Hyperfine Interactions 15/16 (1983) 215-218

EFG SIGN FOR Sn IN Zn, Cd, AND Sb

H. Haas, M. Menningen, Hahn-Meitner-Institut, Berlin-39, Germany
H. Andreasen, S. Damgaard, H. Grann, F.T. Pedersen, J.W. Petersen,
G. Weyer, Institute of Physics, University of Aarhus,
DK 8000 Aarhus C, Denmark, and
ISOLDE Collaboration, CERN, CH 1211 Geneva, Switzerland

Mössbauer spectroscopy on ion-implanted sources of ^{119}Cd in single-crystals was applied to study the electric field gradients (EFG) at ^{119}Sn in three non-cubic metals. The signs and magnitudes determined are in agreement with presently known systematics. The measured isomer shifts and the recoilless fractions are discussed.

1. Introduction

Electric field gradients at impurity nuclei in non-cubic metals are now known for many systems. Of special importance are sp-probe atoms, as their local electronic structure is expected to be rather simple. Most data are available for the group IIb metal matrices Zn, Cd, and Hg. The deviation from ideal packing is strongest for these lattices, so that very large field gradients are found. For Cd and In probe atoms in particular the sign of the EFG is opposite to the one calculated from a lattice sum over positive ion cores (1). For the group Va semimetals As, Sb, and Bi local covalency effects have been invoked to explain EFG systematics found for these lattices (2). The determination of the EFG sign for the group IVa impurity Sn is therefore a valuable check of model predictions in both cases. ^{119}Sn Mössbauer spectroscopy with single-crystal sources offers a rather simple possibility for such measurements.

2. Experiment

Sources of ^{119}Cd were implanted into disk-shaped single-crystals at the ISOLDE on-line isotope separator (3), where this activity is produced by spallation of tin with 600 MeV protons from the CERN synchrocyclotron. The implantation doses were about 10^{11} ions/cm^2 at 60 keV. The Zn and Cd samples were prepared by spark cutting from commercially obtained single-crystals and cleaned by etching with HNO_3, while the Sb samples were prepared by cleaving from a single-crystal grown by the Bridgman technique. As Mössbauer source the decay produced ^{119}In with $T_{1/2}$ = 2.1 min was used. Spectra were recorded with a resonance detector containing $CaSnO_3$ as anode material (4) mounted on a conventional electromagnetic drive system. For measuring temperatures of 77 K the sources were submerged in liquid N_2.

3. Analysis and Results

Data were taken during two separate runs with several crystals. All spectra were fitted with two lines of equal width but variable position (P) and area to background ratio (A/B). The experiments are summarized in Table I.

Table I : Experiments and fit parameters

Sample	T(K)	Run	P_1(mm/s)	A_1/B	P_2(mm/s)	A_2/B	
Zn ⊥	77	1	1.84(2)	1.12(4)	2.79(2)	1.70(5)	
Zn ⊥	293	1	1.85(3)	.26(4)	2.80(3)	.40(4)	
Zn ⊥	77	2	1.88(2)	.79(3)	2.85(2)	1.29(4)	
Cd ∥	77	2	2.40	.33(3)	3.08	.19(2)	a)b)
Cd ⊥	77	2	2.41(2)	.33(3)	3.08(2)	.57(4)	c)
Cd ⊥	77	2	2.39(2)	.48(5)	3.07(2)	.74(6)	b)
Sb ∥	77	1	2.50(3)	.41(2)	2.74(2)	1.23(6)	d)
Sb ∥	293	1	2.46(5)	.11(1)	2.76(3)	.33(3)	d)
Sb ∥	77	2	2.40(3)	.52(5)	2.74(2)	1.64(8)	

a) positions from Cd ⊥
b) weak component at IS = .16 mm/s
c) strong component at IS = .16 mm/s
d) ratio A_2/A_1 = 3 fixed

The expected two-line pattern was clearly resolved for Zn, while for Sb the quadrupole splitting leads only to a broadening of the resonance as documented in Fig. 1. Cd samples were available with the c-axis normal to the surface (γ emission parallel, ∥) and with the c-axis in the surface (γ emission perpendicular, ⊥). Unfortunately the implantations into Cd showed a third component in the Mössbauer spetrum, assigned from the isomer shift to atoms stopped in an oxide layer. Nevertheless, from Fig. 2 it is evident that the line intensity for the quadrupolar split substitutional component is very different along the two directions, showing a strong anisotropy of the recoilless fraction. The determination of the recoilless fractions from spectra recorded with a resonance detector is somewhat complicated, since a possibly time-varying background has to be considered. By comparison with a source prepared by implantation into Pt, however, it was possible to normalize the intensities approximately. In table II the quadrupole coupling constants (e^2Qq/h), isomer shifts (IS) relative to $CaSnO_3$, and recoilless fractions (f) determined are summarized.

Table II: Results

	T	e^2Qq/h(MHz)	IS(mm/s)	f
Zn ⊥	77	-37.1(5)	2.45(2)	.83(5)
Zn ⊥	293	-36.7(10)	2.43(3)	.19(3)
Cd ⊥	77	-25.8(15)	2.82(2)	.54(8)
Cd ∥	77			.22(4)
Sb ∥	77	+11.2(25)	2.68(2)	.87(4)
Sb ∥	293	+11.6(30)	2.68(3)	.23(3)

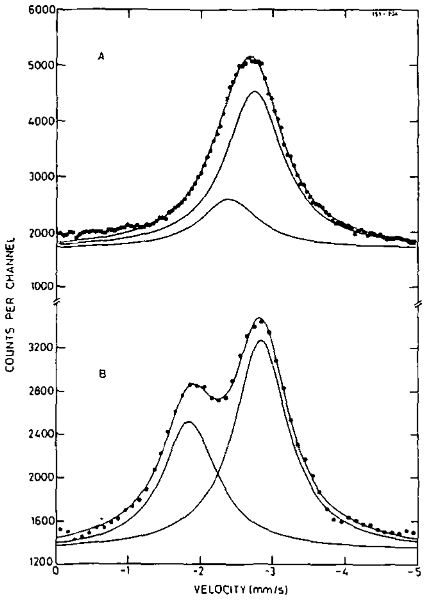

Fig. 1: Spectra for Sb ∥ (A) and Zn ⊥ (B) at 77 K

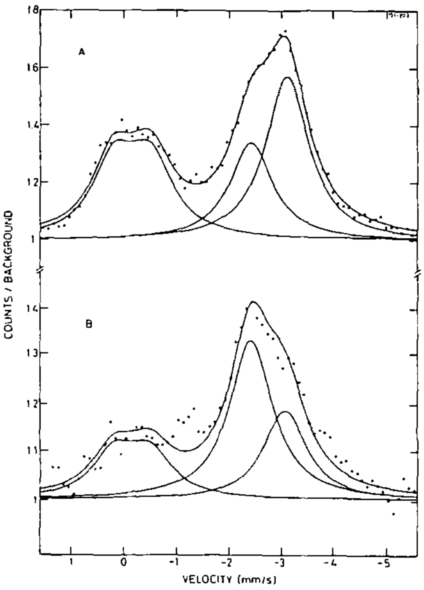

Fig. 2: Spectra for Cd ⊥ (A) and Cd ∥ (B) at 77 K

4. Discussion

To extract the EFG from the quadrupole coupling constants it is necessary to have a reliable value for the nuclear quadrupole moment of the $3/2^+$ isomer in ^{119}Sn. Using the moments for high spin Sn isomers previously determined from PAD experiments in Cd at high temperatures (5) and the measured temperature dependence for this system (6) together with our value for ^{119}Sn in Cd at 77 K one obtains

$$Q = -10.9(8)\ \mathrm{fm}^2$$

which is in the range of earlier results. The negative sign was taken from Ref.7. The EFG's at 77 K calculated are

$$\begin{array}{lr} \mathrm{Zn} & +14.1 \cdot 10^{17}\ \mathrm{V/cm}^2 \\ \mathrm{Cd} & +9.8 \cdot 10^{17}\ \mathrm{V/cm}^2 \\ \mathrm{Sb} & -4.3 \cdot 10^{17}\ \mathrm{V/cm}^2. \end{array}$$

Within the accuracy of the measurements the values at room temperature for Zn and Sb are not significantly different. For Zn no previous value exists, while for Sb our result is somewhat larger than the one to be extracted from a PAC measurement on ^{118}Sn (8).

A negative EFG for Sn in Sb has been predicted using a covalent model for the p electron structure at the impurity (2). A positive EFG similar in value to the group IIb and IIIb impurities is expected from a tight binding description of the band structure of the group IIb metals (9). This is perfectly confirmed by the present data. The values to be compared are: InZn 11.9, InCd +9.4, CdZn +6.7, CdCd +6.2 (all 10^{17}V/cm^2). The larger ratio for the EFG of Sn in Zn and Cd q(SnZn)/q(SnCd) = 1.43 is also found even more pronouncedly for the isovalent impurity Ge: q(GeZn)/q(GeCd) = 1.84.

The isomer shifts measured are in the general range found for ^{119}Sn as impurity in metals (10). For Sb our value agrees with that of Ref.11. The decrease in IS from Cd to Zn (and similarly from Ag to Cu and In to Ga) may be interpreted as an increase in p-character of the Sn valence configuration due to the increased interaction with the neighbours in the denser matrix. This is in accordance with the larger EFG found in Zn.

One interesting aspect of the present measurements may be extracted from the recoilless fractions. If these are converted into Debye temperatures using a simple anisotropic Debye model, one obtains: $\Theta_\perp$(Zn) = 225 (30)K, $\Theta_\parallel$(Cd) = 78 (10)K, $\Theta_\perp$(Cd) = 150 (15)K, $\Theta_\parallel$(Sb) = 230 (40)K. Within the large errors the values for Zn and Sb are in the range of the pure lattice Debye temperatures. For Sb a very small anisotropy may be infered from a single-crystal Mössbauer spectroscopy experiment on ^{121}Sb (12). The very strong anisotropy observed for Cd, in particular, is also found in x-ray scattering experiments (13). Here, however, the overall Θ at the impurity appears to be considerably reduced. A more detailed investigation of this point would be highly desirable.

References

[1] P. Raghavan, E.N. Kaufmann, R.S. Raghavan, E.S. Ansaldo, R.A. Naumann, Phys.Rev. B13 (1976) 2835
[2] H. Haas, M. Menningen, Hyperfine Interactions 9 (1981) 277
[3] H.L. Ravn, Phys. Rep. 54 (1979) 301
[4] G. Weyer, Mössb. Eff. Meth. 10 (1976) 301
[5] H. Bertschat, O. Echt, H. Haas, E. Ivanov, E. Recknagel, E. Schlodder, B. Spellmeyer, M. Ionesco-Bujor, A. Jordachescu, G. Pascovici, D. Plostenara, S. Vajda,Hyperfine Interactions 2 (1976) 326
[6] O. Echt, H. Haas, E. Ivanov, E. Recknagel, E. Schlodder, B. Spellmeyer, Hyperfine Interactions 2 (1976) 232
[7] A.J.F. Boyle, D.St.P. Bunbury, C. Edwards, Proc. Phys. Soc. (London) 79 (1962) 416
[8] K. Krien, B. Klemme, R. Folle, E. Bodenstedt, Nucl. Phys. A228 (1974) 15
[9] H. Haas, to be published
[10] P.A. Flinn in "Mössbauer Isomer Shifts", G.K. Shenoy, E.E. Wagner eds., North Holland 1978, p 593
[11] F. Ambe, S. Ambe, H. Shoji, N. Saito, I. Chem. Phys. 60 (1974) 3773
[12] I.A. Avenarius, R.N. Kus'min, A.A. Opalenko, JETP Letters 14 (1971) 331
[13] G. Toussaint, G. Champier, Phys. Stat. Solidi b54 (1972) 165