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N.M.R. ORBITAL SHIFTS OF ^{125}Te IN SOLIDS, DEPENDENCE ON IONICITY AND LOCAL STRUCTURE

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Résumé. — Le déplacement orbital de la R.M.N., qui mesure la participation des états non-s aux liaisons chimiques, peut être relié directement à l'ionicté dans les composés du tellure. Dans une description moléculaire du solide négligeant les états d, ce déplacement varie de façon parabolique avec le nombre d'électrons p dans les bandes de valence. Ce nombre, qui dépend de façon simple de l'ionicté pour les liaisons du tellure, peut être modifié lors d'un changement de la symétrie locale, en particulier lors de l'amorphisation.

Abstract. — The orbital chemical shift of N.M.R., which measures the weight of non-s states in the chemical bond, can be related directly to the ionicity for tellurium compounds. In a molecular picture of the solid neglecting d states, the shift is a parabolic function of the number of p-electrons in the valence band. This number depends simply on the ionicity for tellurium bonds and can be modified by change in the local symmetry, especially by amorphization.

A number of compounds of tellurium with a large variety of chemical structures have been studied by N.M.R. It is known that the paramagnetic chemical shift (C.S.) of N.M.R. is related to the covalency of the chemical bonds. We present here a recollection of ^{125}Te N.M.R. measurements together with new results and we show that a very simple model relates chemical shifts to ionicities, enabling us to *measure* directly ionicity from chemical shift. In this simplified molecular picture of the solid the chemical shift is a function of the number of p valence electrons around tellurium atoms. This number of p-electrons depends in general on the ionicity and the local symmetry but in the case of tellurium it can be obtained, in a first approximation, from the ionicity only.

The paramagnetic C.S. of the N.M.R. frequency is due to the hyperfine field created on the nuclei by the valence shells in which the orbital momentum has been partially quenched by the external magnetic field [1]. The induced orbital momentum is also responsible for the Van Vleck paramagnetism, a closely related phenomenon [2]. A simplified expression of the paramagnetic C.S. is given by Jameson and Gutowsky [3] for molecules, in a closure approxi-

mation. Neglecting the contribution of d states, the isotropic part of the paramagnetic shift is given by

$$\sigma_p = -\frac{\mu_0}{4\pi} \frac{2}{3} \mu_B^2 \langle r^{-3} \rangle_p \cdot \frac{P_u}{\Delta} \quad (1)$$

where μ_B is the Bohr magneton, Δ is the mean excitation energy between valence and excited states and $\langle r^{-3} \rangle_p$ is the mean value of r^{-3} between outer p orbitals of the atom under consideration.

The quantity P_u is defined by these authors as the *unbalanced content* of the p shell, and involves projectors on p_x , p_y , p_z states. It is zero for an empty or closed p shell which is spherical. In a tetrahedral or cubic site, P_u takes the particularly simple form [4]:

$$P_u = N_p(1 - N_p/6) \quad (2)$$

where N_p is the total weight of tellurium p outer atomic orbitals in the valence states of the compound of interest. We show in this paper that the C.S. is mainly determined by the value of P_u , the mean excitation energy Δ changing only slightly from one compound to the other.

We now relate the quantity N_p to the ionicity. The ionicity represents the sharing of the valence electrons in the bonds between anions and cations. It is defined in the following way by Harrison [5]: If $|h_a\rangle$ and $|h_c\rangle$ are respectively the hybridized atomic orbitals

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of the anion and cation, the bond orbital $|b\rangle$ is written

$$|b\rangle = \left(\frac{1 + \alpha_p}{2}\right)^{1/2} |h_a\rangle + \left(\frac{1 - \alpha_p}{2}\right)^{1/2} |h_c\rangle$$

where α_p is the polarity, or *chemical ionicity*. (Note that α_p is slightly different from the *spectroscopic ionicity* f_i defined by Phillips [6]). It is shown in ref. [5] that :

$$(1 - f_i) = (1 - \alpha_p^2)^{3/2}. \quad (3)$$

In binary compounds for which the values of α_p or f_i have been published [7, 8], we use these values to determine the total weight of tellurium orbitals in the valence states, N_{anion} .

In tellurium compounds we neglect the contribution of tellurium 5s states to the excited states because the splitting between 5s and 5p states of tellurium is large and their hybridization is weak. (The relation (3) still holds in an hybridization different from pure sp^3). Then we write [9] :

$$N_p = N_{\text{anion}} - 2.$$

In zinc blende (N, VIII-N) compounds, such as ZnTe, CdTe, HgTe, the eight valence electrons are in bonding orbitals :

$$N_p = 2 + 4\alpha_p.$$

In IV-VI compounds with rocksalt structure such as PbTe, SnTe, six valence electrons are in the bonding p orbitals with the ionicity α_p , the four other electrons fill deeper orbitals localized around each atom [10] (s_2 , p_3 hybridization) :

$$N_p = 3(1 + \alpha_p).$$

In pure tellurium, within the same approximation we obtain $N_p \sim 4$. We use relation (2) giving P_u to calculate the isotropic part of the paramagnetic C.S. because the structure of crystalline tellurium is not very different from tetrahedral.

We have no ionicity value for the TeCl_2 molecule, but from the chemical properties and the molecule geometry, we evaluate [11] $N_p \sim 3.3$; $P_u \sim 1.6$.

In order to determine a C.S. one needs two frequencies, the N.M.R. frequency of the compound (after correction for a possible Knight shift) and the frequency of a compound with an empty valence shell, here Te^{6+} . Such a compound does not exist (TeCl_2 often quoted as a reference is the most paramagnetic among tellurium compounds and cannot be used as a reference). In the lack of an experimental reference we use a detailed theory of the C.S. in CdTe given elsewhere [12]. This calculation, together with the experimental frequency of CdTe, gives us a theoretical reference :

$$\gamma_{\text{Te}^{6+}} = 13.379 \text{ MHz/T}.$$

We show in table I the experimental and theoretical data on compounds where both chemical structure and N.M.R. results are known. The values of σ_p are obtained from the total chemical shift σ by subtracting the small value of the diamagnetic C.S. which is estimated from the number of valence electrons [12].

TABLE I

Compound	Ionicity f_i	N_p	σ_{exp} (ppm)	σ_p (ppm)	Reference
Te	0	4	- 4 810	- 4 860	[13]
CdTe	0.717	5.01	- 2 800	- 2 860	[4]
HgTe	0.65	4.84	- 2 900	- 2 960	[4]
ZnTe	0.609	4.72	- 2 916	- 2 976	our measurements
PbTe	0.65	5.12	- 2 310	- 2 370	[14]
SnTe	0.49	4.8	- 2 840	- 2 900	[15]
TeCl_2 (Te dissolved in aqua regia)	~ 3.3	~ 3.3	- 5 410	- 5 450	[16]

The values of f_i are taken from ref. [7] for zinc-blende compounds and from ref. [8] for PbTe and SnTe. σ_{exp} is obtained from experiment by deducing the theoretical reference frequency of Te^{6+} discussed in the text. The paramagnetic C.S. σ_p is obtained by correcting σ_{exp} for the (small) diamagnetic C.S.

FIG. 1. — Experimental and theoretical paramagnetic chemical shifts of ^{125}Te N.M.R. in tellurium compounds, as a function of the number of p valence electrons around tellurium : The curve represents the theoretical value calculated from our model for compounds with a tetrahedral or cubic symmetry. The square represents the theoretical value of the shift of the lower symmetry molecule TeCl_2 , using the same model. The experimental points give, for each compounds, the measured paramagnetic chemical shift ; the values of N_p in abscissa are obtained as described in the text.

Comparison between our model and experiment is shown in figure 1. The curve represents the theoretical value of σ_p given by eq. (1) for cubic compounds with $\langle r^{-3} \rangle_p = 11.9$ a.u. [17] and $\Delta = 3.55$ eV. The square represents the theoretical value of σ_p for the case of the lower symmetry molecule TeCl_2 for which the formula (2) is not correct [11]. For all these compounds we plot in the same figure the experimental points (σ_p , N_p). The agreement between such a simplified model and experiment is remarkably good. This shows that the main factor governing C.S. is the content of p orbitals around the nuclei in the solid. A few comments can be made: The mean excitation energy Δ which enters the C.S. is analogous to the mean gap between valence and conduction band E_g although it is not defined through the same kind of average over the Brillouin zone [6, 18]. The values of E_g given by Phillips [6] range from 4.98 eV for BeTe to 5.79 eV for CdTe. This agrees with the quasi constant Δ that we observe. The tellurium experimental point is above the theoretical curve, illustrating that there is no ionic contribution to the gap of homopolar compounds.

A quantity closely related to the paramagnetic C.S. of the N.M.R. is the Van Vleck paramagnetic susceptibility χ_{VV} which measures the macroscopic orbital paramagnetism [19]. Both quantities are simply related by a relation of the form

$$\chi_{\text{VV}} \sim -\frac{1}{\Omega} \left(\frac{\sigma_{\text{pA}}}{\langle r^{-3} \rangle_{\text{A}}} + \frac{\sigma_{\text{pB}}}{\langle r^{-3} \rangle_{\text{B}}} \right) \quad (4)$$

in the case of an AB compound of unit cell Ω . Here σ_{pA} and σ_{pB} are respectively the paramagnetic C.S. of atoms A and B and $\langle r^{-3} \rangle_{\text{A}}$, $\langle r^{-3} \rangle_{\text{B}}$ are the atomic averages over p orbitals in atoms A and B.

Chadi *et al.* [20] have calculated χ_{VV} of several binary compounds, in a model slightly different from ours [9, 21]. A comparison between their results and ours can be made in HgTe, CdTe, and gives good agreement [21].

From the above study we can now predict the effect of a change of N_p on orbital paramagnetism. An increase of N_p will cause an increase of the paramagnetic C.S. when $N_p < 3$; on the contrary if $N_p > 3$ it will cause a decrease of the paramagnetic C.S. hence a *diamagnetic displacement* of the N.M.R. line.

An example of an increase of σ_p with N_p is given by the variation of the C.S. of ^{199}Hg in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys, a case which is extensively studied in ref. [12]. Here the substitution of Cd atoms as second neighbours of Hg increases the p content of the bonds. (N_p changes from 0.3 to 1.2.) An other example of an increase of N_p is that due to the lowering of the local symmetry by amorphization in TlAsSe_2 [22]. Here the ^{205}Tl resonance occurs in higher field in polycrystalline samples than in the amorphous material.

On the contrary the lowering of the local symmetry will cause a decrease of the paramagnetic C.S. if we start from $N_p > 3$. This is the case of the material $\text{Te}_{81}\text{Ge}_{15}\text{As}_4$ which undergoes a diamagnetic shift of the N.M.R. of ^{125}Te between crystalline and amorphous states [23]. In this compound the C.S. value in the crystalline state indicates that $N_p \sim 4$.

The same mechanism could participate in the change of magnetic susceptibility between crystalline and amorphous states [24, 25, 26]. In polyatomic compounds one sees from eq. (4) that it is possible to observe diamagnetic or paramagnetic enhancement depending on which of $|\delta\sigma_{\text{pA}}|$ or $|\delta\sigma_{\text{pB}}|$ is greater when the symmetry is lowered. In the case of germanium [24] we think that the increase of N_p from $N_p = 3$ could partially explain the diamagnetic enhancement between the crystalline and amorphous states [18, 27] although the maximum value $N_p = 4$ accounts for only one fourth of the observed variation. This could be due to the fact that states participating principally to orbital magnetism (not too far in energy) are more strongly perturbed by amorphization than the mean bond orbital, a fact which is out of the simplified picture that we propose.

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$$\left[\left(\frac{P_u}{A} \right)_{\text{anion}} + \left(\frac{P_u}{A} \right)_{\text{cation}} \right]$$

with the equivalent quantity in ref. [20] :

$$\frac{3 \lambda^2 (1 - \alpha_p^2)}{E_a - E_b}$$

parameters involving the cation Hg, Cd are drawn from ref. [4]. Our values are 0.33 (HgTe), 0.298 (CdTe) ; Chadi's values are 0.283 (HgTe), 0.297 (CdTe).

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