Vinogradov Institute of Geochemistry, Academy of Sciences of the USSR, Siberian Branch, Irkutsk[1])

Atomic Hydrogen Centres in LiF–H⁻ and LiF–H⁻, Mg^{2+} Crystals

By

A. V. Egranov, V. V. Otroshok, and B. P. Chernyago

Atomic hydrogen centres in LiF–H⁻ and LiF–H⁻, Mg^{2+} are studied by optical and ESR techniques. X-irradiation of these crystals at 80 K leads to the formation of the H_i^0-centres which are thermally stable up to 110 K. After thermal annealing of the H_i^0-centres in LiF–H⁻, Mg^{2+} crystals a new atomic hydrogen centre is observed which is interpreted as an interstitial hydrogen atom stabilized by a complex of the Mg^{2+} ion and a positive ion vacancy ($H_i^0(Mg)$-centre). Thermal decay of the $H_i^0(Mg)$-centres occurs at 430 K and leads to the formation of a hydrogen atom in the cation vacancy ($H_{s,c}^0(Mg)$-centre).

В кристаллах LiF–H⁻ и LiF–H⁻, Mg^{2+}, с помощью оптических методов и ЭПР, изучены атомарные водородные центры. Рентгеновское облучение этих кристаллов при 80 K приводит к образованию H_i^0-центров, термически устойчивых до 110 K. После отжига H_i^0-центров в крисраллах LiF–H⁻, Mg^{2+} образуются новые центры атомарного водорода, которые были приписаны междоузельным атомам водорода, стабилизированным около примесно-вакансионного диполя — Mg^{2+}-катионная вакансия ($H_i^0(Mg)$-центры). Термическое разрушение последних происходит при 430 K и связано с перемещением атома водорода в катионную вакансию с образованием $H_{s,c}^0$-центров.

1. Introduction

Atomic hydrogen can be trapped at interstitial or substitutional cation and anion sites in alkali halides. Since the hydrogen atom is paramagnetic it could be studied with electron spin resonance (ESR) and electron nuclear double resonance (ENDOR).

H_i^0-centres were observed in almost all alkali halides [11]. The ESR spectrum of these centres shows two proton hyperfine (HF) lines separated by approximately the HF constant of the free hydrogen atom. In many alkali halides, apart from fluorides, each line has an additional structure due to the superhyperfine (SHF) interaction with the four nearest halogen neighbour nuclei, but not with the four nearest alkali nuclei which possess equivalent positions with respect to the hydrogen atom.

In spite of intensive search no interstitial hydrogen atom centres have been observed in LiF–OH⁻ crystals upon UV- or γ-irradiation at low temperature. A paramagnetic hydrogen atom was observed in γ-irradiated LiF containing OH⁻ ions [2]. However, the ESR spectra did not show a large ¹⁹F SHF interaction nor a ⁷Li SHF interaction as should be expected when extrapolating from the results of KF, RbF, and NaF [2]. It seems that the interstitial site is already too small to accomodate a hydrogen atom in LiF [3]. On the other hand, Kamikawa [4], using an unusual treatment of LiF–OH⁻ crystas, has detected the ESR

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[1]) Favorskii str. 1a, P.O. 701, SU-664 033 Irkutsk, USSR.

spectrum of a hydrogen atom centre with resolved SHF structure which was attributed to the H_i^0-centre.

It was shown by Hoentzsch et al. [5] and Studzinski et al. [6], using ESR and ENDOR methods, that the H_i^0-centres are converted to $H_{s,c}^0$-centres on warming above 130 K in the KCl–SH$^-$ and RbCl–SH$^-$ crystals, additionally doped with divalent cations. To produce $H_{s,c}^0$-centres one lets H_i^0-centres diffuse into cation vacancies provided by the doping with divalent cations like Ca^{2+}, Sr^{2+} [5, 6].

This paper reports the results of electron spin resonance measurements of the hydrogen atom centres in LiF–H$^-$ and LiF–H$^-$, Mg^{2+}.

2. Experimental Technique

The LiF–H$^-$ and LiF–H$^-$, Mg^{2+} crystals were grown in hydrogen atmosphere ($\approx 4 \times 10^5$ Pa) from the melt containing LiH and MgF_2 (0.05 to 0.5 wt% in the melt) by the Stockbarger method. Specimens of ^{6}LiF–H$^-$, Mg^{2+} were obtained in a similar fashion. The starting material was polycrystalline LiF enriched to 90% ^{6}Li. The crystals used in this work contained 10^{17} to 10^{20} cm^{-3} U-centres; no trace to OH$^-$-ions could be found by infrared spectroscopy. Absorption measurements were performed with the spectrophotometer "Specord UV/VIS".

The ESR experiments were done on an X-band spectrometer (RE-1306) in connection with a cryostat suitable for temperatures down to 80 K. The microwave frequency was measured by a frequency counter with an accuracy of 1×10^{-6}. The magnetic field strength was controlled by a nuclear magnetic resonance Gauss-meter outside the cavity and a DPPH sample inside.

The crystals were X-rayed using a tungsten tube operating at 50 kV and 50 mA at 80 and 295 K.

3. Experimental Results

3.1 H_i^0-centre

X-irradiation of LiF–H$^-$ crystals at 80 K leads to creation of atomic hydrogen centres which have an ESR spectrum as shown in Fig. 1. The observed two proton HF lines are
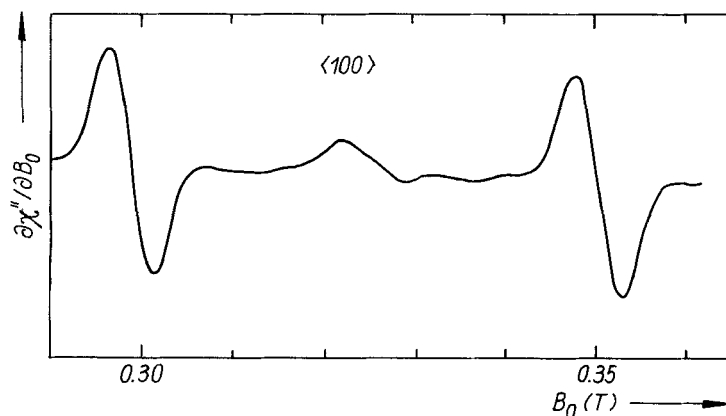

Fig. 1. ESR spectrum of H_i^0-centres in LiF–H$^-$ and LiF–H$^-$, Mg^{2+} after X-irradiation at 80 K for $B_0 \parallel \langle 100 \rangle$, $T = 80$ K, $\nu = 9185$ MHz

Table 1

Proton HF constants a_p, A_p, g-factor, and linewidth (peak to peak) ΔB of hydrogen atom centres in LiF

centre	g	A_p (MHz)	a_p (10^{-4} T)	ΔB (10^{-4} T)	T (K)
H_i^0	2.0032 $\mp$ 0.0004	1440 $\mp$ 4	518 $\mp$ 2	45	80
H_i^0(Mg)	2.0020 $\mp$ 0.0003	1405 $\mp$ 1	504 $\mp$ 2		80, 295
$H_{s,c}^0$(Mg)	2.0018 $\mp$ 0.0002	1423 $\mp$ 1	511 $\mp$ 1	35	295
$H_{s,c}^0$	2.0022 $\mp$ 0.0005		517 $\mp$ 2	47	295 [12]

inhomogeneously broadened by unresolved SHF interactions. The linewidth ΔB (peak to peak) is 45×10^{-4} T. Values of the parameters of the ESR spectrum for this centre are given in Table 1. The centres are thermally stable up to 110 K. In spite of the strong difference of the SHF constants compared to those of other fluoride host crystals, this ESR spectrum was previously [7] explained as due to the H_i^0-centre, because upon above 110 K these centres vanish and the H_2^--centres appear, which was interpreted as a result of the reaction [8]

$$H_i^0 + H_a^- \rightarrow H_2^- . \qquad (1)$$
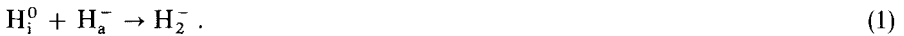
On the basis of a simple estimate of the transition energy it was qualitatively established that the optical transition of the H_i^0-centres is a charge transfer transition, where an electron is excited from the uppermost halogen p-band to the H_i^0 atom forming H_i^- and leaving a hole in the valence band. Because of the T_d symmetry optical dipole transitions are possible for two different linear combinations of halogen p-orbitals with $T_{2\sigma}$ and $T_{2\pi}$ symmetry, where σ is directed along the line joining the halogen ions and the H_i^0 atom. In the iodides and bromides the two corresponding absorption bands are resolved and, furthermore, the σ-polarized band has a lower transition energy and a higher intensity than the π polarized absorption band. In the chlorides only one asymmetrical absorption band was found [9].

In LiF for the H_i^0-centres we observed two absorption bands centred at 2.4 and 3.5 eV with energies considerably lower than expected on the basis of a simple estimate of the transition energy [10]. The energy difference between these bands is 1.1 eV, only slightly higher than the splittings between the $T_{2\sigma}$ and $T_{2\pi}$ states for the H_i^0-centres in alkali halides. If the observed optical absorption transitions of the H_i^0-centre in LiF are considered as related to the $T_{2\sigma}$ and $T_{2\pi}$ states, than $T_{2\pi}$ related absorption has, in contrast to other alkali halides, a lower energy transition than $T_{2\sigma}$, since the absorption band at 2.4 eV is smaller in intensity [7, 8].

3.2 H_i^0 (Mg)-centre

In LiF–H$^-$ crystals containing additional doping with Mg, thermal decay of the H_i^0-centres does not lead to effective formation of H_2^--centres, but to creation of the new hydrogen atom centres.

Fig. 2 shows a doublet ESR spectrum observed in LiF–H$^-$, Mg^{2+} crystals after X-irradiation at 80 K and subsequent heating to room temperature. Each of the lines of the spectrum measured with $\boldsymbol{B}_0 \parallel \langle 100 \rangle$ exhibits a well-resolved structure consisting of five equally spaced $((30 \mp 1) \times 10^{-4}$ T) lines with relative intensities following approximately the sequence $1:4:6:4:1$. This indicates a SHF interaction with four equivalent fluorines.
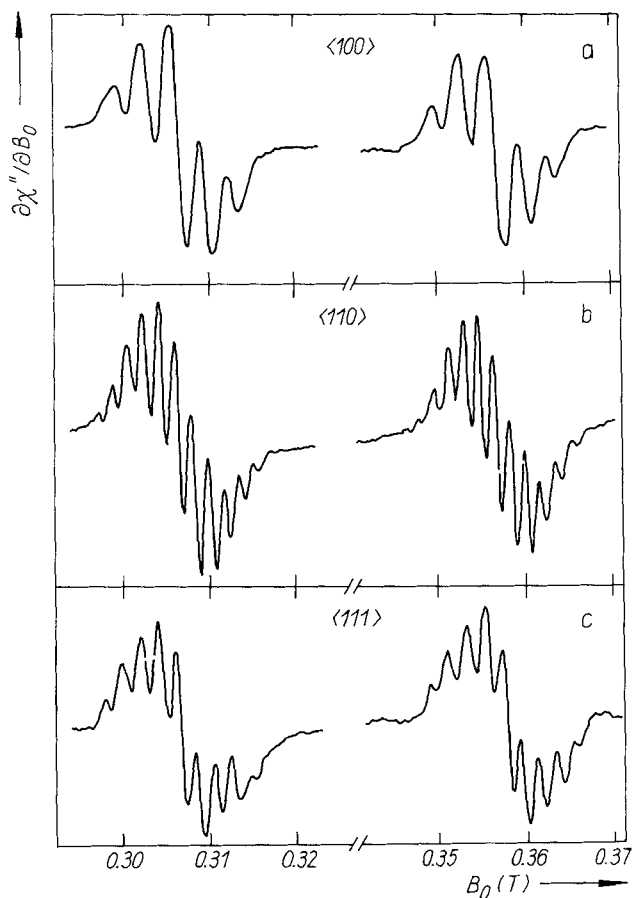
Fig. 2. ESR spectra of H_i^0(Mg)-centres in LiF–H$^-$, Mg^{2+} after X-irradiation at 80 K and subsequent heating to room temperature. a) $B_0 \parallel \langle 100 \rangle$, b) $B_0 \parallel \langle 110 \rangle$, c) $B_0 \parallel \langle 111 \rangle$; $T = 295$ K, $v = 9368$ MHz

Observation of the same SHF structure in crystals enriched in ^{6}Li confirms that the ESR spectrum resolves only the SHF interaction with four fluorine nuclei. When the LiF–H$^-$, Mg^{2+} samples are X-irradiated at room temperature the same ESR signal is observed but with smaller intensity.

The similar ESR spectrum was first observed in LiF–OH$^-$ crystals by Kamikawa [4] who assigned the ESR signal to the H_i^0-centre. However, we found that these hydrogen atom centres are created in Mg-doped LiF–H$^-$ crystals but not in LiF–H$^-$ samples. In LiF the Mg^{2+}-ions are a background impurity, usually present in all crystals with a concentration of the order of 10^{-3} wt%. Therefore, the same centres can be produced in LiF–OH$^-$ (as observed by Kamikawa) but its concentration is very low. It is therefore possible to assume that the observed centre is an interstitial hydrogen atom stabilized by a complex consisting of the Mg^{2+} ion and a positive ion vacancy (Fig. 3).

As mentioned above, X-irradiation of the lithium fluoride containing substitutional H_a^--ions at 80 K produces hydrogen atoms at interstitial sites (H_i^0-centres). On warming
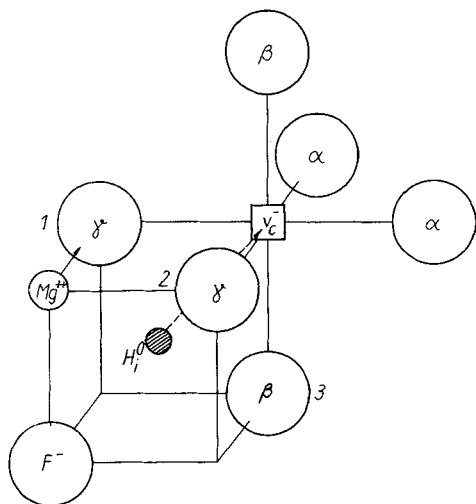
Fig. 3. Model of $H_i^0(Mg)$-centres in LiF–H⁻, Mg^{2+}

to 110 K these atoms move to the $Mg^{2+}v_c^-$-dipole, producing the interstitial hydrogen atom near the $Mg^{2+}v_c^-$-dipole which was first observed by Kamikawa [4],

$$H_i^0 + Mg^{2+}v_c^- \rightarrow H_i^0(Mg). \qquad (2)$$

For $\boldsymbol{B}_0 \parallel \langle 110 \rangle$ each broad line of the ESR spectrum contains eleven resolved lines equally spaced by $(17 \pm 2) \times 10^{-4}$ T (Fig. 2b). If the hydrogen atom would occur at an unperturbed interstitial position, for $\boldsymbol{B}_0 \parallel \langle 110 \rangle$, one would expect nine SHF lines. Furthermore, for $\boldsymbol{B}_0$ aligned parallel to $\langle 111 \rangle$, one expects to observe eight SHF lines. Inspection of the spectrum shows nine lines (Fig. 2c) indicating that the four nearest F⁻ ions are slightly nonequivalent.

These results can be explained by considering the distortions around the $H_i^0(Mg)$ atom due to the effective negative charge of the F⁻ ions surrounding the vacancy and the electrostatic attraction between the negative ions and the divalent cation, which causes a noncubic distortion of the lattice (as in case of the $H_{s,c}^0$-centre [5, 6]).

We have not been able to detect any absorption due to $H_i^0(Mg)$-centres in the range 200 to 800 nm. The optical absorption spectrum of LiF–H⁻, Mg^{2+} crystals after X-irradiation at 80 K and subsequent heating to room temperature consists of the F-band and Mg impurity-related bands at 4.0 and 3.2 eV [11]. Optical bleaching with light of 3.2 to 4.5 eV at 295 K leads to the disappearance of the Mg-related absorption bands, but not to a change of the ESR spectrum.

3.3 $H_{s,c}^0(Mg)$-centre

The $H_i^0(Mg)$-centres are thermally stable up to about 430 K. On warming above 430 K the $H_i^0(Mg)$-centre ESR spectrum decreases and a new ESR spectrum appears which is also associated with a hydrogen atom. The spectrum is shown in Fig. 4 for $\boldsymbol{B}_0 \parallel \langle 111 \rangle$.

The large splitting of $(511 \pm 1) \times 10^{-4}$ T is due to the hyperfine interaction of the unpaired electron with the proton. The analysis of the spectrum taking into account the Breit-Rabi correction yields $g = 2.0018 \mp 0.0002$, and a proton hyperfine constant of $A_p = 1423 \mp 1$ MHz, which is somewhat higher than for the free atomic hydrogen. The linewidth
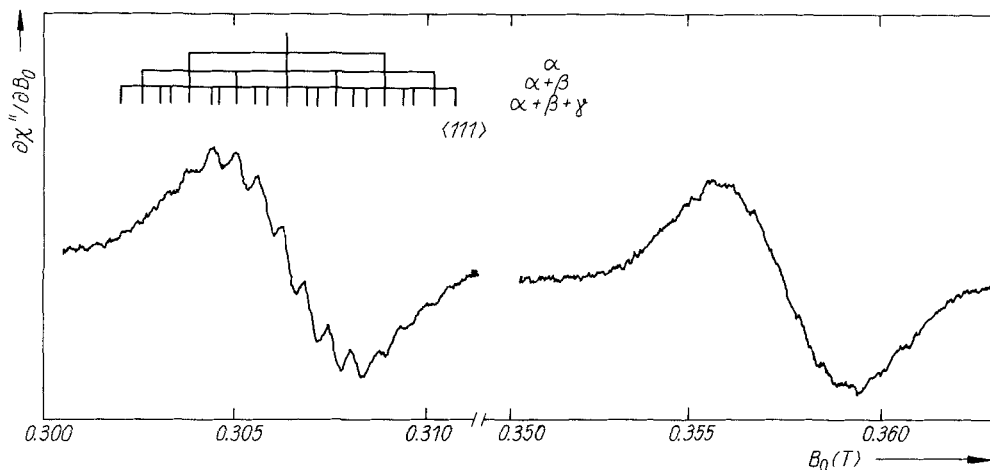
Fig. 4. ESR spectrum of $H^0_{s,c}$(Mg)-centres in normal LiF–H$^-$, Mg^{2+} for $\boldsymbol{B}_0 \parallel \langle 111 \rangle$; $T = 295$ K, $v = 9368$ MHz

(peak to peak) of 35×10^{-4} T is smaller than that for the interstitial hydrogen atom in LiF (Table 1). The partly resolved SHF structure of the low-field band is only observed for $\boldsymbol{B}_0 \parallel \langle 111 \rangle$, but no structure was found for the high-field component. The investigation of LiF–H$^-$, Mg^{2+} crystals enriched in ^{6}Li were also carried out and in these samples the same partially resolved structure is observed. However, in contrast to the normal LiF, the ESR spectrum of ^{6}LiF shows more well-resolved SHF structure when measured with high resolution (Fig. 5). When the magnetic field is away from a $\langle 111 \rangle$ axis the SHF structure
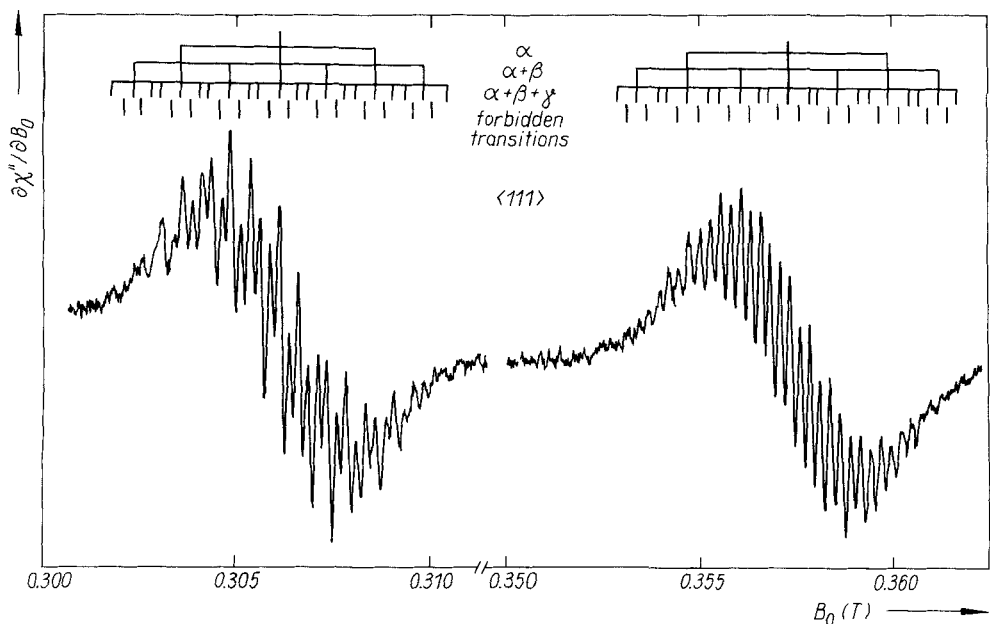

Fig. 5. ESR spectrum of $H^0_{s,c}$(Mg)-centres in LiF–H$^-$, Mg^{2+} crystals enriched with ^{6}Li for $\boldsymbol{B}_0 \parallel \langle 111 \rangle$; $T = 295$ K, $v = 9368$ MHz

is not resolved. These results suggest that the SHF structure is due to interactions with the fluorine nuclei and the centre is associated with a hydrogen atom in a cation vacancy ($H_{s,c}^0$-centre).

The ESR results may be described by a model of the centre that was established by ENDOR in KCl and RbCl crystals [4, 5]. According to this model, the divalent cation is situated on a nearest $\langle 110 \rangle$ site with respect to the hydrogen. Due to the presence of Mg^{2+} along $\langle 110 \rangle$, the six nearest F$^-$ neighbours consist of three pairs of nonequivalent nuclei which were labelled as α, β, and γ. The configuration of α, β, γ ions is the same as reported for the $H_{s,c}^0$(Ca^{2+}) [5, 6] (Fig. 3). However, the difference in the SHF constants between the three kinds of nearest-neighbour nuclei is higher for the $H_{s,c}^0$-centre in LiF than for that in KCl and RbCl (Table 2) [5, 6].

It was also established by Akhvlediani et al. [12] that γ-irradiation of LiF–OH$^-$ crystals leads to the formation of the unperturbed hydrogen atom in cation vacancy. At orientation of the magnetic field along the axis $\langle 111 \rangle$ the seven-line structure is resolved in each component of the doublet spectrum. The observed SHF structure is caused by the interaction with six equivalent nuclei with spin 1/2. This occurs when the hydrogen atom is in a cation vacancy in the environment of six ^{19}F ions. The SHF splitting determined from the spectrum is $(18 \mp 2) \times 10^{-4}$ T and this value is close to that of the β nuclei for which perturbation due to the presence of Mg^{2+} is smallest.

The additional lines observed between the main lines in Fig. 5 arise from "forbidden" transitions. The intensity of forbidden lines increases with external magnetic field B_0. An increase in the relative strengths of the forbidden transitions leads to destruction of the SHF structure of the high-field component of the $H_{s,c}^0$(Mg)-centre in normal LiF-H$^-$, Mg^{2+} crystals (Fig. 4).

The conversion of the H_i^0(Mg)-centres into $H_{s,c}^0$(Mg)-centres indicates that there is a potential barrier between these two configurations. Upon examining the crystal structure, an obvious potential barrier arises when the H_i^0(Mg) hydrogen atom crosses the narrow region surrounded by the three halide ions (1 to 3, Fig. 3) lying perpendicular to the $\langle 111 \rangle$ direction (along the connecting line $H_i^0 - v_c^-$). In LiF crystals the space between the fluorine ions show in Fig. 3 is smaller than the size of the hydrogen atom. This feature is characteristic of the lithium and sodium halides (except NaF). However, $H_{s,c}^0$-centres have been only studied in KCl and RbCl for which the space between the three halide ions is larger than the size of the hydrogen atom and the potential barrier between H_i^0(Me^{2+}) and $H_{s,c}^0$(Me^{2+})-centre configurations could not be observed.

The $H_{s,c}^0$(Mg)-centre perturbed by Mg^{2+} is destroyed at about 510 K and this temperature is close to that of destruction of the unperturbed $H_{s,c}^0$-centre in LiF–OH$^-$ crystals (about 525 K) [12].

Table 2
ESR data of $H_{s,c}^0$-centres in LiF at 295 K

centre	splittings between lines (10^{-4} T)			
	α	β	γ	
$H_{s,c}^0$(Mg)	25	12.5	5.2	
$H_{s,c}^0$	18	18	18	[12]

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(Received April 8, 1991)