP90 Bruker Spectrometer for  $^{55}Mn$  and MSL-300 Bruker Spectrometer for Cd and Te in  $Cd_{1-x}Mn_xTe$ . The shifts for  $^{113}Cd$  and  $^{125}Te$  are reported against single-crystal CdTe, taken as reference. For  $^{55}Mn$ , a solution of  $KMnO_4$  in water is taken as the reference. All data were taken at room temperature under static conditions. Apart from pure CdTe (reference), four different samples ranging from comparatively dilute ( $x = 0.01$ ) through  $x = 0.125, x = 0.3$  to the more than 50% substituted  $x = 0.6$  were studied.  $x = 0.01$  is not quite the upper limit of almost isolated spins; whereas from  $x = 0.125$ , exchange interactions play an important role and above  $x = 0.2$  for  $x = 0.3$  and  $0.6$  we probably have domain clusters, within which antiferromagnetic exchange occurs. The samples were chosen to get a kaleidoscopic effect.

$^{55}Mn$  (100% abundance) NMR was first detected at 22.198 MHz [Fig. 2(a)] for the sample  $x = 0.6$  in the CXP90 Bruker Fourier-transform-NMR spectrometer, provided with a high-resolution (HR) electromagnet at Central Leather Research Institute (CLRI), Madras, which enabled narrow lines to be obtained. Later,  $^{55}Mn$  NMR for the three different samples ( $x = 0.6, 0.3, \text{ and } 0.125$ ) were detected in CXP90 with a wide-line (WL) electromagnet at Tata Institute of Fundamental Research (TIFR), Bombay. Again, two lines of unequal intensities were found, but due to magnetic field inhomogeneity, the individual lines are rather broad [Fig. 2(b)]. However, the shifts change sign (positive to negative) from  $x = 0.6$  to  $x = 0.3$ . The shift was positive again for  $x = 0.125$ .

In spite of repeated and prolonged efforts to detect  $^{55}Mn$  at high frequencies in MSL-300, there was no success. It appears that magnetic broadening at the higher frequency broadens the line beyond detection.

$^{125}Te$  NMR (6.5% abundance) in a CdTe single crystal was detected at 28.437 MHz in a single-crystal CdTe on CXP90 (HR magnet) and revealed a triplet due to anisotropic  $J$  coupling from Cd.<sup>6</sup> The narrow dipolar line from low-abundance  $^{125}Te$  enables the detection of  $J$  coupling. However, at MSL-300 (94.831 MHz), due to higher conduction-electron polarization by the high magnetic field, no splitting in the Te line was observed, though the coupling manifests itself as humps on either side of the line [Fig. 3(a)].

$^{113}Cd$  NMR in CdTe single crystal (12.25% abundance) was detected at 66.577 MHz on the MSL-300 spectrometer and though no splittings could be observed, the line showed strong chemical-shift anisotropy [Fig. 3(b)].

$^{113}Cd$  and  $^{125}Te$  in  $Cd_{1-x}Mn_xTe$  at MSL-300.  $Mn^{2+}$  substitutes for  $Cd^{2+}$  randomly for different  $x$  values, while the Te lattice is only indirectly affected. Thus Te is surrounded by four cations consisting of Cd and Mn. Five different cation configurations are possible for  $Cd_xMn_{4-n}$  where  $n = 0, 1, \dots, 4$ . Each different cation configuration should give different shifts for associated Te, but because of paramagnetic broadening due to transferred hyperfine interaction from  $Mn^{2+}$ , these may not be resolved. However, in the diamagnetic  $Cd_{1-x}Zn_xTe$ , the  $^{125}Te$  lines have been resolved.<sup>7</sup> The Te shift in the present case is

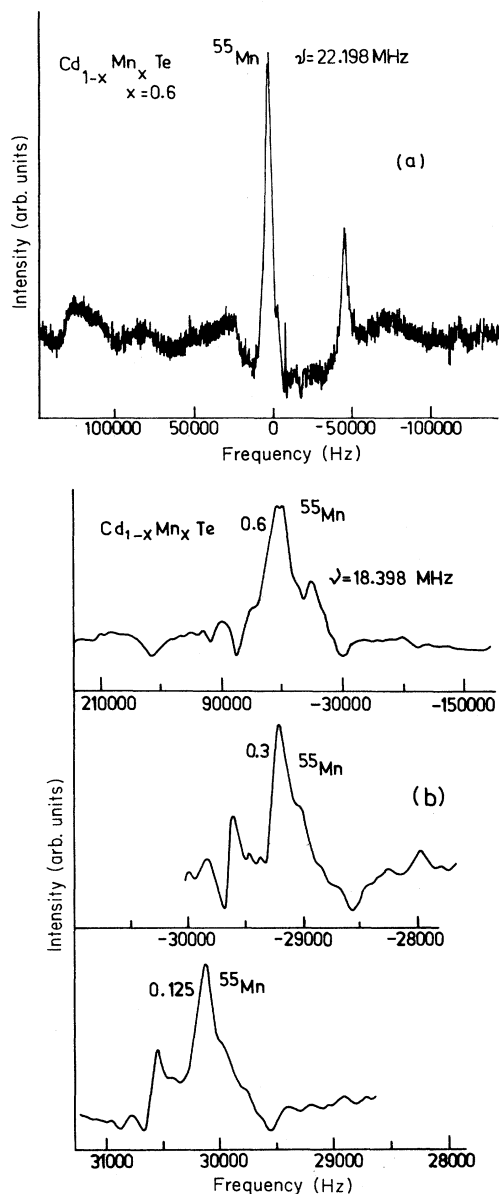


FIG. 2. (a)  $^{55}\text{Mn}$  NMR spectrum for  $\text{Cd}_{0.4}\text{Mn}_{0.6}\text{Te}$  at 22.198 MHz in CXP90 Bruker Spectrometer (HR magnet). (b)  $^{55}\text{Mn}$  NMR spectra for  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  at 18.398 MHz in CXP90 Bruker Spectrometer (WL magnet).

primarily determined by nearest-neighbor  $\text{Mn}^{2+}$  ions. For large  $x$ , superexchange leads to smaller  $\langle S_z \rangle$  of  $\text{Mn}^{2+}$  as experienced by  $^{125}\text{Te}$ , whereas at low  $x$  values,  $\langle S_z \rangle$  is large. Thus in MSL-300,  $^{125}\text{Te}$  NMR (Fig. 4) could be observed only for  $x=0.6$  and  $0.3$  and that also with a large number of scans due to low  $^{125}\text{Te}$  abundance and strong contact interaction from  $\text{Mn}^{2+}$ . Interestingly, the shifts change sign (negative to positive) from  $x=0.6$  to  $x=0.3$  (Table I). Core-polarization effects can be positive or negative and are difficult to predict unless calculated.

However, in  $^{113}\text{Cd}$ , where it is not directly bonded to Mn, signals could be detected for all four different con-

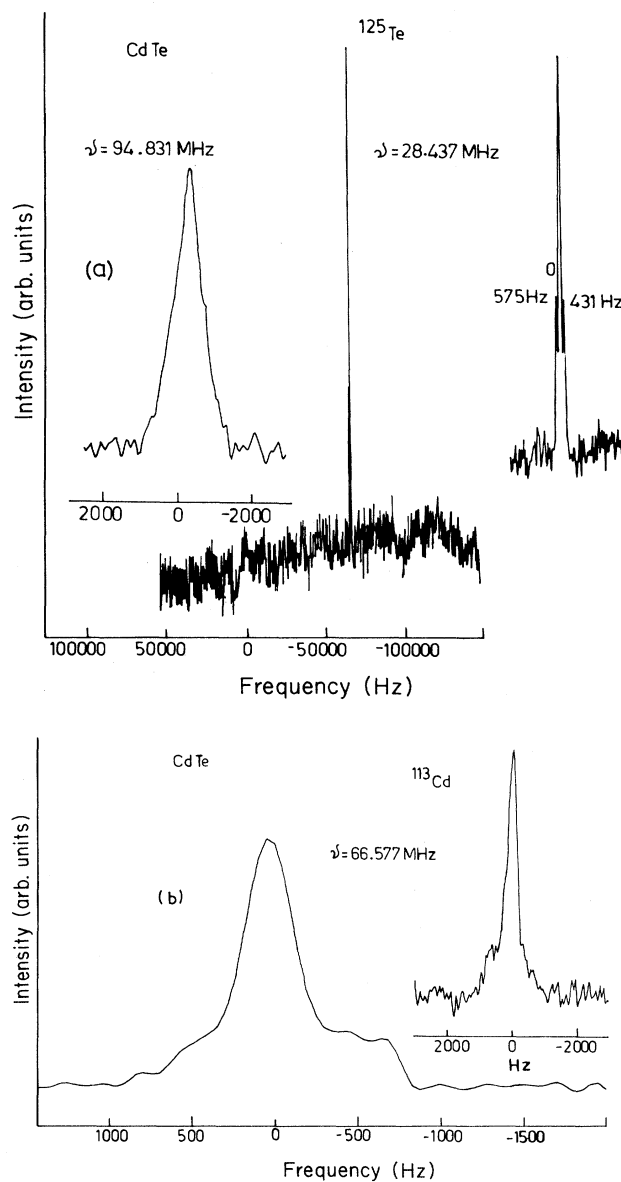


FIG. 3. (a)  $^{125}\text{Te}$  NMR spectra for CdTe at 28.437 MHz (HR magnet) and at 94.831 MHz. (b)  $^{113}\text{Cd}$  NMR spectra for CdTe at 66.577 MHz.

centrations. In case of Cd, there is the direct dipolar interaction from  $\text{Mn}^{2+}$ , together with a pseudocontact interaction from Mn, though there is no direct contact term. Thus for the comparatively dilute system  $x=0.01$ , a single line was observed, whereas for  $x=0.125$  and  $0.3$ , two separate lines with different shifts were observed. For  $x=0.6$ , where there is strong antiferromagnetic exchange interaction between the  $\text{Mn}^{2+}$  ions in the clusters, a single (Fig. 5) shifted line was observed. Also in this case the shift changed sign (positive to negative) from  $x=0.6$  to  $x=0.3$ . It may be mentioned in this connection that Zamir *et al.*<sup>8</sup> in their NMR studies of II-VI semiconductors report that  $^{113}\text{Cd}$  and  $^{125}\text{Te}$  have been detected in the range  $0 < x < 0.1$  in dilute  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ . Additional

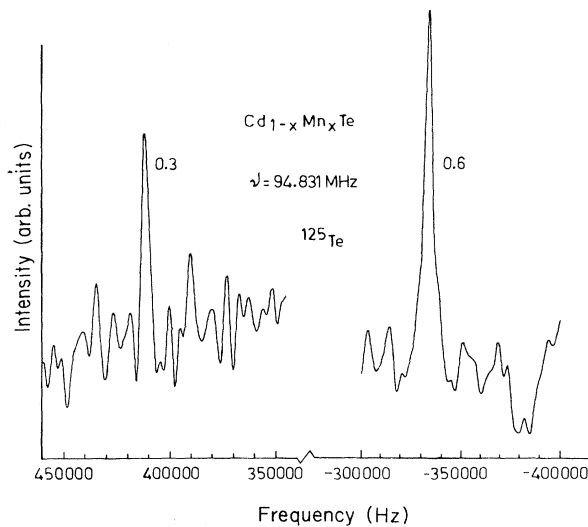


FIG. 4.  $^{125}\text{Te}$  NMR spectra for  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  at 94.831 MHz.

lines have been observed for  $^{113}\text{Cd}$  at higher frequencies for Mn concentrations up to  $x=0.1$ . However, no details have been given regarding  $^{125}\text{Te}$ .

In summary,  $^{55}\text{Mn}$ ,  $^{113}\text{Cd}$ , and  $^{125}\text{Te}$  NMR signals have been detected in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  (DMS).  $^{55}\text{Mn}$  NMR signals have been detected for  $x=0.125, 0.3$ , and  $0.6$  at the low frequency of 22 MHz, but not in the high frequency of 74.021 MHz.  $^{113}\text{Cd}$  NMR has been observed for all four  $x$  values at 66.577 MHz.  $^{125}\text{Te}$  NMR has only been observed for  $x=0.6$  and  $0.3$ , where exchange interactions are large. Finally, room-temperature results indicate perfect correlation between  $^{55}\text{Mn}$ ,  $^{125}\text{Te}$ , and  $^{113}\text{Cd}$  shifts as is expected from  $\text{Mn}^{2+}\text{-Mn}^{2+}$  exchange and polarization of the  $sp$  conduction band in DMS by  $\text{Mn}^{2+}$ .

Thus though the detection of NMR signals of  $^{55}\text{Mn}$ ,  $^{113}\text{Cd}$ , and  $^{125}\text{Te}$  in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  system is gratifying, further work has to be done in optimizing the signals to obtain the true line shape and linewidths, and also low-temperature studies should be conducted to further the understanding of the spin dynamics of the system.

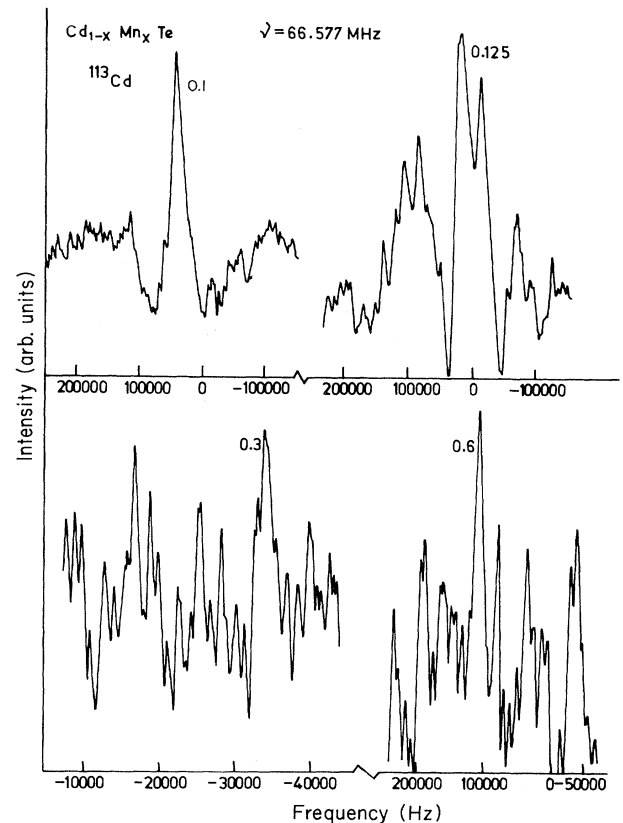


FIG. 5.  $^{113}\text{Cd}$  NMR spectra for  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  at 66.577 MHz.

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