NMR CHEMICAL SHIFTS IN THE SILVER HALIDES

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Measurements of the NMR chemical shifts of ^{109}Ag, ^{19}F, ^{35}Cl, ^{81}Br, and ^{127}I in the silver halides are reported in the temperature range from about 180 K to 670 K. At room temperature, the cation chemical shifts span a relatively large range of 800×10^{-6} and decrease in the order AgF > AgBr > AgCl > AgI. In AgCl and AgBr, the temperature dependences of the cation shifts are in good agreement with theoretical calculations accounting for the decrease of overlap of atomic orbitals with increasing lattice parameters. In AgI, measurements were performed on the hexagonal β-phase and a cubic polytype, both giving rise to different quadrupolar and chemical shift interactions. The shielding constant of ^{109}Ag can be rationalized using a simple tight binding description of chemical bonding. At the transition to the structurally disordered α-phase, the decreasing paramagnetism of the silver chemical shift is consistent with a distorted tetrahedral coordination of the cations in α-AgI.

1. Introduction

The NMR chemical shifts of copper nuclei in the cuprous halides and in Cu(I) chalcogen compounds have recently been shown to be dominated by contributions from the 3d-states to chemical bonding [1, 2]. Silver ions with 4d valence electrons are however better candidates for a systematic investigation of such d-electron contributions to the magnetic shielding. Nuclei of ^{107}Ag and ^{109}Ag possess nuclear spin $I = 1/2$ and are therefore insensitive to quadrupolar interactions. Thus, in contrast to cuprous ions, the determination of the chemical shifts of Ag$^+$ ions is not limited to crystals with cubic or nearly cubic structures and the shifts of Ag$^+$ ions can be studied in a wide variety of compounds. Due to the complex crystal chemistry of Ag$^+$, a whole range of different local environ-

ments is available, varying from twofold to eightfold coordination. In this paper, we present data on cation (^{109}Ag) and anion (^{19}F, ^{35}Cl, ^{81}Br, ^{127}I) chemical shifts in the silver halides together with their temperature dependences. This is a particularly interesting class of compounds with AgF, AgCl and AgBr, though considerably less ionic than the corresponding alkali halides [3, 4], crystallizing in the ionic NaCl structure. In contrast, the low temperature phase of AgI possesses a covalent tetrahedral structure. The transition to the cation disordered high temperature phase deserves special attention because little is known about chemical bonding in such structurally disordered systems. In addition, data are reported for the halogen shifts in LiBr, LiI, NaBr and NaI, which were remeasured for comparison with the silver halides.

2. Experimental

AgF (Merck, p.a.) was recrystallized in an aqueous solution of acetone and carefully dried. The products obtained were still brown in colour, indicating contamination with metallic Ag, Ag_2O and probably with AgF_2. The other Ag halides were prepared by slow precipitation from dilute solutions of $AgNO_3$ (Merck, p.a.) and the corresponding acid (Merck, suprapur). The dried products were melted and investigated in polycrystalline form. In the case of AgI, experiments were also carried out on the dry precipitate. LiBr, LiI, NaBr and NaI (Merck) are extremely hygroscopic substances. In order to obtain them free of water of crystallization, oxide and hydroxide, we carefully dried and repeatedly treated these compounds with a mixture of H_2 and the appropriate hydrogen halide gas at high temperatures.

As reference for the silver nuclei an aqueous solution 9.08 molal in $AgNO_3$ and 0.24 molal in $Fe(NO_3)_3$ was used. Except for the fluorine shift in AgF, which was referred to solid NaF, 0.10 m aqueous solutions of the corresponding sodium halide were taken as references for the anion shifts. Spectra of the ^{109}Ag nuclei were recorded at

4.193 MHz on a modified Bruker BK-322s Fourier spectrometer equipped with a Nicolet (BNC-12) computer. The low sensitivity and the relatively long spin-lattice relaxation times of ^{109}Ag necessitated values of data accumulation of the order of 10000 with a pulse delay varying between 2 and 10 s. Data for the halogen nuclei were taken with a crossed coil wide-line spectrometer at fixed frequencies of 16 MHz (^{19}F, ^{81}Br), 12.1 MHz (^{127}I), 8 MHz (^{127}I), 7.2 MHz (^{81}Br) and 4 MHz (^{35}Cl). The temperature of the samples was varied by vacuum-isolated flow systems using gaseous nitrogen. Such gas flow systems possess the advantage of producing no additional magnetic fields at the position of the samples.

3. Results and discussion

Data on anion and cation chemical shifts $\delta = (v_{ref} - v)v_{ref}^{-1} = (B - B_{ref})B_{ref}^{-1}$ of the four silver halides are given in table 1. At room temperature chemical shifts of ^{109}Ag decrease in the order AgF > AgBr > AgCl > AgI. This progression does not agree with that observed for the cation shifts in the Rb and Cs halides [7, 13, 14], which decrease

Table 1
The results of NMR measurements on the silver and the halogen nuclei in the solid silver halides. δ is the chemical shift for the absorptions of ^{109}Ag, ^{19}F, ^{35}Cl, ^{81}Br and ^{127}I measured at 300 K. The silver shifts are referenced to AgBr, to show the difference between AgCl and AgBr. The other shift references used are described in section 2. For the evaluation of the shifts relative to the free atoms σ^*, data from [11, 12, 5] were used for ^{109}Ag, ^{35}Cl and ^{19}F, respectively. δ' is the rate of change with temperature of the chemical shift in the quoted temperature range. Supplementary data are presented for the halogen nuclei in the bromides and iodides of lithium and sodium

Crystal	Nucleus	$\delta \times 10^6$		$\sigma^* \times 10^6$	$\delta' = (d\delta/dT) \times 10^9$	Temperature range (K)
		this work	previous work			
AgF	^{109}Ag	475 ± 5		-840	-18	300–420
	^{19}F	90 ± 20	83[5]	33/26[5]	$|\delta'| < 15$	300–430
AgCl	^{109}Ag	-3.5 ± 0.5		-1315	-11	300–420
	^{35}Cl	10 ± 3	20[6]	$-160/-150[6]$	7	300–670
AgBr	^{109}Ag	0		-1310	-8	200–420
	^{81}Br	-210 ± 3	$-190[6]$		17	300–540
AgI	^{109}Ag	-330 ± 3		-1640	33	300–420
	^{127}I	80 ± 10			-60	180–350
LiBr	^{81}Br	95 ± 10	$-109[7]/ -93[8]$			
NaBr	^{81}Br	20 ± 5	6[7]/ 24[8]			
LiI	^{127}I	-340 ± 5	$-330[9]/-245[10]$			
NaI	^{127}I	-200 ± 10	$-213[7]/-200[8]$			

with increasing atomic number of the halogen, nor is it in line with the shifts of ^{23}Na in the sodium halides [15]. Likewise, there is no agreement with the behaviour encountered in a number of typical II–IV and III–V semiconductors [16–19] and in copper(I) chalcogen compounds [2], in which the cation shifts increase with increasing atomic number of the more electronegative partner. The unusual behaviour in the silver halides has its only parallel in the shift of ^{63}Cu in the cuprous halides [1], which possess the tetrahedrally coordinated zincblende structure. The temperature dependences of δ, which are also presented in table 1, indicate that at low temperatures the progression of the silver shift in the chloride and in the bromide is reversed. Cation shifts then decrease with increasing atomic number of the halogen atom, as do the shifts in the heavy alkali halides [7, 13, 14]. In contrast to the Ag halides, such an inversion at low temperatures is not observed for the cation shifts in the Cu(I) halides [1]. As a further distinction between 3d cuprous and 4d silver halides, the ranges spanned by the cation shifts differ considerably. In the Cu(I) halides the variations are very small, $\approx 60 \times 10^{-6}$, compared to a shift difference of 800×10^{-6}, between AgF and AgI.

In addition to the room temperature chemical shifts we also determined the temperature dependences of the anion and cation shifts. These are also presented in table 1. For the cation shifts in AgF, AgCl and AgBr a negative temperature dependence is observed, whereas for the fluorine, chlorine and bromine shifts $(d\delta/dT) > 0$ was found. AgI exhibits quite the opposite behaviour with a positive temperature dependence of δ for the silver resonance and a negative one for the anion absorption. Apart from the cuprous halides for which $(d\delta(Cu^+)/dT) > 0$ and $(d\delta(X^-)/dT) < 0$, there exist no other measurements on anion *and* cation chemical shifts in simple crystals to which these results can be compared. In the alkali halides only the anion shifts have been investigated which were invariably found to possess negative temperature dependences [10]. While AgCl and AgBr behave differently from the alkali halides as well as from the cuprous halides, in AgI, $d\delta/dT$ is in accordance with the behaviour encountered in the cuprous halides [1]. In conclusion, the above phenomenological comparison indicates that a

meaningful discussion of chemical shifts in the silver halides should be possible, in which the transition from octahedral to tetrahedral structure is taken into account. The discussion will therefore be divided accordingly.

NMR chemical shift data in simple crystals, such as of type MX, usually have been analysed by two different interpretation schemes: using the framework of the Kondo–Yamashita overlapping ion theory [20] and using the localized LCAO MO approach of Pople, Karplus and Das [21, 22]. Inherent to both theories is the use of an average energy approximation. In this approximation the paramagnetic contribution to magnetic shielding of a nucleus is given by an expression of the form

$$\sigma^{(p)} = -\frac{\mu_0}{4\pi} 16\mu_B^2 \frac{\langle r^{-3} \rangle}{\Delta E} f, \tag{1}$$

where μ_B is the Bohr magneton, $\langle r^{-3} \rangle$ is an appropriate average over the valence electrons and ΔE is an average excitation energy between occupied electronic ground states and unoccupied excited states. The quantity f depends solely on details of the chemical bonding in which the atoms under consideration are involved.

3.1. AgF, AgCl, AgBr

For ionic crystals, Kondo and Yamashita (KY) [20] derived an expression for f containing overlap integrals between atomic orbitals of neighbouring ions. The KY theory, which in its extended form also includes contributions to $\sigma^{(p)}$ from π-bonding and from next nearest neighbours [23], has been applied to interpretation of chemical shifts and of their pressure and temperature dependences in the alkali and alkaline earth halides. Nevertheless, even in this class of highly ionic compounds evidence has been presented for the necessity to account for covalency contributions to magnetic shielding, see e.g. refs. [5, 15].

Within the framework of the KY formalism, Bouznik and Avkhutsky et al. [5, 24] have derived an expression for halogen chemical shifts in NaCl-type crystals with metal ions having a rare gas configuration of d-electrons. Unfortunately, a quantitative discussion of chemical shifts in the silver halides along these lines is hampered by the fact

that there are not calculations available of overlap integrals between silver and halogen ions, except for AgF [5, 24]. However, these authors have shown that $\sigma^{(p)}$ is dominated by the contribution σ^{NNN} from next nearest neighbours involving halogen–halogen overlap integrals only. In general, this theory requires that the halogen resonances in AgX are always shifted less paramagnetically than those in isostructural crystals with a similar lattice parameter, containing a metal ion of comparable size with a closed shell of p-valence electrons. This is however not observed experimentally. While AgF conforms to these expectations [5, 24], the halogen shifts in AgCl and AgBr become increasingly paramagnetic, i.e. more negative relative to *all* corresponding resonances in the alkali halides. Fig. 1 shows this for the shifts in AgX and in the corresponding lithium, sodium and potassium halides. The change of the halogen shifts in the silver halides relative to the corresponding shifts in the alkali compounds is quite distinct. While $\delta(Ag^{19}F)$ is larger than that of all the anion shifts in the alkali fluorides, $\delta(Ag^{81}Br)$ is smaller than all the anion shifts in the alkali bromides. This observation cannot be accounted for by the above mentioned theory and, at least for AgBr, is calling for the inclusion of covalency and/or polarization effects into (1). In a first attempt, ΔE might be chosen smaller than the values appropriate to the free ions. However, reductions of 20 to 40%, required to reproduce experimental findings, seem to be quite large for a theory of the KY type, which

essentially is a free ion theory. As is clearly visible from fig. 1, the iodine resonance in AgI does not follow the trend observed for the NaCl-type silver halides. We will take this as further reason for the separate discussion of AgI, which will be given below.

The temperature dependences of the halogen shifts in AgCl and AgBr are shown in fig. 2. The most salient feature of these data is the curvature exhibited by the bromine resonance shift at temperatures above 520 K. To our knowledge this is the first case in which such a deviation from a linear temperature dependence is observed in simple crystals of the MX type. In all previous work, chemical shifts were found to depend linearly on temperature [1, 10, 26], as is also observed for the other anion and the cation shifts investigated in this study.

According to Ngai's theory of the temperature dependence of chemical shifts [10], $d\sigma^{(p)}/dT$ is given by the difference of two contributions arising from the thermal vibrations and the thermal expansion of the lattice. As a consequence of the above mentioned lack of overlap data, only NNN contributions can be evaluated which are expected to dominate $d\sigma/dT$. Using the results of Hafemeister and Flygare [27] for halogen–halogen overlaps and choosing appropriate data for the various parameters, it turns out that the vibrational and the
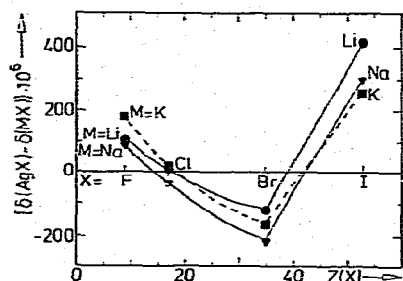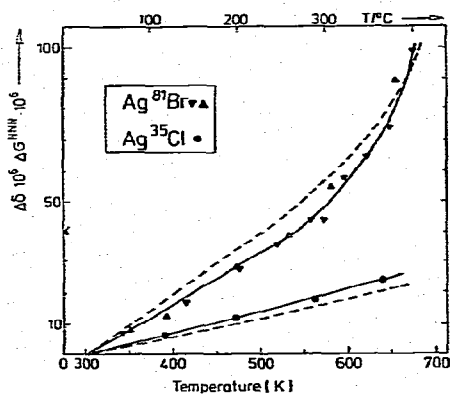

Fig. 1. The difference between anion shifts in the silver halides and in the corresponding halides of lithium, sodium and potassium as a function of the halogen atomic number Z. Data for the halogen shifts not determined in this work, table 1, were taken from refs. [7, 25]. Lines are drawn only to serve as guides.

Fig. 2. The halogen chemical shifts in AgCl ($\bullet$, 4 MHz) and AgBr ($\blacktriangle$, 7.2 MHz/$\blacktriangledown$, 16 MHz) as a function of temperature, $\Delta\delta = \delta(T) - \delta(300$ K); –––– theoretical calculation of $\Delta\sigma^{NNN} = \sigma^{NNN}(T) - \sigma^{NNN}(300$ K) according to (2), see text.

dilatational contribution nearly cancel each other. The values of $d\sigma^{NNN}/dT$ thus determined are too small and of the wrong sign.

As has already been pointed out by Ngai [10], the Debye model used for the description of the vibrational properties of the lattice, is a poor approximation for the calculation of NNN contributions. Because of this and since $(d\delta/dT) > 0$ indicates that the dilatation of the lattice dominates the temperature dependence of δ, σ^{NNN} was calculated from [23]

$$\sigma^{NNN} = -\frac{\mu_0}{4\pi} 64\mu_B^2 \frac{\langle r^{-3}\rangle}{\Delta E}$$
$$\times [|S^{\sigma\sigma}|^2 + |S^{\pi\pi}|^2 + |S^{\sigma\pi}|^2 - 2S^{\sigma\sigma}S^{\pi\pi}], \qquad (2)$$

completely neglecting the vibrational contribution. Here $S^{\alpha\beta}$ are halogen–halogen overlap integrals between α and β type orbitals, depending on the interatomic distances. Using Lawn's results for the temperature dependence of the lattice parameters [28] and taking the overlap data, ΔE and $\langle r^{-3}\rangle$ from [23, 27], $(\sigma^{NNN}(T) - \sigma^{NNN}(300\,K))$ can be compared to the experimentally determined difference $(\delta(T) - \delta(300\,K))$. As can be seen in fig. 2, there is good agreement between both quantities for the bromine as well as for the chlorine shift. Especially the agreement in the high temperature region of $\Delta\delta(^{81}Br)$ gives strong support to the validity of the present approach, according to which the curvature in AgBr results from an anomalous increase in the lattice constant. This high temperature anomaly is much more pronounced in AgBr than in AgCl [28]. Accordingly, in the temperature range investigated the halogen shift in AgCl increases linearly. The remaining small discrepancies may be ascribed to the neglect of nearest neighbour and/or covalency contributions to $d\sigma^{(p)}/dT$. For AgF no data on the temperature dependence of the lattice parameter seem to have been reported.

Cation chemical shifts usually are dominated by nearest neighbour contributions involving anion–cation overlap integrals. Due to the lack of these data only the following comments will be made on the silver chemical shifts. At 300 K, the striking feature of these shifts presented in table 1, is the small difference between the ^{109}Ag shift in AgCl and AgBr, and the fact that $\delta(^{109}AgCl) < \delta(^{109}AgBr)$,

which is at variance with expectation. In the KY theory such irregularities may be attributed to changes in the relative magnitude of the contributions from nearest and next nearest neighbours. According to Ngai's theory [10], the negative temperature dependences of the shifts show that $\delta(T)$ is determined by vibrational contributions. Owing to the slightly different temperature dependences, the silver shifts in AgCl and AgBr are expected to be identical at a temperature between 70 K and 120 K. Below this temperature the shifts decrease in the order AgF > AgCl > AgBr > AgI. This reversal of order clearly demonstrates the importance of the vibrational contribution to the cation chemical shift.

3.2. AgI

In the Phillips–van Vechten theory of chemical bonding in crystals [3, 4], AgI is one of the border line cases with a ionicity $f_i = 0.770$ very near to the empirically determined value of $f_i^* = 0.785$ for which the transition occurs from ionic octahedral to covalent tetrahedral structures. The stable low temperature form, β-AgI, possesses the hexagonal wurtzite structure. However, in polycrystalline material the actual structure was often found to depend on sample preparation and the thermal and mechanical history of the substance, though the existence of a pure phase of cubic γ-AgI with zinc-blende structure has been questioned [29]. In more recent X-ray [30] and NMR [31] work on single crystalline AgI, the existence of extended poly-typism was demonstrated.

In our experiments we also encountered phenomena resulting from this polytypism. In the precipitated powder material an almost symmetrical absorption signal of ^{127}I was observed. At 300 K a linewidth of $\Delta B = 0.19$ mT was determined ($\nu_L = 8$ MHz). This value as well as the observed increase of ΔB with rising temperature is in good agreement with the data reported by Herzog and Richtering [32] for a similarly prepared substance. The temperature dependence of the linewidth was attributed by these authors to broadening effects caused by quadrupolar interactions. Since the shape of the signal is nearly symmetrical, a dynamic quadrupolar interaction dominates giving rise to a

temperature dependent lifetime broadening of the absorption. However, the existence of an additional static contribution cannot be ruled out. For this interaction, which is characterized by the nuclear quadrupole coupling constant χ of ^{127}I, only an upper limit can be deduced from the observed powder spectra. At room temperature $\chi < 0.7$ MHz is derived. Therefore, the precipitated powder material is either of the cubic γ-structure with $\chi = 0$ or of a nearly cubic polytype with a coupling constant much smaller than those given in ref. [31] for single crystals. After heating the sample to 480 K or melting it (870 K), at room temperature only a very broad and weak absorption could be detected. This behaviour can easily be understood since in β-AgI, which is known to be produced by the heat treatment [33], quadrupolar interactions are so large, $\chi(^{127}$I$) \approx 8$ MHz [31], that absorption signals are extremely broadened in polycrystalline material.

Nuclei of ^{109}Ag possess spin $I = 1/2$ and are therefore insensitive to quadrupolar interactions. As shown in fig. 3, silver chemical shifts measured at room temperature depend on the thermal treatment of the compound. In comparison with the absorptions in the two other samples, in the substance heated to 480 K the amplitude of the signal is reduced and its width is increased by about a factor of two. This observation may be caused by an unresolved superposition of absorptions from silver nuclei experiencing different chemical shifts. It
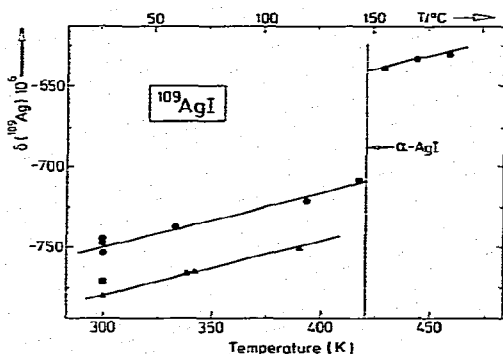

Fig. 3. The NMR chemical shift of ^{109}Ag in AgI as a function of temperature for the precipitate ("cubic" AgI, ▲), for the melted substance (β- and α-AgI, ●), and for a sample heated to 480 K (■). The reference is an aqueous solution of 9.08 m AgNO$_3$ and 0.24 m Fe(NO$_3$)$_3$.

therefore may be understood as a result of the well known "memory effect" [33] and provides further evidence for the complex phase behaviour of low temperature AgI. A further clue to the nature of the "cubic" AgI modification can be obtained from the temperature dependence of the linewidth Δv of the ^{109}Ag absorption. In contrast to AgCl and AgBr, which show marked motional narrowing phenomena, in the two low temperature modifications of AgI the linewidths were found to be almost identical, $\Delta v \approx 130$ Hz, and not to depend on temperature. In view of the fact that the mean jump frequencies of the silver ions in these phases are of about the same magnitude as those in AgCl and AgBr (for a review see ref. [34]) and because the dipolar spin–lattice relaxation time T_1 of the ^{109}Ag nuclei is expected to be long, $T_1 > 10$ s, the absence of a detectable narrowing of Δv with temperature is ascribed to inhomogeneous broadening effects caused by anisotropic chemical shift interactions. By this the possibility is excluded that the "cubic" modification is the pure γ-AgI phase with the cubic zincblende structure. Hence, one is led to the conclusion that the untreated precipitate either is a pure phase of a polytype of high cubicity or a mixture of such phases. From the absorption signal lineshape a value of 50×10^{-6} can be deduced for an upper limit of the chemical shift anisotropy in low temperature AgI. The data presented in table 1 for ^{109}Ag apply to β-AgI, those given for ^{127}I strictly apply to "cubic" AgI.

In predominantly covalent crystals with tetrahedral structures, simple LCAO MO descriptions of chemical bonding in a number of cases [1, 2, 35] have been shown to account successfully for experimental findings. In crystals with cations having a filled d-valence shell and anions with a complete shell of p-electrons, MO's can be constructed from tetrahedral sd^3 and sp^3 hybrid orbitals centered on cations and anions with mixing coefficients c and a, respectively. Using this simple tight binding description of chemical bonding, in the localized approach of Jameson and Gutowsky [36],

$$f_M^{MO} = c^2(3 - c^2)C, \tag{3}$$

$$f_X^{MO} = a^2(1 - a^2)C', \tag{4}$$

is deduced [1]. C and C' are orbital reduction factors.

Neglecting small diamagnetic contributions to the magnetic shielding, $\sigma^{(p)}(Ag^+)$ as obtained from (1) and (3) can be compared to the silver shift $\sigma^*(Ag^+)$ relative to the free atom (cf. table 1). We used a value of 8.3 au for $\langle r^{-3} \rangle$ estimated from the corresponding value for the free atom [37] and a d-admixture $c^2 = 0.34$ deduced from photoelectron spectra of the uppermost valence band in β-AgI [38]. As value of ΔE we took the average energy gap $E_g = 6.49$ eV from the Phillips–van Vechten theory of chemical bonding [3, 4]. With these data a reduction factor $C = (0.24 \pm 0.02)$ is deduced; which compares favourably with $C = (0.19 \pm 0.01)$ found appropriate in a similar treatment of cation shifts in the cuprous halides [2]. The stated errors only account for the uncertainties introduced by the atomic beam measurements needed to establish the atomic σ^* scales [11, 39].

As shown in fig. 3, the silver absorption in β-AgI is shifted less paramagnetically by 30×10^{-6} relative to the position in the "cubic" substance. The rate of change with temperature of $\delta(Ag^+)$ is practically identical in both modifications. The magnitude of the slopes is similar to the value obtained in the low temperature phase of CuI, $(d\delta(Cu^+)/dT) = 28 \times 10^{-8}$ K^{-1}. In the cuprous halides, the positive temperature dependences of the cation shifts and the negative ones of the anion shifts were accounted for by the change of vibrational overlap with temperature. This interpretation is expected to be valid in the case of AgI too, though the present approach differs slightly from that taken in ref. [1] where the data for the p- and d-admixtures were obtained from Harrison's bond orbital model [40]. In the present work and in ref. [2] use is made of experimental data for c^2.

The observation that the silver shift is less paramagnetic in β-AgI, the crystal with lower symmetry around the cations, is in perfect agreement with results obtained for the copper shifts in the cuprous halides, e.g. at the transitions from the cubic zincblende to the hexagonal wurtzite phases and to the cation disordered cubic high temperature phases [1]. Hence, it appears that chemical shifts of these d^{10} ions in tetrahedral structures sensitively differentiate between structures with different anion arrangements, as for example fcc and hcp.

At $T_c = 420$ K, AgI undergoes a transition to a high temperature phase with an unusually high ionic conductivity [34]. According to Strock [41], who first determined the structure of α-AgI, the anions form a body centered cubic lattice with the very mobile Ag$^+$ ions distributed over sites with octahedral, tetrahedral and trigonal bipyramidal coordination. The silver chemical shift increases by $\Delta\delta(Ag^+) = 65 \times 10^{-6}$ at the phase transition from β- to α-AgI, fig. 3. Though it is difficult to assess, this change appears to be too small to be caused by a change in the type of coordination, i.e. from tetrahedral to octahedral. The only estimate presently available of such a change is that given by $\delta(^{109}AgBr) - \delta(^{109}AgI) = 330 \times 10^{-6}$. The increase of $\delta(Ag^+)$ observed at T_c corresponds to a change in magnetic shielding of only 4%. This implies that chemical bonding undergoes only a small change at the transition to the disordered α-phase. A similar deduction was recently drawn from photoelectron spectroscopy [42]. According to the above discussion the decrease of the paramagnetism of the cation shift at T_c is indicative of a lowering of local symmetry around the silver ions. It is tempting therefore, to correlate $\Delta\delta(Ag^+)$ with the fact that the tetrahedral positions in α-AgI possess a strongly distorted coordination. The observed increase of $\delta(Ag^+)$ then mainly reflects the transition from perfect to distorted tetrahedral coordination. This conclusion is also fully consistent with recent results from X-ray [43], neutron scattering [44], and EXAFS [45] studies.

4. Conclusions

NMR chemical shifts of the anions and cations in the silver halides are discussed in the framework of two interpretation schemes allowing for the different types of chemical bonding existing in this class of compounds. The overlapping ion theory of Kondo and Yamashita (KY) is used for the crystals with the ionic NaCl type structure. In contrast, chemical shifts in the covalent tetrahedral AgI are discussed, and accounted for by an LCAO MO approximation to the local paramagnetic shielding.

It is shown from a comparison with the corresponding alkali halides that the KY theory for compounds containing a d^{10} cation fails to predict

the observed increase of the paramagnetism of the anion shift in crystals with increasing covalency. Despite these discrepancies, the temperature dependences of the anion shifts in AgCl and AgBr are in good agreement with those calculated from the KY theory taking into account halogen–halogen overlaps only. In particular, the reproduction of the curvature in the temperature dependence of the bromine shift confirms the underlying assumption that the increase of the anion shifts with temperature is due to a decrease of overlap caused by the thermal expansion of the lattice.

In AgI, two low temperature modifications were investigated the occurrence of which depends on the sample preparation. Besides the stable hexagonal β-phase, an almost cubic polytype was identified. These modifications give rise to different quadrupolar and chemical shift interactions, as monitored by the quadrupole-sensitive resonance of ^{127}I and the chemical shift of the the ^{109}Ag absorption. The magnitude of the silver chemical shift can be rationalized in the framework of the simple LCAO MO approach which was also appropriate in the case of the cuprous halides. Furthermore, the silver shifts in these two tetrahedral modifications confirm the observation already made in the Cu(I) halides that a decrease of symmetry around the d^{10} ions results in a decrease of the paramagnetism of the cation chemical shift.

At the transition to the structurally disordered α-phase, the paramagnetism of the silver shift decreases by 65×10^{-6}. This corresponds to a change in the magnetic shielding of only 4 %, implying that chemical bonding changes only slightly at the phase transition. The reduction of local symmetry, indicated by the increase of the shift, is in accordance with the model that the Ag^+ ions possess a distorted tetrahedral coordination in α-AgI.

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