12 February 1999

ELSEVIER

Chemical Physics Letters 300 (1999) 613–618

CHEMICAL PHYSICS LETTERS

Nuclear quadrupole resonance of mixed-valence charge-ordered dimers

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Received 25 March 1998; in final form 7 December 1998

Abstract

The influence of an external magnetic field on the conditions of charge ordering of mixed-valence dimer clusters Ni^{2+}–Ni^{+} is considered. The manifestations of charge ordering in the spectra of nuclear quadrupole resonance are elucidated. These spectra are shown to give information on the key parameters of charge-ordered crystals. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Mixed-valence (MV) clusters contain two or several different valency ions of transition metals bridged by ligands in a molecular system. Each cluster contains 'extra' (tunnelling) electrons or holes that migrate within the cluster. Recently isolated MV clusters have been the subject of interest in theory and experiment. Meanwhile, a wide class of crystals comprising MV clusters is known for which the concept of isolated MV clusters is inapplicable. Experimental investigations using ESR, Mössbauer and X-ray spectroscopy as well as thermodynamic measurements indicate phase transitions to the charge-ordered state [1–6] wherein the 'extra' electron is completely or partially localized on one of the cluster ions. In papers [7–12] the interrelation between the temperature behaviour of ESR and Mössbauer spectra including their hyperfine structures and the modifications in the electronic density distribution accompanying phase transitions has been revealed. The manifestations of the effects of the redistribution of the electronic density in MV crystals are to be expected also in other phenomena resulting from the interaction of nuclei with valence electrons, including nuclear quadrupole resonance (NQR). From experiments on NQR information about the extent of 'extra' electron localization in different phase states of a crystal may be drawn.

The goal of the present Letter is to show the possibility of investigating the charge-ordering phenomenon and phase transitions in MV crystals with the help of NQR spectra. So far as NQR spectra can be observed for nuclei whose ground state has a spin I which exceeds $1/2$, for the demonstration of the effect we confine ourselves to the case of dimer MV clusters Ni^{2+}–Ni^{+} with the electronic configuration d_a^8–d_b^9 and nuclear spins $I_a = I_b = 3/2$ (where a and b denote cluster ions). In passing, the peculiarities of charge ordering in an external magnetic field are examined.

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PII: S0009-2614(98)01416-X

2. Hamiltonian of the crystal

The exchange-tunnel multiplets $^2A_{2g,1u}$, $^4A_{2g,1u}$ are assumed to make up the group of low-lying states of the isolated MV dimer d^8–d^9 cluster (Fig. 1) [13]. The energies of the levels $^2A_{2g,1u}$ and $^4A_{2g,1u}$ are defined by the parameters J and P of Heisenberg-type and double exchange, respectively. The Hamiltonian of a crystal consisting of interacting clusters can be written in the form

$$H = H_e + V_e + V_N + H_Q\,, \tag{1}$$

where H_e is the Hamiltonian of the electronic subsystem

$$H_e = \sum_n H_n - \frac{1}{2}\sum_{n,m} K\left(\vec{R}_n - \vec{R}_m\right) d_n^z d_m^z\,, \tag{2}$$

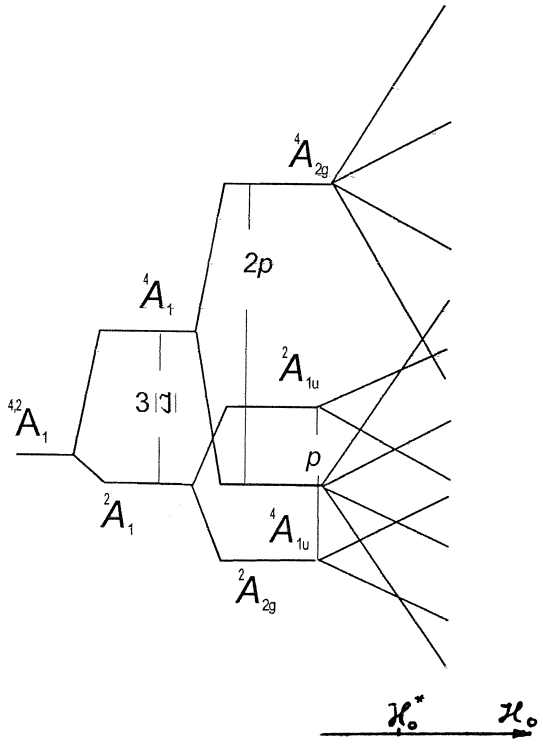


Fig. 1. Energy levels of the dimer MV cluster d^8–d^9 in the magnetic field $\vec{\mathcal{H}}_0$ for $p>0$, $J<0$, $1/6<|x|<1/2$.

with

$$H_n = \begin{array}{c} \begin{matrix} {}^4A_{2g} & {}^4A_{1u} & {}^2A_{2g} & {}^2A_{1u} \end{matrix} \\ \begin{pmatrix} -3J+p & 0 & 0 & 0 \\ 0 & -3J-p & 0 & 0 \\ 0 & 0 & -\frac{p}{2} & 0 \\ 0 & 0 & 0 & \frac{p}{2} \end{pmatrix} \end{array}, \tag{3a}$$

and

$$d_n^z = d_0 \begin{array}{c} \begin{matrix} {}^4A_{2g} & {}^4A_{1u} & {}^2A_{2g} & {}^2A_{1u} \end{matrix} \\ \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \end{array}. \tag{3b}$$

H_n is the Hamiltonian of the isolated cluster with the eigenvalues found in [13]. The second term in Eq. (2) describes the dipole–dipole interaction [8] between clusters leading to the charge-ordered state, d_n^z is the z-component of the operator of the cluster dipole moment, m and n number interacting clusters, $\vec{R}_n$ and $\vec{R}_m$ are their position vectors, and $K(\vec{R}_n - \vec{R}_m)$ is the structural factor [8] depending on the mutual positions of clusters in the crystal lattice. $d_0 = eR_{ab}/2$ is the dipole moment of the cluster with the localized 'extra' electron with the mid-point between a and b as origin. The operators V_e and V_N respectively describe the interactions of electronic cluster spins $\vec{S}_n$ and nuclear cluster spins $\vec{I}_a^n$ and $\vec{I}_b^n$ with the external magnetic field $\vec{\mathcal{H}}_0$:

$$V_e = g\beta\sum_n \vec{S}_n\vec{\mathcal{H}}_0\,, \tag{4a}$$

$$V_N = -g_N\beta_N\sum_n\left(\vec{I}_a^n + \vec{I}_b^n\right)\vec{\mathcal{H}}_0\,. \tag{4b}$$

For simplicity these interactions are assumed to be isotropic. The consideration of the anisotropy of the electronic g-factor leads to an 'inclination' of the electronic spin with respect to the direction of the external magnetic field. However while calculating

the stationary states and NQR spectrum this effect will be neglected for the sake of simplicity.

The Hamiltonian of electron–nuclear quadrupole interaction for each cluster can be written in the form

$$H_{\mathrm{Q}} = \frac{e^2 Q_{\mathrm{n}}}{4I(2I-1)} \sum_{c=\mathrm{a,b}} q_c \left[3\left(I_c^z\right)^2 - I(I+1) \right], \tag{5}$$

where Q_{n} is the nuclear quadrupole moment, I is the nuclear spin, $q_c = \sum_i (3z_{ic}^2 - r_{ic}^2)/r_{ic}^5$ is the operator of the electric field gradient at the nucleus c, $\vec{r}_{ic}$ is the radius-vector of the ith electron relative to nucleus c.

3. Molecular field approximation. Charge-ordered states

Intra- and intercluster interactions are supposed to exceed considerably the interactions H_{Q} and V_{N}. This approximation may be justified by the fact that phase transitions in MV coordination compounds are observed at temperatures $T \geq 200$ K [1–3]. Therefore we neglect those interactions while calculating the numerical characteristics of charge ordering.

In the molecular field approximation the Hamiltonian $H_{\mathrm{e}} + V_{\mathrm{e}}$ decomposes into the sum of single-cluster Hamiltonians:

$$\mathscr{H}_n = H_n - L\bar{d}d_n^z + g\beta\vec{S}\vec{\mathscr{H}}_0, \tag{6}$$

where $\bar{d}(T)$ is the thermal average value of the dipole moment (order parameter) that satisfies the self-consistent equation:

$$\bar{d} = \frac{\mathrm{Tr}\left[\exp\left(-\frac{H_{\mathrm{e}} + V_{\mathrm{e}}}{kT}\right) d_n^z\right]}{\mathrm{Tr}\left[\exp\left(-\frac{H_{\mathrm{e}} + V_{\mathrm{e}}}{kT}\right)\right]}. \tag{7}$$

The eigenvalues of the Hamiltonian (6) and the corresponding wavefunctions have the form:

$$\varepsilon_{1(2)}(SM_S) = -3J\left[S(S+1) - S_{\mathrm{a}}(S_{\mathrm{a}}+1) - S_{\mathrm{b}}(S_{\mathrm{b}}+1)\right] + g\beta\mathscr{H}_0 M_S \pm W(S), \tag{8}$$

$$\Psi_{1(2)}(SM_S) = \left[\frac{1}{2}\left(1 \mp \frac{L\bar{d}d_0}{W(S)}\right)\right]^{1/2} \varphi_{\mathrm{a}} \mp (-1)^{S-1/2}\left[\frac{1}{2}\left(1 \pm \frac{L\bar{d}d_0}{W(S)}\right)\right]^{1/2} \varphi_{\mathrm{b}}, \tag{9}$$

where

$$W(S) = \left[\frac{p^2(S+1/2)^2}{4} + \left(L\bar{d}d_0\right)^2\right]^{1/2},$$

$$L = \sum_n K\left(\vec{R}_n - \vec{R}_m\right).$$

S_{a} and S_{b} are the electronic spins of the cluster ions, M_S is the projection of the cluster full spin S ($S = 1/2, 3/2$), φ_c is the cluster wave function with the 'extra' electron localized on the ion c ($c = \mathrm{a,b}$). The system behaviour is characterized by three non-dimensional parameters: $x = J/|p|$, $y = |p|/Ld_0^2$, and $z = \beta g\mathscr{H}_0/|p|$.

In the absence of an external magnetic field in d^1–d^2 crystals a single phase transition takes place for two parameter regions: (1) $J < 0$, $y < 1$ and arbitrary values of x; and (2) $J < 0$, $1 \leq y \leq 2$, $|x| = 1/6$. Under conditions $J < 0$, $1 < y \leq 4/3$, $|x(y)| < |x| < 1/6$ (where $x(y)$ is determined numerically) two phase transitions may be realized [8]. Sufficiently strong magnetic fields leading to the ground ferromagnetic state ($S = 3/2$, $M_S = -3/2$) promote the 'extra' electron delocalization and the destabilisation of the charge-ordered phase. The latter manifests itself in the following effects:

(a) The increase of the maximum dipole moment $\bar{d}_{\max}$ with growth of the external field (Fig. 2).

(b) The appearance of two phase transitions instead of one for fields $\mathscr{H}_0 > \mathscr{H}_0^*$ ($\mathscr{H}_0^* = (g\beta)^{-1}(3|J| - |p|/2)$ in the range of parameters $|x| > 1/6$, $1 \leq y \leq 3/2$, $J < 0$. In consequence the range of parameters y wherein the charge ordering is possible narrows (Fig. 2, curves 3, 4, 7). So for the fields $\mathscr{H}_0 < \mathscr{H}_0^*$ and $\mathscr{H}_0 > \mathscr{H}_0^*$ this range is defined by the inequalities $y < 2$ and $y < 3/2$, respectively. At the same time one phase transition takes place for $\mathscr{H}_0 < \mathscr{H}_0^*$, $y < 2$, and for $\mathscr{H}_0 > \mathscr{H}_0^*$, $y < 1$. Thus the system with the parameters $|x| > 1/6$, $1 \leq y < 3/2$ may be identified by its behaviour in an

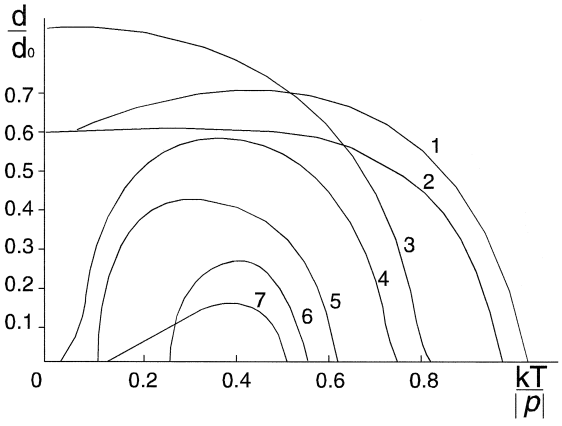


Fig. 2. Temperature dependence of the order parameter for $J<0$ in the presence of the external magnetic field $\mathscr{H}_0$: (1) $z=0$, $x=-0.025$, $y=0.8$; (2) $z=1.5$, $x=-0.025$, $y=0.8$; (3) $z=0$, $x=-0.375$, $y=1.0$; (4) $z=1.0$, $x=-0.375$, $y=1.0$; (5) $z=0$, $x=-0.09$, $y=1.05$; (6) $z=0.5$, $x=-0.09$, $y=1.05$; and (7) $z=2.0$, $x=-0.375$, $y=1.0$.

external magnetic field. The physical interpretation of this result is as follows: for magnetic fields $\mathscr{H}_0 > \mathscr{H}_0^*$ and positive double exchange values the ground antiferromagnetic state $({}^2\mathrm{A}_{2g}, M_S=-1/2)$ is replaced by the ferromagnetic one $({}^4\mathrm{A}_{1u}, M_S=-3/2)$ (Fig. 1). Therefore at low temperatures for $1\le y<3/2$ the 'extra' electron localization in the system with the tunnel parameter $2p$ is impossible. The population of the Zeeman sublevel $({}^2\mathrm{A}_{2g}, M_S=-1/2)$ softens the conditions for charge-ordered phase stabilization. Further increase of temperature results in the population of the sublevel ${}^2\mathrm{A}_{1u}$, $M_S=-1/2$, and the system passes again to the paraelectric state.

(c) The field dependence of phase transition temperatures: a decrease of the temperature T_c with the field growth in the case of one phase transition (Fig. 2, curves 1, 2). An increase of the temperature T_{c1} and a decrease of the temperature T_{c2} in the case of two phase transitions (Fig. 2, curves 4–7). For example, for $1\le y<3/2$, $1/6<|x|<1/2$ (Fig. 1) the growth of the field intensity $\mathscr{H}_0$ ($\mathscr{H}_0>\mathscr{H}_0^*$) leads to the increase of the energy gap

$$\Delta\varepsilon_1=\varepsilon\left({}^2\mathrm{A}_{2g}, M_S=-\frac{1}{2}\right)-\varepsilon\left({}^4\mathrm{A}_{1u}, M_S=-\frac{3}{2}\right)=g\beta\mathscr{H}_0-3|J|+p/2,$$

therefore the temperature T_{c1} of first phase transition rises. At the same time the energy

$$\Delta\varepsilon_2=\varepsilon\left({}^2\mathrm{A}_{1u}, M_S=-\frac{1}{2}\right)-\varepsilon\left({}^2\mathrm{A}_{2g}, M_S=\frac{1}{2}\right)=p-g\beta\mathscr{H}_0,$$

and for fields $\mathscr{H}_0>|p|/g\beta\mathscr{H}_0$ the level $({}^2\mathrm{A}_{1u}, M_S=-1/2)$ turns out to be lower than the level $({}^2\mathrm{A}_{2g}, M_S=1/2)$, but higher than the levels $({}^2\mathrm{A}_{2g}, M_S=-1/2)$, $({}^4\mathrm{A}_{1u}, M_S=-1/2)$, $({}^4\mathrm{A}_{1u}, M_S=-3/2)$. It is evident that in this case the temperature of the second phase transition falls. For $|x|<1/6$, $p>0$ and arbitrary values $\mathscr{H}_0$ the Zeeman sublevel $({}^4\mathrm{A}_{2g}, M_S=-3/2)$ remains the ground one. Thus in the indicated range of parameters an external magnetic field does not cause dramatic changes in the temperature dependence of $\bar{d}(T)$ (Fig. 2, curves 1, 2, 5, 6). Nevertheless with the growth of the magnetic field the gap between the states $({}^2\mathrm{A}_{2g}, M_S=-1/2)$ and $({}^4\mathrm{A}_{1u}, M_S=-3/2)$ increases, and the conditions of appearance of two phase transitions become more rigid.

The experiments on dimeric MV clusters reveal different relations between the parameters of Heisenberg exchange and electron transfer [14]. The transfer parameter takes on the values from 0.1 to 10^3 cm^{-1}. The exchange parameter is a value of the order of 10–10^2 cm^{-1}. As to the parameter Ld_0^2, its value can be estimated using X-ray data. For distances $R_{ab}\approx 2$–5 Å between metal ions in the cluster and distances $R\approx 10$–20 Å between adjacent clusters the parameter $Ld_0^2\sim e^2(R_{ab}/2)^2/R^3$ ranges from 14 to 720 cm^{-1}. Meanwhile it should be borne in mind that for fields ~ 200 kOe the energy $g\beta\mathscr{H}_0$ amounts to 20 cm^{-1}. Therefore the results obtained are valid for systems wherein the transfer parameter and the characteristic energy of intercluster interaction are of the order of the Zeeman interaction energy.

4. Energy levels of cluster nuclei

The quadrupole splitting of nuclear energy levels in the definite cluster state with the wavefunction $\psi_i(SM_S)$ $(i=1,2)$ can be obtained by the averaging

of the Hamiltonian H_Q (Eq. (5)) over the electronic coordinates

$$H_Q^{(1,2)} = \langle \psi_{1,2}(SM_S)/H_Q(\vec{r},\vec{R})/\psi_{1,2}(SM_S)\rangle . \tag{10}$$

In strong enough magnetic fields for which the magnitude $g_N\beta_N\mathscr{H}_0$ exceeds considerably the constant of quadrupole interaction, the spins of the cluster nuclei are quantized along the field direction and make up angles Ω_a and Ω_b with the cluster axis. If the cluster ions occupy equivalent positions, then $\Omega_a = \Omega_b = \Omega$. In this case for the energies of cluster nuclear levels in the electronic state $\Psi_{1,2}(SM_S)$ we get:

$$E_a^{(1,2)}(S) = -g_N\beta_N\mathscr{H}_0 m_a + \frac{e^2Q_n}{16I(2I-1)} \times (3\cos^2\Omega - 1)\left[3m_a^2 - I(I+1)\right] \times \left[q^*\left(1 \mp \frac{L\bar{d}d_0}{W(S)}\right) + q\left(1 \pm \frac{L\bar{d}d_0}{W(S)}\right)\right], \tag{11a}$$

$$E_b^{(1,2)}(S) = -g_N\beta_N\mathscr{H}_0 m_b + \frac{e^2Q_n}{16I(2I-1)} \times (3\cos^2\Omega - 1)\left[3m_b^2 - I(I+1)\right] \times \left[q\left(1 \mp \frac{L\bar{d}d_0}{W(S)}\right) + q^*\left(1 \pm \frac{L\bar{d}d_0}{W(S)}\right)\right], \tag{11b}$$

where m_c ($c = a, b$) is the projection of the nuclear spin, q and q^* are the mean electric field gradients on the nuclei of the d^8 and d^9 ions, i.e. of cluster ions with the completely localized 'extra' electron.

5. Temperature transitions in the NQR spectra

Since in NQR spectra only transitions are allowed for which the selection rule $\Delta m_{a(b)} = \pm 1$ holds the transition frequencies for nuclei a and b are determined by the following relations:

$$h\nu_{1(2)}^a(S) = g_N\beta_N\mathscr{H}_0 - \frac{3e^2Q_n}{16I(2I-1)}(2m_a - 1) \times (3\cos^2\Omega - 1)\left[q^*\left(1 \mp \frac{L\bar{d}d_0}{W(S)}\right) + q\left(1 \pm \frac{L\bar{d}d_0}{W(S)}\right)\right], \tag{12a}$$

$$h\nu_{1(2)}^b(S) = g_N\beta_N\mathscr{H}_0 - \frac{3e^2Q_n}{16I(2I-1)}(2m_b - 1) \times (3\cos^2\Omega - 1)\left[q\left(1 \mp \frac{L\bar{d}d_0}{W(S)}\right) + q^*\left(1 \pm \frac{L\bar{d}d_0}{W(S)}\right)\right]. \tag{12b}$$

The observed spectrum may be obtained by the summation of spectra originating from different electronic Zeeman sublevels in the molecular field (8) taking into account their thermal populations. Carrying out this averaging and using the equation for the order parameter we obtain:

$$h\nu^a = g_N\beta_N\mathscr{H}_0 - \frac{3e^2Q_n}{16I(2I-1)} \times \left[q + q^* - (q - q^*)\frac{\bar{d}}{d_0}\right] \times (2m_a - 1)(3\cos^2\Omega - 1), \tag{13}$$

$$h\nu^b = g_N\beta_N\mathscr{H}_0 - \frac{3e^2Q_n}{16I(2I-1)}(2m_b - 1) \times (3\cos^2\Omega - 1)\left[q + q^* + (q - q^*)\frac{\bar{d}}{d_0}\right]. \tag{14}$$

The NQR spectrum represents the superposition of two spectra with different temperature-dependent electric field gradients on the nuclei. From Eqs. (13) and (14) it is seen that for integral values I of the nuclear spin and $3\cos^2\Omega - 1 \neq 0$, $4I$ transitions are possible in the ordered phase. For fractional values I of the nuclear spin the frequency of the line corre-

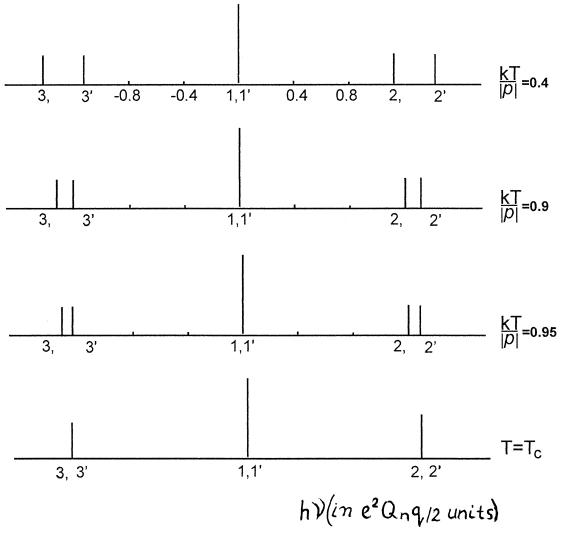


Fig. 3. Temperature dependence of the NQR spectrum of the dimer Ni^{2+}–Ni^{+} (d^8–d^9) for $z = 1.5$, $x = -0.025$, $y = 0.8$. The lines 1–3, 1′–3′ correspond to the following transitions: $(1,1')$ $m_{a(b)} = -1/2$, $m'_{a(b)} = 1/2$; $(2,2')$ $m_{a(b)} = 1/2$, $m'_{a(b)} = 3/2$; and $(3,3')$ $m_{a(b)} = -3/2$, $m'_{a(b)} = -1/2$.

sponding to the transition $-1/2 \rightarrow 1/2$ is the same for the two cluster nuclei, and for $3\cos^2 \Omega - 1 \neq 0$ the spectrum consists of $4I - 1$ lines. In the NQR spectrum the distance between the lines corresponding to the transitions $m_a - 1 \rightarrow m_a$ and $m_b - 1 \rightarrow m_b$ on the nuclei a and b, respectively, is equal to

$$h\Delta\nu_{ab} = \frac{3e^2Q_n}{8I(2I-1)}(3\cos^2\Omega - 1) \times \left[(q+q^*)(m_b - m_a) + (q-q^*)(m_a + m_b - 1)\frac{\bar{d}}{d_0}\right]. \quad (15)$$

While studying the dependence of the distance $h\Delta\nu_{ab}$ on the orientation of the external magnetic field one may obtain information about the electric field gradients on nuclei a and b as well as information about the characteristics of charge ordering. In Fig. 3 the temperature dependence of the NQR spectrum of the MV dimer Ni^{+}–Ni^{2+} (d^9–d^8, $I = 3/2$) is presented. The spectrum simulation was carried out by the use of relations (13) and (14) with the following parameter values: $x = -0.025$, $y = 0.8$, $z = 1.5$, $q^*/q = 1.5$, $\Omega = 0$. In the disordered phase the electronic density is uniformly distributed between cluster ions, and the NQR spectrum consists of the three lines with the intensity ratio 3:4:3. In the charge-ordered state the intensity and the frequency of the central line does not change, but the lines originating from the transitions $1/2 \rightarrow 3/2$ and $-3/2 \rightarrow 1/2$ split. With temperature decrease the distance between these split lines corresponding to the transitions between the same Zeeman sublevels of nuclei a and b increases. At $T < T_c$ the spectrum consists of 5 lines with the intensity distribution: 3:3:8:3:3. Thus in the charge-ordered state the superposition of spectra characteristic for ions a and b can be observed.

It is worth noting that the splittings in the NQR spectrum allow the mean value of the electronic density on each cluster nucleus to be determined and thus conclusions about the degree of ordering can be drawn. The results obtained may turn out to be useful while investigating charge-ordered states in MV coordination compounds.

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