NMR study of the perovskite-like compounds $Ba_2ScCuO_{4.5}$, $Ba_3Sc_4Cu_3O_{12}$, and $Ba_2Sc_2O_5$

A. A. Gippius, V. P. Denisov, V. V. Moshchalkov, Yu. M. Petrusevich, O. P. Revokatov, E. V. Antipov, A. L. Kharlanov, L. M. Kovba, and L. N. Lykova

M. V. Lomonosov State University, Moscow

The temperature dependence of the NMR spectra of ^{45}Sc nuclei has been measured in the perovskite-like compounds $Ba_2ScCuO_{4.5}$, $Ba_3Sc_4Cu_3O_{12}$, and $Ba_2Sc_2O_5$. The first two of these compounds are found to have identical NMR spectra, which stem from the electron–nucleus exchange interaction between the unpaired $3d^9$ electron of copper and the ^{45}Sc nucleus. The Knight shift of the ^{45}Sc NMR line is negative for these two samples in the temperature intervals 140–250 K and 250–380 K and varies in accordance with $K = -K_0/(T - \theta)$. This behavior corresponds to a negative sign of $A/\gamma_n\hbar$, the constant of the electron–nulceus exchange interaction. The compound $Ba_2Sc_2O_5$ exhibits the characteristic quadrupole broadening of the ^{45}Sc line, which can be described in first–order perturbation theory. This circumstance corresponds to the filling of oxygen positions with a probability of 5/6 in the ScO_6 octahedron. In addition, the temperature dependence of the spin–spin and spin–lattice relaxation times of the ^{45}Sc nuclei has been measured for all of the compounds studied.

INTRODUCTION

Since the discovery of high–temperature superconducting,[1] the properties of the Y–Ba–Cu–O system and of related componds have become the subject of a huge number of studies. The mechanism for the high–temperature superconductivity nevertheless remains unknown. It is thus important to carry out a systematic search for other metal–oxide superconductors in the $BaO–M_2O_3–CuO$ system, where M is a metal. Analysis of those crystal structures of high–temperature superconductors containing copper which are known at this point reveals the following basic structural features:

1. The structures of the high–temperature superconductors are derived from the ion–deficient perovskite ABO_{3-y}. These layered structures accordingly have a substantial number of anion vacancies, so the oxygen concentration in a compound can be varied over a substantial range by firing the compound in media with various oxygen partial pressures.

2. The copper atoms occupy B positions of the perovskite ABO_{3-y}. All of the structures necessarily contain Cu–O planes oriented perpendicular to the z axis.

The high-temperature superconductors which have been synthesized so far contain only copper atoms in the B sublattice. In an effort to determine whether it is possible to synthesize new superconducting materials we have solved the problem of modeling perovskite–like structures which contain barium, oxygen, and two types of metal atoms in the B sublattice. As the atoms of the second type we used scandium. We have also synthesized and studied single–phase metal–oxide compounds based on scandium: $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$.

The nuclear–magnetic–resonance (NMR) method makes it possible to obtain important information about both the crystal structure and the electronic properties of these compounds. The absence of conduction electrons ($Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$ are insulators) makes these compounds convenient models for studying electron–nucleus exchange interactions casued in perovskite–like structures by localized $3d^9$ electrons of Cu^{2+} ions.

1. SAMPLES

As the initial materials for synthesizing the samples of $Ba_2ScCuO_{4.5}$, $Ba_3Sc_4Cu_3O_{12}$, and $Ba_2Sc_2O_5$ we used $BaCO_3$ (analytically pure), Sc_2O_3, and CuO (chemically pure). The synthesis was carried out by a two–step firing: first at 900 °C for 12 h and then at 1000 °C for 40–60 h, with intermediate regrinding. We used x–ray diffraction to verify that the samples consisted of a single phase (in an FR-552 monochromator chamber with Cu $K\alpha_1$ radiation).

It was established by x–ray structural analysis that the compound $Ba_2ScCuO_{4.5}$ crystallizes in tetragonal symmetry with unit–cell parameters $a = b = 8.193(1)$ Å, $c = 7.960(2)$ Å. The structure of $Ba_3Sc_4Cu_3O_{12}$ is more complex and has not been completely determined, but it has been established to be a derivative of the perovskite structure, like that of $Ba_2ScCuO_{4.5}$.

Figure 1 shows the crystal structure of the compound $Ba_2ScCuO_{4.5}$. We see that Sc–O layers alternate with Cu–O layers. The scandium ions occupy hexacoordination crystal positions at lattice sites, forming a stable ScO_6 octahedron. Note that the probability for the filling of the vertices of this octahedron by oxygen ions is unity; i.e., it can be asserted that there is essentially no electric field gradient at the center of the ScO_6 octahedron, which is the position of the Sc ion. In the Cu–O layers, in contrast, the filling of the oxygen positions amounts to 0.25, as follows from the stoichiometry. This circumstance is very important for a subsequent analysis of the spectra of ^{45}Sc in these compounds.

There are no Cu–O layers in $Ba_2Sc_2O_5$, so the unit–cell parameters are half those of $Ba_2ScCuO_{4.5}$: $a = b = 4.160$ Å, $c = 3.994$ Å. The ScO_6 octahedra are retained, but we conclude from the composition of the compound $Ba_2Sc_2O_5$ that the probability for the filling of any oxygen position in the octahedron is 5/6.
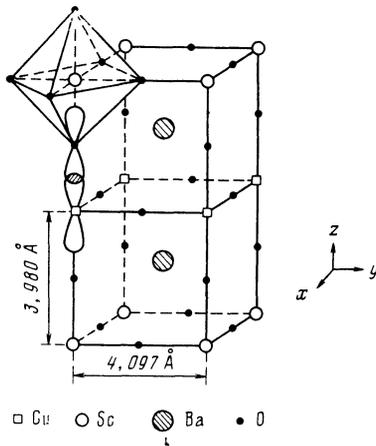
0038-5646/89/061229-06$04.00

FIG. 1. Fragment of the crystal structure of $Ba_2ScCuO_{4.5}$.

□ Cu   ○ Sc   ◉ Ba   ● O

FIG. 3. Temperature dependence of the reciprocal of the Knight shift, $1/K = f_L/(f - f_L)$, for the compounds (○) $Ba_2ScCuO_{4.5}$ and (●) $Ba_3Sc_4Cu_3O_{12}$.

2. KNIGHT SHIFT

Figure 2 shows NMR spectra measured at ^{45}Sc nuclei ($f_L = 72.914$ MHz) for the compound $Ba_3Sc_4Cu_3O_{12}$ at various temperatures. These measurements were carried out with a CXP-300 spectrometer (manufactured by Bruker, FRG), combined with a flow–through CF-1200 cryostat (manufactured by Oxford Innstruments, England). The samples were crushed beforehand to a particle size on the order of 20–50 μm. It can be seen from Fig. 2 that the spectrum consists of a wide line and a narrow line, so we used the "solid–echo" method to detect this spectrum. That method makes it possible to distinguish the wide-component signal from the "ringing" of the detector. A line of exactly the same shape is observed in the NMR spectrum of ^{45}Sc in the compound $Ba_2ScCuO_{4.5}$, so we will take a more detailed look at the characteristics of this line.

Figure 3 shows the temperature dependence of the reciprocal of the Knight shift, $1/K$, for $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$. It can be seen from this figure that the values of $1/K$ for these two compounds are essentially the same over the entire temperature range. This agreement is evidence that the crystals of the two materials contain the same structures, which is responsible for the narrow line in the NMR spectrum of ^{45}Sc of these compounds. In additio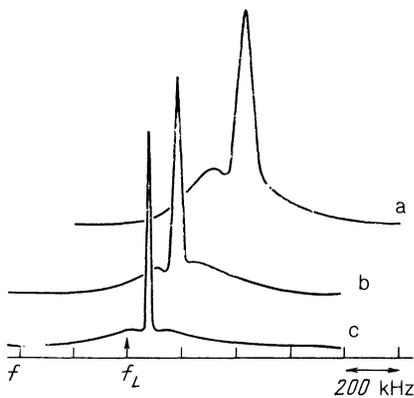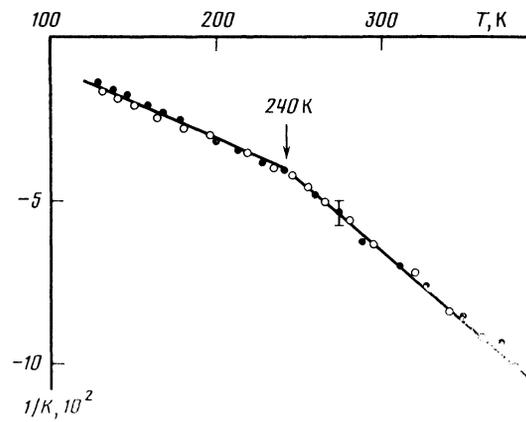n, the same physical mechanism governs the temperature dependence of this line in the two materials. This structural basis in $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$ is the ScO_6 octahedron. Let us examine the mechanism for determining the negative Knight shift of the line of ^{45}Sc nuclei in these compounds. It can be seen from Fig. 1 that the crystal structure of $Ba_2ScCuO_{4.5}$ has a regular alternation of Sc^{3+} and Cu^{2+} ions along the z axis. In all cases, these ions are separated by an O^{2-} oxygen ion. Since the Cu-O distance along the z axis ($c/2 = 1.99$ Å) is smaller than the Cu-O distance in the ab plane ($a/2 = b/2 = 2.049$ Å), the greatest overlap will be that of the wave functions of the p_z orbitals of oxygen and the d_{z^2} orbitals of copper, which correspond to the half-filled highest level of the Cu^{2+} ion in the $3d^9$ electron configuration. In turn, the p_z orbital of the O^{2-} ion overlaps the p_z orbital of the Sc^{3+} ion; this overlap gives rise to a hyperfine exchange interaction between the magnetic moment of a $3d^9$ electron (this moment is localized at the Cu^{2+} ion) and the ^{45}Sc nuclear spin.

The Hamiltonian of the direction of nuclear spin $\mathbf{I}$ (^{45}Sc) and the electron spin $\mathbf{S}$ ($3d^9$, Cu^{2+}) in the magnetic field $\mathbf{H}_0$ can be written

$$H = -\gamma_n \hbar \mathbf{I}\mathbf{H}_0 - \gamma_e \hbar \mathbf{S}\mathbf{H}_0 + \mathbf{I}[A]\mathbf{S} + H_Q, \tag{1}$$

where $[A]$ is a symmetric second–rank tensor, and γ_e and γ_n are the gyromagnetic ratios of the electron and the ^{45}Sc nucleus, respectively, and H_Q is the Hamiltonian of the quadrupole interactions.[2] Here we are not considering the term which describes the interaction of spin $\mathbf{I}$ with the conduction electrons, since $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$ are insulators. Furthermore, we can ignore the quadrupole contribution H_Q in the Hamiltonian (1) because, as we mentioned earlier, there is no significant electric field gradient at the center of the ScO_6 octahedron. The spin Hamiltonian (1) ignores interactions which are responsible for relaxation in the electron spin system. It can be assumed, however, that the correlation times τ_e for fluctuations of the electron spins are shorter than the Larmor precession period of the nuclear spin in the field of the electrons (i.e., $\tau_e^{-1} > |AS/\hbar|$).[2] For this reason, the nuclear magnetization is acted upon only by the average strength of this field, which is in turn proportional to the average value of the spin, $\langle \mathbf{S}\rangle$. The effective Hamiltonian for the nuclear spin can thus be written

FIG. 2. NMR spectra of ^{45}Sc in the compound $Ba_3Sc_4Cu_3O_{12}$, measured at (a) 140, (b) 230, and (c) 375 K.

$$H_n = -\gamma_n \hbar I H_0 + I[A]\langle S\rangle. \tag{2}$$

Using only the z component of the tensor $[A]$ (i.e., ignoring the partial polarization of the p_x and p_y orbitals of the Sc^{3+} ion), we find an expression for the resonant frequency:

$$\omega = |\gamma_n H_0 - \langle S_z\rangle A/\hbar|. \tag{3}$$

The average value of the spin, $\langle S_z\rangle$, is related to the average value of the spin magnetic moment, $\langle \mu_z\rangle$, by

$$\langle S_z\rangle = \langle \mu_z\rangle / \gamma_e \hbar,$$

where $\langle \mu_z\rangle = \chi H_0$, and χ is the magnetic susceptibility. We thus find from (3)

$$\omega = \gamma_n H_0 |1 - A\chi/\hbar^2 \gamma_n \gamma_e|. \tag{4}$$

The relative Knight shift is

$$K = \Delta\omega/\omega_0 = -A\chi/\hbar^2 \gamma_n \gamma_e. \tag{5}$$

To determine the reduced electron–nucleus interaction constant $A/\gamma_n \hbar$, we carried out an independent measurement of the magnetization M with a PARC-153 vibration magnetometer (manufactured in the US). Figure 4 shows the temperature (T) dependence of $1/M$. It can be seen from this figure that in the temperature range 50–300 K the susceptibility per magnetic Cu^{2+} ion obeys the Curie–Weiss law

$$\chi = \frac{\mu_B^2 p^2}{3k_B(T-\Theta)}, \tag{6}$$

where our measurements yield the following values for the parameters p (the number of Bohr magnetons per magnetic center) and Θ (the Curie temperature): $p = 1.55$ (the theoretical value is $^3p = 1.73$) and $\Theta \approx 20$ K. At $T_N \approx 13$ K, there is a transition to an antiferromagnetic state. Substituting (6) into (5), we find

$$K = \frac{A}{\hbar^2 \gamma_n \gamma_e} \frac{\mu_B^2 p^2}{3k_B(T-\Theta)} = -\frac{K_0}{T-\Theta}. \tag{7}$$

The electron–nucleus interaction constant is therefore

$$A/\gamma_n \hbar = \frac{\mu_B^2 \hbar \gamma_e}{3k_B p^2} K_0. \tag{8}$$

The parameter K_0 can be found from the slope of the linear region of the $K^{-1} = K_0^{-1}(T - T_0)$ dependence (Fig. 3). The constants $A/\gamma_n \hbar(kOe)$ calculated in this fashion for the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$ are as follows:

Temperature interval	$Ba_2ScCuO_{4.5}$	$Ba_3Sc_4Cu_3O_{12}$
140–250 K	15	12
250–380 K	7	7

The abrupt change in the electron–nucleus interaction constant near $T_c \approx 250$ K apparently results from a change in the overlap of the wave function of the Sc^{3+}, Cu^{2+}, and O^{2-} ions. It may be that this effect stems from an order-disorder phase transition in the filling of oxygen vacancies in the Cu–O layers, accompanied by an abrupt change in the polarization of the electron shells.

3. LINESHAPE

The asymmetry of the ^{45}Sc line (see the inset in Fig. 5) appears to be a consequence of an anistropy of the dipole fields produced by localized magnetic moments of Cu^{2+} ions at the position of the ^{45}Sc nucleus. Let us consider the field produced by the two Cu^{2+} ions nearest a ^{45}Sc nucleus (these ions lie on the z axis along with the scandium nucleus; (Fig. 1):

$$H_{dip} = \frac{2\langle \mu(T)\rangle}{r^3}(3\cos^2\theta - 1) = H_{dip}(T)(3\cos^2\theta - 1), \tag{9}$$

where θ is the angle between the z axis and the direction of magnetic field H_0. The resonant frequency is given by

$$f = f_0 + \tfrac{1}{2}\alpha(3\cos^2\theta - 1) \tag{10}$$

[the isotopic shift is incorporated in f_0; $\alpha/2 = H_{dip}(T)\gamma_n/2\pi$]. Under condition (10), the spectrum of a powdered sample assumes the characteristic asymmetric shape in the inset in Fig. 5, with a width $\Delta f = (3/2)\alpha$ (Ref. 4). The
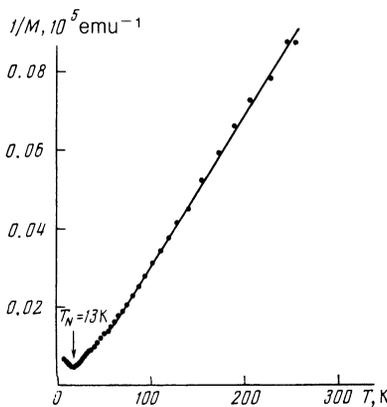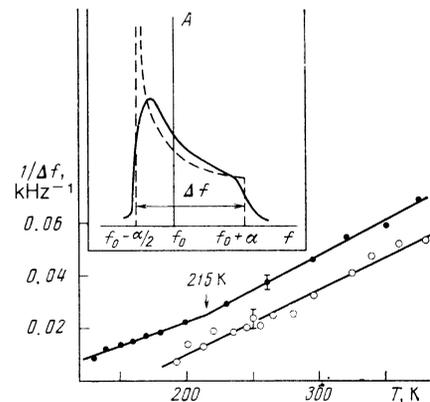

FIG. 4. Temperature dependence of the reciprocal magnetization $1/M$ of the compound $Ba_2ScCuO_{4.5}$, measured in a static magnetic field $H = 2.2$ kOe.

FIG. 5. The reciprocal width $(1/\Delta f)$ of the narrow line in the NMR spectrum of ^{45}Sc in samples of (○) $Ba_2ScCuO_{4.5}$ and (●) $Ba_3Sc_4Cu_3O_{12}$. The inset shows a theoretical prediction (the dashed line) and the actual shape of the line (solid line) for anisotropic NMR spectra of powdered samples.[4]

temperature dependence of the anisotropic width of the spectrum is determined by the quantity

$$H_{dip}(T) = \frac{2\langle\mu(T)\rangle}{r^3} = \frac{2\mu_B^2 \; H_0 p^2}{3k_B T r^3},$$

$$\Delta f(T) = {}^3/_2\alpha(T) = \frac{\gamma_n \mu_B^2 \; H_0 p^2}{\pi k_B r^3 T} = F_0/T. \quad (11)$$

Substituting the values $r = r_z$ (Sc–Cu) $= 3.980$ Å (for the compound $Ba_2ScCuO_{4.5}$) and $p = 1.55$ (p was found from independence measurements of the magnetic susceptibility; Sec. 2) into (11), we find that the constant $1/F_0$ has the value 2.7×10^{-4} $kHz^{-1} \times K^{-1}$. Figure 5 shows the temperature dependence of the reciprocal width $1/\Delta f$ of the narrow ^{45}Sc spectral line of the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$. These plots are linear, in accordance with (11); for the $Ba_2ScCuO_{4.5}$ sample we find the following value from the slope: $1/F_0(expt.) = \tan\alpha = 2.4 \times 10^{-4}$ $kHz^{-1}\cdot K^{-1}$, in good agreement with the calculated value. For the $Ba_2Sc_4Cu_3O_{12}$ sample the linear dependence of $1/\Delta f$ on T changes slope slightly at $T \approx 215$ K. The value of $1/F_0(expt.)$ for the high–temperature region is 2.6×10^{-4} $kHz^{-1}\cdot K^{-1}$, and that for the low-temperature region is 1.8×10^{-4} $kHz^{-1}\cdot K^{-1}$.

Up to this point we have considered only the narrow line in the NMR spectrum of ^{45}Sc in the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$. The origin of the broad line ($\Delta \sim 350–550$ kHz), present in the spectra of both compounds, is not completely clear, but it can be suggested that this line results from a quadrupole splitting of the ^{45}Sc line due to large electric field gradients which arise at lattice defects.

4. LONGITUDINAL AND TRANSVERSE RELAXATION OF ^{45}Sc NUCLEI IN THE COMPOUND $Ba_3Sc_4Cu_3O_{12}$

Figure 6 shows the temperature dependence of the longitudinal relaxation rate $R_1(T) = 1/T_1(T)$ for the compound $Ba_3Sc_4Cu_3O_{12}$ (curves 2 and 3). The relaxation was measured from the height of the maximum of the narrow line, by the saturation recovery method. In analyzing the experimental saturation–recovery curve, we made a least–squares fit of this curve by the five–parameter, two–exponential function.

$$I = I_0 - I_1 \exp(-t/T_1^{(1)}) - I_2 \exp(-t/T_1^{(2)}).$$

The presence of two exponential functions (curves 2 and 3 in Fig. 6) is evidence of either two relaxation mechanisms or the existence of different relaxation rates for the transitions between the Zeeman levels E_m and E_{m-1}, where $m = \pm\frac{7}{2}$, $\pm\frac{5}{2}$, $\pm\frac{3}{2}$, $\pm\frac{1}{2}$. The position of the broad minimum on the $R_1^{(1)}(T)$ and $R_1^{(2)}(T)$ curves coincides with the temperature of the slope change on the curves of the reciprocal Knight shift $K^{-1}(T)$ (Fig. 3). In the same temperature region we see a structural feature on the temperature dependence of the transverse relaxation rate $R_2(T)$ (curve 1 in Fig. 6). This circumstance is indirect support for the suggestion of a structural transition at $T \sim 240–250$ K in the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$. Unfortunately, the origin of the high–temperature structural features on the $R_1(T)$
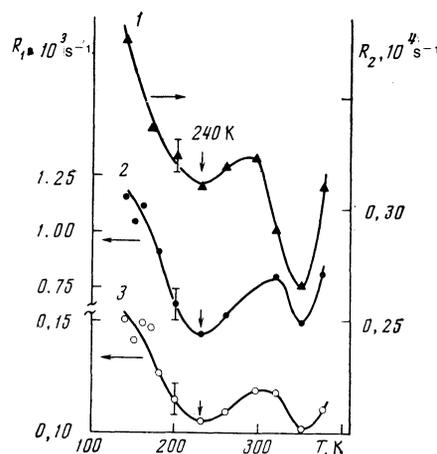

FIG. 6. Temperature dependence of the longitudinal ($R_1 = 1/T_1$) and transverse ($R_2 = 1/T_2$) relaxation rates of ^{45}Sc nuclei in the compound $Ba_3Sc_4Cu_3O_{12}$. 1—Transverse relaxation; 2—fast longitudinal relaxation; 3—slow longitudinal relaxation.

and $R_2(T)$ curves is not clear at this point.

5. SPECTRUM OF THE COMPOUND $Ba_2Sc_5O_5$

In addition to the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$, we studied the NMR spectra of ^{45}Sc in ceramic $Ba_2Sc_2O_5$ over the temperature range 130–375 K. This compound is another insulator, and, as we mentioned back in Sec. 1, its structure is analogous to the perovskite structure of $Ba_2ScCuO_{4.5}$ (Fig. 1), in which there are no Cu–O layers. Furthermore, this ceramic has the important distinguishing feature that there is a single oxygen vacancy in the ScO_6 octahedron. These aspects of the crystal structure qualify the compound $Ba_2Sc_2O_5$ as an interesting model for NMR studies: First, the absence of copper atoms makes it possible to test the hypothesis (mentioned above) that the paramagnetic Cu^{2+} ions influence the Knight shift and line-shape of the ^{45}Sc spectrum of the ceramics $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$, which do contain copper. Second, the defectiveness in terms of oxygen makes it possible to study the mobility of oxygen among vacancies in a perovskite-like structure which is similar to the structure of high–temperature superconductors.

Figure 7 shows the NMR spectrum of ^{45}Sc in ceramic $Ba_2Sc_2O_5$ measured at 135 K (curve 1). Note the following features of this spectra: 1) The Knight shift is very small and positive, given by

$$K = \Delta f/f \approx 4 \text{ kHz}/72914 \text{ kHz} \approx 0.005\%;$$

2) the position of the central line in the spectrum does not depend on the temperature. It appears to us that each of these features can be linked in a natural way with the absence of paramagnetic Cu^{2+} ions from the crystal structure of the ceramic $Ba_2Sc_2O_5$. Those ions cause a negative Knight shift, substantial in magnitude and inversely proportional to the temperature, in the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$, which do contain copper (Sec. 2).

The lineshape in Fig. 7 (curve 1) is characteristic of the spectrum of a powdered sample in the presence of a quadrupole broadening in first-order perturbation theory.[5] In this approximation, and in the case of an axisymmetric tensor of the electric field gradient, the rate of the transition between levels m and ($m - 1$) is determined by[5]
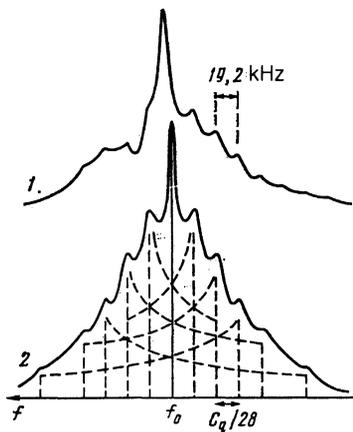
1232   Sov. Phys. JETP **68** (6), June 1989

Gippius *et al.*   1232

FIG. 7. 1—NMR spectrum of ^{45}Sc in the compound $Ba_2Sc_2O_5$, measured at 135 K; 2—theoretical spectrum calculated in the approximation of first-order quadrupole broadening for a spin $J = 7/2$.

$$f_{m,(m-1)}=f_L+\frac{3(2m-1)}{4J(2J-1)}\frac{eQq_{zz}}{h}\frac{3\cos^2\theta-1}{2},\qquad(12)$$

where q_{zz} is the z component of the field gradient tensor, $J(^{45}Sc) = 7/2$ is the magnetic moment of the nucleus, $Q(^{45}Sc) = -0.22\times10^{-24}$ esu is the nuclear quadrupole moment, and f_L is the Larmor frequency. Substituting the value $J = 7/2$ into (12), we find

$$f_{m,(m-1)}=f_0+(C_q/56)(2m-1)f(\theta),\qquad(13)$$

where $f(\theta) = 3\cos^2\theta - 1$, and $C_q = eQq_{zz}/h$ is the quadrupole interaction constant. Since the projection of the nuclear magnetic moment $J = 7/2$ onto the z axis can take on the values $m = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \pm\frac{7}{2}$, we find from (13)

$$f_{+\frac{1}{2},-\frac{1}{2}}=f_0,\quad f_{\pm\frac{3}{2},\pm\frac{1}{2}}=f_0\pm(C_q/28)f(\theta),\qquad(14)$$

$$f_{\pm\frac{5}{2},\pm\frac{3}{2}}=f_0\pm(C_q/14)f(\theta),\quad f_{\pm\frac{7}{2},\pm\frac{5}{2}}=f_0\pm(3C_q/28)f(\theta),$$

The expressions for the transition frequencies in (14) are of the form

$$f=f_0\pm\tfrac{1}{2}\alpha(3\cos^2\theta-1).$$

The lineshape of a powdered sample for a frequency dependence of this type was discussed back in Sec. 3 and is shown in the inset in Fig. 5 (Ref. 4). Taking all the transitions in (14) into account, we find the resultant theoretical lineshape shown by curve 2 in Fig. 7.

It can be seen from Fig. 7 that the theoretical shape of the spectrum generally reflects the basic features of the experimental spectrum measured at $T = 135$ K (curve 1 in Fig. 7): the presence of a central peak, which is evidence of a small asymmetry parameter $\eta = |(q_{xx} - q_{yy})/q_{zz}|$ (Ref. 4), and an equidistant spacing of the main satellites. There are some distinctions, which possibly stem from the existence of additional forbidden transitions with $\Delta m = 1$ and also the influence of a second-order quadrupole broadening.

The average distance between the peaks in the spectrum is $C_q/28 = 19.2$ kHz; i.e., the quadrupole interaction constant C_q is 538 ± 8 kHz. We can thus determine the z component of the field gradient tensor:

$$|q_{zz}|=C_qh/e|Q|\approx0.33\cdot10^{14}\text{ esu.}$$

Knowing the Sc–O distance along the z axis(1.997 Å; Sec. 1), we can calculate the parameter q_{zz} in the point-charge approximation: $|q_{zz}| = 2e/r^3 = 1.21\cdot10^{14}$ esu. In other words, this parameter is predicted to have a value 3.6 times its experimental value. The discrepancy may stem from some averaging of the field gradient tensor due to fast vibrational motions of the ScO_6 octahedron[6] and also abrupt transitions of oxygen vacancies from one vertex of an octahedron to another. This question will be studied in more detail in the following section of this paper.

6. SPIN-LATTICE RELAXATION IN CERAMIC $Ba_2Sc_2O_5$

As was shown above, the spectrum of the compound $Ba_2Sc_2O_5$ indicates that the interaction of the ^{45}Sc nucleus with the oxygen atoms at the vertices of the ScO_6 octahedron is of a purely quadrupole nature. The literature (e.g., Refs. 7 and 8) reveals that in high-temperature superconductors, and also in a nonsuperconducting metal–oxide ceramic with an oxygen deficiency, the mobility of oxygen among vacancies is quite high. In the compound $Ba_2Sc_2O_5$, for example, the position of an oxygen vacancy in the ScO_6 octahedron may change abruptly, because of the mobility of the oxygen atoms. Such abrupt changes cause fluctuations in the electric field gradient.

Analyzing possible mechanisms for the nuclear relaxation of ^{45}Sc in ceramic $Ba_2Sc_2O_5$, we should note the following.

1. Since there are no conduction electrons ($Ba_2Sc_2O_5$ is an insulator), we can completely ignore the Korringa relaxation involving free electrons.

2. The Sc–Sc distance in the ab plane is 4.160 Å (Sec. 1), so the intensity of the dipole-dipole relaxation ($\propto 1/r^3$) is low, and that relaxation mechanisms can also be ignored.

3. Since $Ba_2Sc_2O_5$ contains no copper atoms, there is absolutely no nulcear relaxation mechanism as a result of fluctuations in the hyperfine field induced at the ^{45}Sc nucleus by the polarization of the electron orbitals by the localized magnetic moment of the Cu^{2+} ion.

It can thus be suggested that the primary mechanism for nuclear relaxation in $Ba_2Sc_2O_5$ is quadrupole relaxation caused by the mobility of oxygen at the vertices of the ScO_6
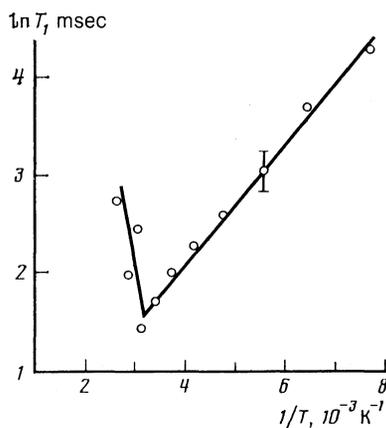

FIG. 8. Temperature dependence of the spin–lattice relaxation time of ^{45}Sc nuclei in the compound $Ba_2Sc_2O_5$, in the coordinates $\ln T_1 = F(1/T)$.

octahedron. In this case the longitudinal relaxation can be described by the Arrhenius law[5]

$$T_1 \sim \exp(\pm V_0/k_B T), \qquad (15)$$

where T_1 is the spin–lattice relaxation time, and V_0 is the potential barrier which opposes the motion of oxygen. The plus sign in (15) corresponds to very slow displacements of the oxygen ($\omega_0 \tau_c \gg 1$), and the minus sign to fast hops ($\omega_0 \tau_c \ll 1$). Here τ_c is the correlation time of the fluctuations in the electric field gradient, which is equal to the average lifetime of an oxygen vacancy at some fixed vertex of an ScO_6 octahedron, and $f_q = \omega_q/2\pi$ is the quadrupole relaxation frequency, which for the transition $\pm 3/2 \leftarrow \rightarrow \pm 1/2$ is on the order of $C_q/28 \approx 20$ kHz, according to (14).

Figure 8 shows the temperature dependence of the spin–lattice realxation time of ^{45}Sc in the compound $Ba_2Sc_2O_5$ in the coordinates $\ln T_1 = F(1/T)$. The relaxation was measured by the saturation recovery method (Sec. 2) on the basis of the height of the central peak. It can be seen from this figure that the Arrhenius law (15) holds for slow reorientations ($\omega_0 \tau_c \gg 1$) in the temperature range 130–320 K. The height of the potential barrier found from the slope of the linear region of the plot of $\ln T_1 = F(1/T)$ is $V_0^{(1)} \approx 600$ K. The second linear region (320–375 K) corresponds to fast motions of the oxygen atom ($\omega_0 \tau_c \ll 1$) with a potential barrier $V_0^{(2)} \approx 2300$ K. Near the minimum ($T_{min} = 320$ K) the relation $\omega_0 \tau_c \sim 1$ apparently holds; i.e., the characteristic lifetime of an oxygen vacancy at a fixed site is $\sim 10^{-8}$–10^{-9} s.

In addition to the component due to the hopping mobility of oxygen, there may be a component of the nuclear relaxation due to fast vibrational motions of the entire ScO_6 octahedron around the fourfold tetragonal c axis[6], which would also cause fluctuations of the electric field gradient at the ^{45}Sc nucleus. For the perovskite $BaTiO_3$, of similar structure, the time scale of these fluctuations is[6] $\sim 10^{-13}$–10^{-14} s.

CONCLUSION

We have carried out a complex study of a new Ba–Sc–Cu–O perovskite system by the method of NMR spectroscopy. The temperature dependence of the reciprocal of the Knight shift, $K^{-1}(T)$, and that of the longitudinal and transverse relaxation rates $R_1(T)$ and $R_2(T)$ of the compounds $Ba_2ScCuO_{4.5}$ and $Ba_3Sc_4Cu_3O_{12}$ have structural features in the temperature region 230–250 K. We believe that these features can be linked with the existence of a structural transition (e.g., an order–disorder transition) in this temperature interval, which causes changes in the degree of overlap of the wave functions of electrons localized at ions of scandium, oxygen, and copper. In the process there would be an abrupt change in the electron–nucleus exchange interaction constant. Confirming this suggestion and identifying the nature of this transition, which is characteristic of perovskite–like metal–oxide compounds, will reqiuire further and more detailed research (in particular, low-temperature x–ray structural measurements).

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] A. Narat, *Hyperfine Interactions in Solids* (Russ. Transl. Mir, Moscow, 1970).

[3] S. V. Vonsovskiĭ, *Magnetizm*, Nauka, Moscow, 1971, p. 90 (Magnetism, Halsted, New York, 1975).

[4] J. Winter, *Magnetic Resonance in Metals*, Oxford, Univ. Pree, London, 1971 (Russ. Transl. Mir. Moscow, 1971, p. 124).

[5] V. S. Grechishkin, *Yadernye kvadrupol'nye vzaimodeĭstviya v tverdykh telakh (Nuclear Quadrupole Interactions in Solids)*, Nauka, Moscow, 1973.

[6] R. Blinz and B. Jacksch, *Ferroelectrics and Antiferroelectrics: Lattice Dynamics* (Russ. Transl. Mir, Moscow, 1975).

[7] L. T. Willie, A. Berera, and D. de Fontaine, Phys. Rev. Lett. **60**, 1065 (1988).

[8] W. K. Ford, C. T. Chen, and J. Anderson *et al.*, Phys. Rev. B **37**, 6924 (1988).

Translated by Dave Parsons