A ^{35}Cl NQR Study on $Cs_2[Au^ICl_2][Au^{III}Cl_4]$*

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A pair of ^{35}Cl NQR spin echo signals has been observed for the mixed valence complex $Cs_2[Au^ICl_2][Au^{III}Cl_4]$ between 77 and 243 K. At 77 K, two resonance lines with the half widths $\Delta\nu_Q \sim 50$ kHz were located at $\nu_{Q1} = 17.28$ MHz for the Au^I-Cl chlorine and at $\nu_{Q2} = 27.10$ MHz for the Au^{III}-Cl chlorine in accordance with the crystal structure. The chlorine ionic characters of the Au^I-Cl and Au^{III}-Cl bonds are estimated as 0.63 and 0.42, respectively. The central gold atom carries a fractional protonic charge of 0.26 in $[Au^ICl_2]^-$ and 0.68 in $[Au^{III}Cl_4]^-$. The charge distributions in the complex anions differ insignificantly from those in the isolated $[AuCl_2]^-$ and $[AuCl_4]^-$ for ordinary complexes, indicating that the charge transfer interactions between the anions are weak in the mixed valence complex. The observed linear temperature dependencies of ν_Q and $\log T_{1Q}$ are well explained by the lattice vibration. When the temperature was increased from 77 K, the resonance lines became gradually weak without changing $\Delta\nu_Q$ and immeasurable above 215 K. ESR spectra taken at various temperatures revealed the presence of paramagnetic sites of ca. 5×10^{20} mol^{-1} arising from Au(II). The small but finite concentration of Au(II) or some other reason should be responsible for the fade out phenomenon and the large $\Delta\nu_Q$ observed.

Key words: ^{35}Cl NQR Frequency, ^{35}Cl NQR Spin-lattice Relaxation, Mixed Valence Gold Complex, Charge Transfer Interaction, ESR.

Introduction

$Cs_2[Au^ICl_2][Au^{III}Cl_4]$ crystallizes in the tetragonally distorted perovskite structure, space group I4/mmm with axes $a = 749.5$ and $c = 1088.0$ pm, $Z = 2$ [1–3]. In the crystal, linear and symmetric $[Au^ICl_2]^-$ and square planar $[Au^{III}Cl_4]^-$ are stacked alternately, forming the chlorine bridged networks of Au^I-Cl–Au^{III} along the c-axis and of Au^{III}-Cl–Au^I in the plane perpendicular to the c axis, as shown in Figure 1. The reported rather long interatomic distances of Cl–Au^{III} (315.9 pm) and Cl–Au^I (300.5 pm) compared with the bond lengths of Au^I-Cl (228.1 pm) and Au^{III}-Cl (229.5 pm) suggest that the Au^I–Au^{III} charge transfer interactions are weak [2]. Although the ordinary gold (I, III) complexes form colorless ($[AuCl_2]^-$) or pale yellow ($[AuCl_4]^-$) crystals, the title compound crystallizes in an astonishingly jet black color as described by the discoverer [4], indicating the Au^I–Au^{III} interaction to be present in the crystal. Therefore the complex may be classified as a class II mixed valence compound [5].

Since the discovery of super conductivity in perovskite type oxides, the mixed valence system $R_2[Au^IX_2][Au^{III}X_4]$ (R = Cs, Rb; X = Cl, Br, I) has been extensive-

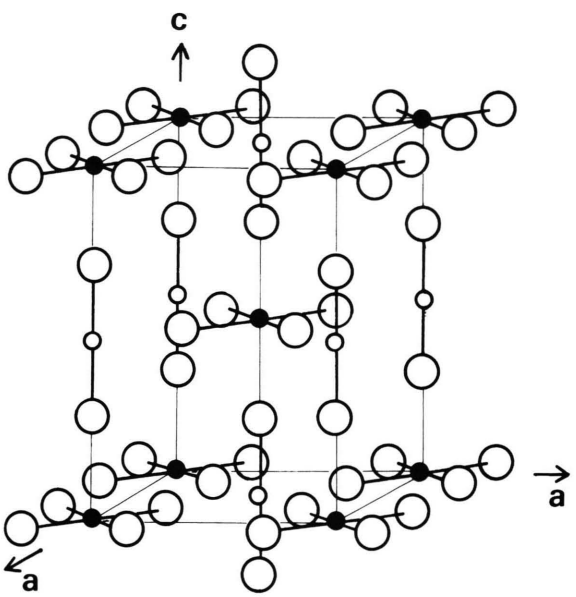

Fig. 1. The crystal structure of $Cs_2[Au^ICl_2][Au^{III}Cl_4]$. Large circles represent chlorine atoms, small open circles Au^I, and small full circles Au^{III}. Cesium ions are omitted.

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ly studied by workers including one of the present authors [6–8]. However, no study has been carried out about this system by NQR technique. The present experiments have been undertaken to clarify the charge distribution in $[Au^ICl_2]^-$ and $[Au^{III}Cl_4]^-$ and the lattice dynamics of the complex anions.

Experimental

A home made pulsed spectrometer was used for the observation of ^{35}Cl NQR [9]. The line shape of the resonances was determined by monitoring the dependence of the spin echo amplitudes on the rf frequencies. The pulse sequence $\pi/2-\tau-\pi/2-\tau_e-\pi$ was employed for the measurements of the spin-lattice relaxation time T_{1Q}, where τ_e was set to be ca. 350 μs throughout the experiments. The signal amplitudes decreased exponentially with τ in all measurements.

ESR spectra were recorded on a JEOL JES-FE1XP X-band spectrometer. The spectra were calibrated using the spectrum of Mn^{2+} diluted in MgO.

Magnetic susceptibilities were measured by a vibrating sample magnetometer VSM-5/5SC from Toei Industry.

Two kinds of polycrystalline samples were employed. One (I) was prepared by the Bridgman method [2] and successively purified in concentrated hydrochloric acid by the thermal diffusion method. The other (II) was prepared in a similar way as described in [4] and then purified by sublimation.

Results and Discussion

^{35}Cl NQR ν_Q

At 77 K, two ^{35}Cl NQR spin echo signals arising from $Cs_2[Au^ICl_2][Au^{III}Cl_4]$ were observed at $\nu_{Q1}=17.28$ MHz and $\nu_{Q2}=27.10$ MHz (Fig. 2), indicating that there are two kinds of nonequivalent chlorine atoms in the crystal. This agrees with the results of X-ray analyses [1–3]. (Two other signals, located at 13.61 and 21.34 MHz, were assigned to corresponding ^{37}Cl NQR.) The large difference between ν_{Q1} and ν_{Q2} suggests that the two kinds of chlorine have clearly distinguishable bonding characters in the crystal. Since the crystal consists of fairly isolated complex anions, linear and symmetric $[Au^ICl_2]^-$ and square planer $[Au^{III}Cl_4]^-$, one of the ν_Q should be assigned to the Au^I-Cl and the other to the Au^{III}-Cl chlorine. ^{35}Cl NQR studies [10–13] have been accompanied by X-ray analyses in a wide variety of tetrachloroaurates(III) (Table 1). When the reported ^{35}Cl NQR ν_Q are plotted against the Au(III)-Cl bond lengths L, a good linear correlation is obtained, as shown in Figure 3. The observed $\nu_{Q2}=27.10$ MHz and reported $L=229.5$ pm [2] corroborate this correlation. Therefore ν_{Q2} is attributable to the Au^{III}-Cl chlorine. The signal at $\nu_{Q1}=17.28$ MHz falls within the range of ^{35}Cl NQR $\nu_Q=17-18$ MHz in the various linear dichloroaurates(I) [14, 15] and can be assigned to the Au^I-Cl chlorine.

The ionic characters i of the Au^I-Cl and Au^{III}-Cl bonds have been estimated as 0.63 and 0.42, respectively, by the Townes and Dailey method [16]. The central gold atom carries a fractional protonic charge ρ of 0.26 in $[Au^ICl_2]^-$ and 0.68 in $[Au^{III}$-$Cl_4]^-$. The charge distribu-

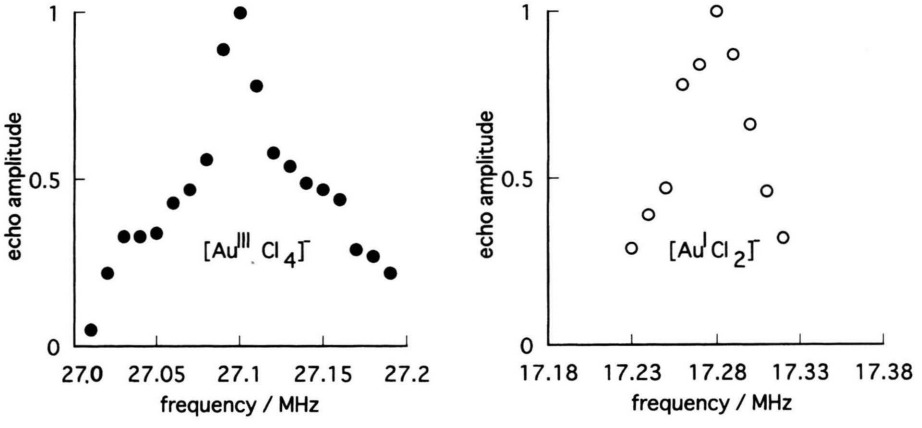

Fig. 2. ^{35}Cl NQR spectra for ν_{Q1} ($[Au^ICl_2]^-$) and ν_{Q2} ($[Au^{III}Cl_4]^-$) lines at 77 K.

Table 1. Au(III)-Cl bond length L and ^{35}Cl NQR frequencies ν_Q at 77 K in tetrachloroaurates(III).

Compound	L/pm	Ref.	ν_Q/MHz	Ref.
$Na[AuCl_4] \cdot 2H_2O$	226.0	a	29.47	[10, 11]
	227.8	a	28.87	[10, 11]
	228.3	a	28.00	[10, 11]
	228.8	a	25.36	[10, 11]
$Rb[AuCl_4]$	227.8	b	28.32	[11]
	228.6	b	27.65	[11]
$K[AuCl_4]$	228.5*	c	27.76*	[11]
$K[AuCl_4] \cdot 2H_2O$	228.5	d	28.18	[11]
	229.1	d	27.14	[11]
$SeCl_3[AuCl_4]$	226.6	e	32.67	[12]
	228.9	e	26.98	[12]
	229.4	e	26.92	[12]
	230.1	e	24.04	[12]
$guH[AuCl_4]$	228.8	f	28.15	[13]
	228.8	f	28.30	[13]
	229.1	f	28.06	[13]
	229.3	f	27.88	[13]
$Cs_2[Au^ICl_2][Au^{III}Cl_4]$	229.5	[2]	27.10**	

[a] M. Bonamico et al., Atti. Accad. Naz. Lincei. Rend. Cl. Sci. Fis. Mater. Nat. **39,** 504 (1966).
[b] J. Strähle and H. Bärnighausen, Z. Naturforsch. **25b,** 1186 (1970).
[c] M. Bonamico and Dessy, Acta Cryst. **29B,** 1735 (1973).
[d] P. F. Théobald and H. Omrani, Acta Cryst. **36B,** 2932 (1980).
[e] P. G. Jones et al., Acta Cryst. **43C,** 607 (1987).
[f] H. Kiriyama et al., Acta Cryst. **42C,** 277 (1986).
* average value.
** present study.

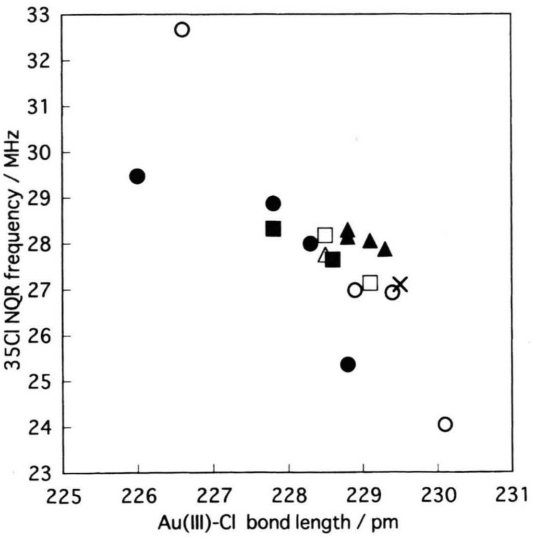

Fig. 3. Relation between Au(III)-Cl bond length and ^{35}Cl NQR frequency. Full circles represent $Na[AuCl_4] \cdot 2H_2O$, open circles $SeCl_3[AuCl_4]$, full squares $Rb[AuCl_4]$, open squares $K[AuCl_4] \cdot 2H_2O$, full triangles $guH[AuCl_4]$, open triangle $K[AuCl_4]$, and cross $Cs[Au^ICl_2][Au^{III}Cl_4]$.

tions in the complex anions differ insignificantly from those in the isolated $[AuCl_2]^-$ and $[AuCl_4]^-$ for the ordinary complexes. The charge transfer interactions between the Au^I and Au^{III} atoms are therefore considered to be small in the present mixed valence complex. The charge distributions in the complex anions are comparable to those in $[Au^I\text{-}I_2]^-$ ($i=0.60$, $\rho=0.20$) and $[Au^{III}\text{-}I_4]^-$ ($i=0.38$, $\rho=0.52$) recently studied by ^{129}I Mössbauer spectroscopy for $Cs_2[Au^ICl_2][Au^{III}Cl_4]$ [17].

Echo Spectra

The ^{35}Cl NQR spin echo amplitudes for (I) are plotted against the rf frequencies as shown in Figure 2. The intensity of the echoes was strong enough to determine the line shapes in the range of ±50 kHz around the central part of the spectra. However, weak signals were observable over the range of ±100 kHz. Practically the same spectra were obtained for (II) at 77 K. Therefore NQR measurements were restricted to (I) at the other temperatures. The observed spectra are extraordinarily broad. Line widths within 10 kHz were observed on $Cs[AuCl_4]$ [18]. In order to seek the causes of the line broadening, ESR first derivative spectra have been recorded for (I) at various temperatures between 153 K and room temperature. The intensity of the spectra increased with decreasing temperature in accordance with Curie's law, keeping the peak to peak width almost constant at ca. 260 G. From the intensity of the spectra, a concentration of the paramagnetic sites of ca. 5×10^{20} mol^{-1} was estimated. Both (I) and (II) yielded the same ESR line shape at room temperature. However, (II) showed only about 10% of the intensity of (I).

The mixed valence compound $Cs_2[Au^ICl_2][Au^{III}Cl_4]$ is known as diamagnetic with mass magnetic susceptibility $\chi_g=-0.30\times10^{-6}$ emu g^{-1} [19, 20]. In order to confirm the magnetic purity, χ_g was measured for both (I) and (II). The results are in good agreement with the reported value of χ_g mentioned above, assuring the purity of (I) and (II). The existence of the paramagnetic sites revealed by ESR measurements is intrinsic to the mixed valence compound and attributable to Au(II) having the configuration $5d^9$. The observed fairly broad line width in ESR spectra may largely arise from the site asymmetry at the position Au(II) in the tetragonal system. The existence of paramagnetic sites of Au(II) causes imperfections in the crystal lattice and results in a wider distribution of EFG at the chlorine nuclei, which causes the ^{35}Cl NQR spectra to broaden.

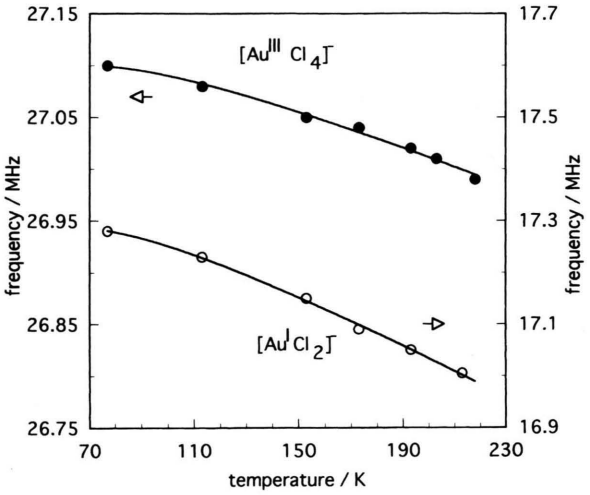

Fig. 4. Temperature dependence of ^{35}Cl NQR ν_{Q1} ($[Au^ICl_2]^-$) and ν_{Q2} ($[Au^{III}Cl_4]^-$). Solid lines represent the best fitted theoretical curve (1).

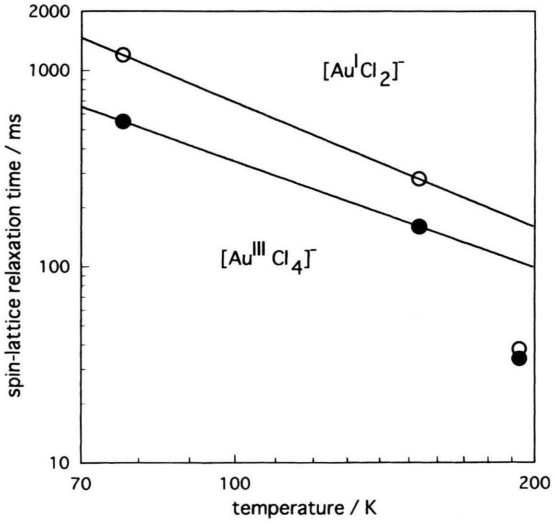

Fig. 6. Temperature dependence of ^{35}Cl NQR spin-lattice relaxation time T_{1Q} for ν_{Q1} ($[Au^ICl_2]^-$) and ν_{Q2} ($[Au^{III}Cl_4]^-$).

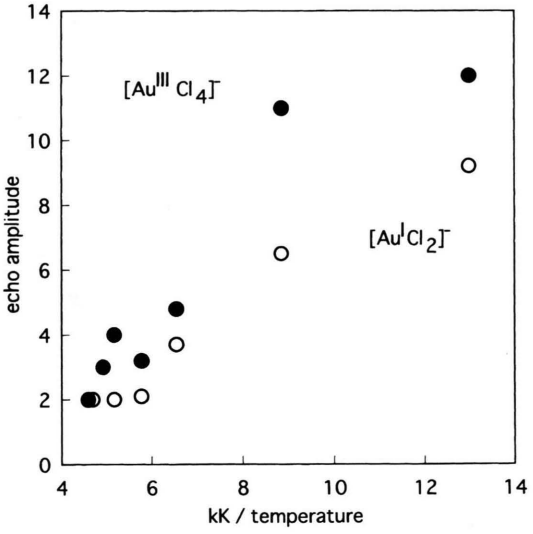

Fig. 5. Temperature dependence of ^{35}Cl NQR spin echo amplitude for ν_{Q1} ($[Au^ICl_2]^-$) and ν_{Q2} ($[Au^{III}Cl_4]^-$).

Temperature Dependence of ν_Q and T_{1Q}

The temperature dependence of ^{35}Cl NQR ν_{Q1} and ν_{Q2}, determined from the spin echo signals of $Cs_2[Au^ICl_2][Au^{III}Cl_4]$, is shown in Figure 4. When the temperature was increased from 77 K, the spectra became gradually weaker without changing $\Delta\nu_Q$ (Figure 5). The echo signals were observable up to 243 K, although the frequencies were indeterminable above 215 K. The temperature coefficient of ν_{Q1} is roughly twice as large as that of ν_{Q2}. This means that the libration of $[Au^ICl_2]^-$ is more easily exited in the crystal lattice. The temperature dependence of ν_Q can be expressed by the Bayer-Kushida equation [21]. By introducing the effective angular frequency ω_{eff} of the lattice vibration and the effective moment of inertia I_{eff} associated with the vibration, in the high temperature approximation, the equation can be rewritten as

$$\nu_Q = \nu\,[1-(3\,kT/2\,I_{eff}\,\omega_{eff}^2)-(\hbar^2/8\,I_{eff}\,kT)]\,, \quad (1)$$

where ν represents the NQR frequency in a fictitious vibrationless state. Applying (1) on the data shown in Fig. 4, $\nu = 17.64$ MHz, $\omega_{eff}/2\pi = 154$ cm^{-1} and $I_{eff} = 1.6\times 10^{-46}$ kg m^2 have been obtained for ν_{Q1} and $\nu = 27.25$ MHz, $\omega_{eff}/2\pi = 168$ cm^{-1} and $I_{eff} = 5.4\times 10^{-46}$ kg m^2 for ν_{Q2}. The value of I_{eff} for $[Au^{III}Cl_4]^-$ motion is about three times larger than I_{eff} for $[Au^ICl_2]^-$ motion. The well separated values of ω_{eff} and I_{eff} between the complex anions suggest that the associated motions are isolative. The smaller value of the effective force constant, $I_{eff}\,\omega_{eff}^2$ for $[Au^ICl_2]^-$ than for $[Au^{III}Cl_4]^-$ suggests that the interaction between the anions are stronger in the plane perpendicular to the c axis than those along the c axis, in accordance with the crystal structure [2, 6].

^{35}Cl T_{1Q} was determined as 1.2 and 0.55 s for ν_{Q1} and ν_{Q2}, respectively at 77 K on the center frequency of the resonance lines. Upon heating, the difference in the T_{1Q}

became small and nearly the same of 34 ms at 193 K, as shown in Figure 6. Above 193 K, the signal intensities were too weak to determine T_{1Q}. Below 153 K, T_{1Q} was proportional to T^{-n}, where n was determined as 2.1 for ν_{Q1} and 1.8 for ν_{Q2}. The close value of the exponent $n = 2.0$ suggests that the lattice vibration of the complex anions is responsible to the relaxation [22]. Above 153 K, T_{1Q} deviates from the proportionality suggesting the presence of other relaxation mechanisms. A rapid ^{35}Cl NQR T_{1Q} decrease, observed in $CsPbCl_3$ (perovskite structure) above 300 K, was attributed to the reorientation of $[PbCl_6]^{2-}$ octahedra [23]. Sharp decreases of ^{35}Cl NQR T_{1Q} caused by the reorientation of the complex anions have been reported even at relatively low temperatures in various octahedral [24, 25] and square planer [26] metal complexes as well. The migration of the lattice defects also contributes to the reduction T_{1Q} [27]. The ^{35}Cl NQR T_{1Q} above 153 K can be considered to be strongly affected by the reorientational motion of the complex anions or/and the existence of paramagnetic sites as lattice defects.

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[1] N. Elliott and L. Pauling, J. Amer. Chem. Soc. **60,** 1846 (1938).
[2] J. C. M. Tindemans-v. Eijndhoven and G. C. Verschoor, Mater. Res. Bull. **9,** 1667 (1974).
[3] D. Denner, H. Schulz, and H. d'Amour, Acta Cryst. **35A,** 360 (1979).
[4] H. L. Wells, Amer. J. Sci. **3,** 315 (1922).
[5] M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem. **10,** 247 (1967).
[6] H. Kitagawa, N. Kojima, and H. Sakai, J. Chem. Soc. Dalton Trans. **1991,** 3211, and references cited therein.
[7] N. Kojima, M. Hasegawa, H. Kitagawa, T. Kikegawa, and O. Shimomura, J. Amer. Chem. Soc. **116,** 11368 (1994), and references cited therein.
[8] S. S. Hafner, N. Kojima, J. Stanek, and Li Zhang, Phys. Lett. **A192,** 385 (1994).
[9] A. Sasane, M. Shinha, Y. Hirakawa, and A. Ishikawa, J. Mol. Struct. **345,** 205 (1995).
[10] C. W. Fryer and J. A. S. Smith, J. Chem. Soc. A, **1970,** 1029.
[11] A. Sasane, T. Matuo, D. Nakamura, and M. Kubo, J. Magn. Reson. **4,** 257 (1971).
[12] Z. A. Fokina, S. I. Kuznetsov, N. I. Timoshchenko, and E. V. Bryukohova, Zh. Fiz. Khim. **53,** 146 (1979).
[13] S. Gima, Y. Furukawa, R. Ikeda, and D. Nakamura, J. Mol. Struct. **111,** 189 (1983).
[14] G. A. Bowmaker and R. Whiting, Aust. J. Chem. **29,** 1407 (1976).
[15] P. G. Jones and A. F. Williams, J. Chem. Soc. Dalton Trans. **1977,** 1430.
[16] E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, New York 1969.
[17] N. Kojima, H. Sakai, M. Seto, S. Kitao, and Yu. Maeda, Soc. Ital. Fis. **50,** 47 (1996).
[18] A. Ishikawa, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **44a,** 125 (1989).
[19] N. Elliott, J. Chem. Phys. **2,** 419 (1934).
[20] B. Brauer and G. Sleater, J. Less-Common Met. **21,** 283 (1970).
[21] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104,** 1364 (1956).
[22] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **39,** 440 (1963).
[23] R. L. Armstrong, J. Magn. Reson. **20,** 214 (1975).
[24] K. Horiuchi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **88,** 546 (1987).
[25] A. Ishikawa, K. Horiuchi, R. Ikeda, and D. Nakamura, J. Mol. Struct. **192,** 237 (1989).
[26] Y. Furukawa and D. Nakamura, Z. Naturforsch. **41a,** 416 (1986).
[27] C. A. Martín and M. J. Zuriaga, Z. Naturforsch. **41a,** 378 (1986).