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Quasi-one-dimensional magnetic properties of the $(In;Sc;Lu;Y)_2Cu_2O_5$ oxides

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Abstract. The intrachain and interchain magnetic interactions in the $(In;Sc;Lu;Y)_2Cu_2O_5$ ternary oxides have been estimated on the basis of the Heisenberg chain model for $S = 1/2$, taking into account only the high-temperature experimental data of the magnetic susceptibility. We have also calculated the first three coefficients in the high-temperature expansion series of the magnetic susceptibility for the three-dimensional model of weakly coupled Heisenberg chains. The temperature dependence of the magnetic susceptibility has been compared with the predictions of the models mentioned above. The theoretical values of T_N, obtained by numerical calculations of the Oguchi expression, are in good agreement with experiment. The applied model of the ferromagnetic chains being mutually weakly coupled antiferromagnetically turns out to be a good approximation for the real magnetic system existing in the $(In;Sc;Lu;Y)_2Cu_2O_5$ oxides.

1. Introduction

The discovery of the high-T_c superconductivity in ceramic oxides has intensified the study of the related non-superconducting parent compounds as well. On the basis of recent results it appears that this magnetism may play an essential role in the high-T_c superconductivity mechanism and hence numerous physicists have shown a considerable interest in the magnetic properties of copper-based oxides [1].

Numerous members of the family of isomorphous oxides with the general chemical formula $R_2Cu_2O_5$ (where R = Y, In, Lu, Sc or one of the heavy rare-earth elements from Tb to Yb), crystallize in the $Ho_2Cu_2O_5$-type structure [2–4], where the copper atoms have the 4 + 1 oxygen coordination sphere (see figures 1 and 2). Four oxygen atoms with short Cu–O bonds (1.9–2.1 Å) form a diagonally broken CuO_4 'square', where the Cu–O distance with the fifth oxygen atom is quite large, ranging from 2.7 to 2.9 Å. The distances given above refer to the $Y_2Cu_2O_5$ case [3, 4]. As figure 1 indicates, the Cu(1)–Cu(2) dimer units are linked by the O(3) atoms in zig-zag alternating chains along the b-axis. For the Cu^{2+} d^9 configuration, the $d_{x^2-y^2}$ orbitals (lying approximately in the deformed CuO_4 plane) are expected to be half filled, while the d_{z^2} orbitals are oriented towards the O(3) atoms and are expected to be completely filled (see figure 2). Taking into account the direct intrachain distances between the Cu(1) and Cu(2) atoms, which are well separated, that is 2.8–3.2 Å, we see that only the superexchange interactions via oxygen atoms come into play. The intrachain superexchange paths via only one oxygen atom are nearly identical, with the Cu–O–Cu angle being approximately

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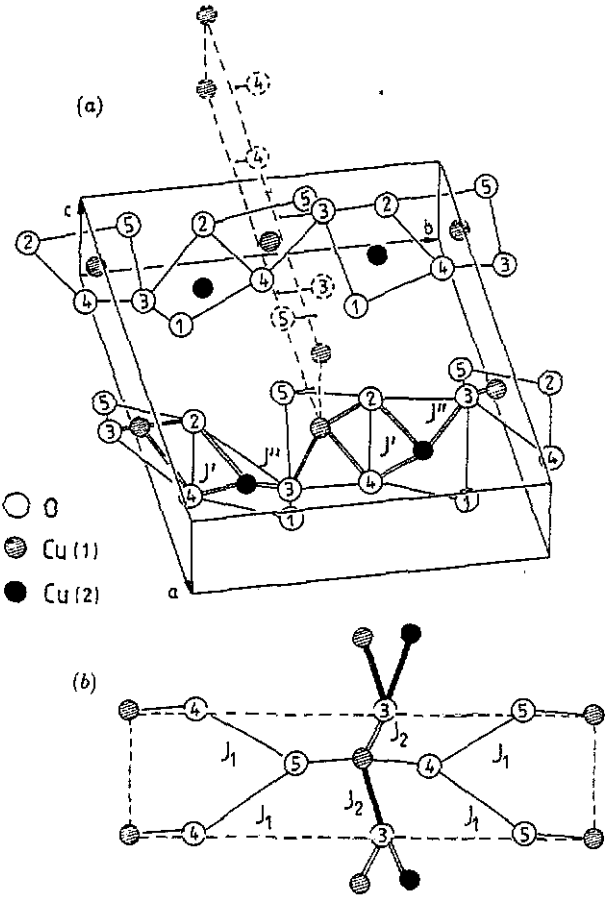

Figure 1. The $Ho_2Cu_2O_5$ type of structure of space group $P2_1nb$. (*a*) The unit cell is illustrated by the full lines. The Cu(1) and Cu(2) atoms, each surrounded by four oxygen atoms, arranged in the diagonally broken 'squares', form the pronounced chains along the *b*-axis. The intrachain superexchange interactions, designated by *J'* and *J''*, are illustrated by the double full lines. The interchain superexchange interactions, described by the integrals J_1 and J_2, are presented by means of the projection of the intervening oxygen atoms (4 and 5) onto the plane containing five Cu(1) atoms. This is shown by the broken lines. (*b*) The full projection onto the plane described above, where the possible interchain ferromagnetic superexchange interactions between the Cu(1) and Cu(2) or the Cu(1) atoms along the *c*-axis are shown by means of the half-filled $d_{x^2-y^2}$ orbitals (denoted by the double full line) and completely filled d_{z^2} orbitals (denoted by the bold full line). For details also see figure 2.

90°. These ferromagnetic interactions involve two half-filled $d_{x^2-y^2}$ orbitals of adjacent copper ions. The possible interchain superexchange interactions are as follows:

(i) the ferromagnetic interactions along the *c*-axis, via the O(3) atom, between half-filled $d_{x^2-y^2}$ and filled d_{z^2} orbitals (we believe we may neglect these interactions) and

(ii) the antiferromagnetic ones acting on the long paths

Cu(1)–O(4)–O(5)–Cu(1)–O(4)– . . .

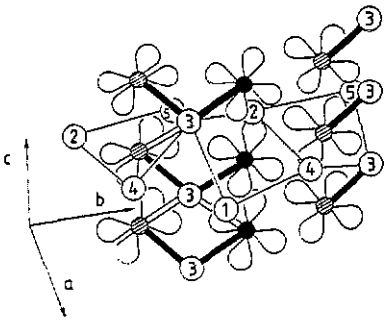

Figure 2. The spatial orientation of the $d_{x^2-y^2}$ orbitals which lie within the deformed CuO_4 'square' is shown schematically. The d_{z^2} orbitals are shown by means of the bold full line and are directed towards the O(3) atoms.

and

$$Cu(2)–O(1)–O(2)–Cu(2)–O(1)–\ldots$$

between two half-filled $d_{x^2-y^2}$ orbitals (see figure 1).

All these interactions we show in figure 1, namely the intrachain ones are illustrated by the double full lines and are designated by the corresponding exchange parameters J' and J'' (see figure 1(a)). In turn, the interchain interactions are designated by J_1 and J_2 (see figure 1(b)). We note that J' is associated with two intrachain superexchange paths Cu(1)–O(2)–Cu(2) and Cu(1)–O(4)–Cu(2), whereas J'' corresponds to one path Cu(2)–O(3)–Cu(1). Hence, we may expect that $J' \simeq 2J''$. We have tried to evaluate these magnetic interactions, that is the intrachain interactions described by only one effective parameter J and the sum of the interchain interactions zJ (see below), taking into account the experimental data for the powder magnetic susceptibility, $\chi(T)$, measured in the temperature range 4.2–1000 K, except for $Lu_2Cu_2O_5$. In the latter case we have utilized the experimental data for the magnetic susceptibility of the powder, measured in the temperature range 4.2–300 K only [5, 6].

A careful examination of the Cu–O bonds [3, 4] leads one to the conclusion that the distinct dominance of the intrachain ferromagnetic interactions over those acting between chains can be sufficient to cause the one-dimensional magnetic behaviour in the $(In;Sc;Lu,Y)_2Cu_2O_5$ oxides. Hence it seems justified to use the $S = 1/2$ Heisenberg chain model. In this model, which appears to be very appropriate for a number of Cu^{2+}-containing compounds [7], the temperature dependence of the susceptibility may be compared with that of the theoretical prediction. Previously, a similar investigation to that proposed above has been carried out by Ramakrishna *et al* [8], who have also interpreted the magnetic susceptibility of $Y_2Cu_2O_5$ on the basis of the $S = 1/2$ Heisenberg chain model. Very recently Paillaud *et al* [9] have also determined the values of the parameters J', J'' and zJ, for all the compounds considered here, on the basis of the numerical solution of the J-alternating, Heisenberg finite-chain model [10]. The authors of [8, 9] have taken into account the susceptibility data obtained in the temperature range only between 4.2 and 300 K. Our theoretical results, found by fitting the experimental susceptibility in the range 4.2–1000 K, are in good agreement with those given by Ramakrishna and co-workers and do not agree with the data given above by Paillaud and co-workers.

2. Experimental details

Syntheses of the powder samples of the considered compounds were carried out as described elsewhere [5, 6]. The magnetic susceptibility measurements of the ternary

oxides considered here were made over the temperature range 4.2–300 K on an RH Cahn electrobalance, whereas at temperatures 300–1000 K an Obuszko electrobalance was used.

3. Results and discussion

Since there is no theoretical work in the literature treating an alternating chain model, except for some numerical results obtained by Duffy and Barr [10], we have used a uniform chain model with only one effective parameter J describing the intrachain interactions. Using the mean-field approximation (MFA) argument only, in the alternating chain model, the paramagnetic Curie temperature is $\theta_p = (J' + J'')/2k_B$ [10] and hence we may expect that $J \simeq (J' + J'')/2$. Thus the temperature dependence of the magnetic susceptibility is [11]

$$\chi_{ch}(T) = [Ng^2\mu_B^2 S(S+1)/3k_BT]F(K) \qquad K = J/2k_BT \tag{1}$$

$$F(K) = [(1 + 5.7979916\,K + 16.902653\,K^2 + 29.376885\,K^3 + 29.832959\,K^4 + 14.03618\,K^5)/(1 + 2.7979916\,K + 7.008678\,K^2 + 8.6538644\,K^3 + 4.5743114\,K^4)]^{2/3}. \tag{2}$$

If we also take into account the interchain interactions in the MFA the magnetic susceptibility for the considered system can be expressed as follows [12]:

$$\chi(T)^{-1} = \chi_{ch}(T)^{-1} - 2zJ/Ng^2\mu_B^2 \tag{3}$$

where $zJ = 4J_1 + 2J_2 + \ldots$.

This equation was fitted to the experimental points using the two-point (g fixed), nonlinear, least-squares Levenberg–Marquart method. As an initial value of J/k_B we have taken the value of the paramagnetic Curie temperature θ_p, estimated roughly from the slope of the $\chi(T)^{-1}$ curve (in the $S = 1/2$ chain model $\theta_p \equiv J/k_B$). The minimal fitting error has been obtained for the values of the parameters given in table 1.

It is interesting to note that we have also found a nearly identical geometry for the superexchange path to that considered here, that is one involving the two intervening oxygen atoms, in the Bi_2CuO_4-type structure [13]. The value of the corresponding parameter J_1 in Bi_2CuO_4 is in the range 4.5–5.5 K and this value is surprisingly close to that determined in this work for $Sc_2Cu_2O_5$ (see table 1). Moreover, we have also considered the superexchange path, involving only one intervening oxygen atom and designated in this paper by J', in the $BaCuO_2$-type structure [14]. Thus, for this compound the value of parameter J' is 110 K. Therefore, this value appears to be surprisingly close to those determined for the $R_2Cu_2O_5$ oxides, which range between 77 and 163 K.

As seen in figure 3 the Curie–Weiss behaviour is not followed over the whole temperature range investigated. This 'breakdown' of the MFA is caused by neglecting the short-range order (SRO). Since the ratio of the interchain interactions to the intrachain ones is small, only the spin correlations within the chains play a key role at high temperatures. As the temperature is lowered the correlation length becomes sufficiently large and the clusters of ferromagnetically coupled spins are probably formed within the chains. It is well known that the relative importance of SRO is greatly enhanced by lowering the lattice dimensionality. The amount of SRO taken at given k_BT/J for our quasi-1D case is relatively much larger than in the 2D or 3D systems. In addition, the SRO

Table 1. The magnetic characteristics of the $(In;Sc;Lu;Y)_2Cu_2O_5$ oxides.

Compound	$Sc_2Cu_2O_5$	$In_2Cu_2O_5$	$Lu_2Cu_2O_5$	$Y_2Cu_2O_5$
g	2.17	2.075	2.02	2.14 2.108†
	2.09‡	2.18‡	2.22‡	2.19‡
μ_{eff} [μ_B]	1.88	1.80	1.75	1.85 1.82†
	1.81‡	1.89‡	1.92‡	1.90‡
J/k_B [K]	58.2	116.1	122.5	88.2 72†
J'/k_B [K]	242‡	215‡	200‡	100‡
J''/k_B [K]	167‡	157‡	103‡	81‡
zJ/k_B [K]	−18.0	−12.8	−2.8	−1.6 −3.2†
	−32.2‡	−28.9‡	−12.3‡	−12.4‡
$I(\eta)$	2.3	3.7	7.7	9.0
$T_{N,exp}$ [K]	16	30	21	13
$T_{N,calc}$ [K]	25 65‡	31 59‡	16 34‡	10 27‡

† Taken from [8].

‡ Taken from [9]. We have reduced the values of the exchange parameters reported by Paillaud *et al* [9] by a factor of two. This reduction is caused by using a different type of normalization for the exchange parameters.

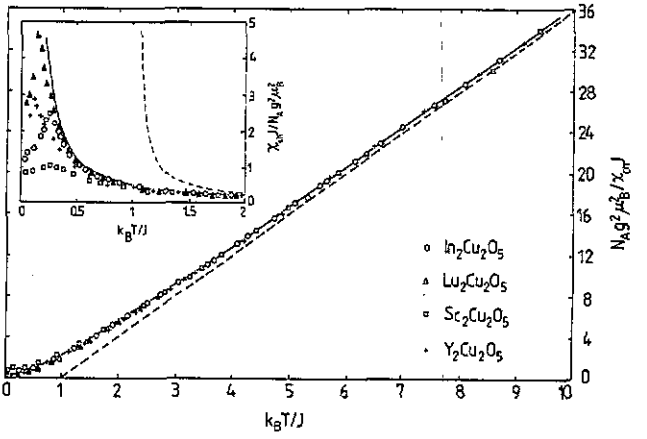

Figure 3. A plot of $N_Ag^2\mu_B^2/\chi_{ch}J$ against kT_B/J where χ_{ch} and J are the susceptibility and the intrachain interaction parameter, both associated with the chain of Cu^{2+} atoms. The full curve is drawn according to equation (1), while the broken curve represents the asymptotic behaviour of the inverse magnetic susceptibility; that is the Curie–Weiss law, $3(k_BT/J - 1)/S(S + 1)$. We have corrected the values for the experimental magnetic susceptibility with respect to the presence of the interchain interactions. Thus, in accordance with equation (3) we have that $N_Ag^2\mu_B^2/\chi_{ch}J = N_Ag^2\mu_B^2/\chi J + 2zJ/J$.

effects are also enhanced by lowering the spin value and they are more pronounced for the isotropic Heisenberg-type interactions than the anisotropic interactions of Ising type [7]. The temperature at which the transition to the 3D magnetic long-range ordering occurs can be well defined from the susceptibility peak, which is also in good agreement with the determination of T_N from the heat capacity experiment [15]. The positive sign of θ_p is consistent with the model of antiferromagnetically coupled ferromagnetic chains. This model, which has been proposed earlier in [8] seems to be verified by neutron diffraction studies of $Y_2Cu_2O_5$ [3, 4], $In_2Cu_2O_5$ [16] and $Lu_2Cu_2O_5$ [17]. We have also verified our estimates of the integrals J and zJ by calculating the theoretical value of T_N. By using the expression obtained by Oguchi for an isotropic model of weakly interacting chains with four interchain bounds per spin [18]

$$k_B T_N/|J| = \tfrac{4}{3}S(S+1)/I(\eta) \tag{4}$$

where $\eta = |J_1/J|$ and

$$I(\eta) = \frac{1}{\pi^3}\int_0^\pi \int_0^\pi \int_0^\pi \frac{1}{\eta(1-\cos q_x)+\eta(1-\cos q_y)+1-\cos q_z}\,dq_x\,dq_y\,dq_z \tag{5}$$

we found the values of T_N to be in good agreement with the experimental ones (see table 1). We carried out numerical calculations for $I(\eta)$ by assuming that we could neglect the ferromagnetic interchain interactions J_2; that is that we may put

$$J_1 = zJ/4. \tag{6}$$

As one can see in table 1 the values of T_N calculated by us, but using the parameters of Paillaud *et al*, considerably exceed the experimental ones. It should also be noted that a nearly linear behaviour of $\chi(T)^{-1}$ at the highest temperatures, observed for all the compounds studied by us (see figures 3 and 4), strongly suggests that we have to deal with the 'true' high-temperature region. On the other hand, in the case of such large values of the interaction parameters, reported by Paillaud and co-workers, we expect a pronounced nonlinear, low-dimensional behaviour of $\chi(T)^{-1}$ almost throughout the entire temperature region studied; that is up to about 1000 K. Thus, for example, in the $Sc_2Cu_2O_5$ case the value of k_BT/J in the temperature range 300–1000 K is between 5 and 17 for $J/k_B = 58$ K (our calculation), whereas this value is between 1.5 and 5.0 for $J/k_B = 204.5$ K, as reported by Paillaud and co-workers (see figure 3).

We have also calculated the first three coefficients in the high-temperature series for the magnetic susceptibility using the Oguchi model considered above, using the moment method [19]. Thus, the temperature dependence of $\chi(T)$ takes the following form:

$$\chi(T) = (Ng^2\mu_B^2/4k_BT)(1 + 3K_1 + 6K_1^2 - \tfrac{8}{3}K_2^2 + 11K_1^3 - 6K_1K_2^2 + \tfrac{1}{2}K_2^3 + \ldots.)$$
$$K_1 = (J + 2J_1)/3k_BT \qquad K_2 = 2(J - J_1)/3k_BT. \tag{7}$$

In figure 4 we present the temperature dependence of the theoretical susceptibility (denoted as a full curve), calculated by using the previously found J- and J_1-values. It should be emphasized that equation (7) obtained without use of the MFA confirms the fitting obtained on the basis of equation (3) well. Hence, we believe that the results obtained from the Oguchi equation are quite reasonable. Moreover, we plan to calculate the higher coefficients in equation (7), to make this equation valid in the low-temperature region also where the three-dimensional correlations become important. As the inset of figure 3 indicates, this region concerns the temperatures between T_N and $T \cong 1.0$–$1.5\,J/k_B$, depending on the compound considered.

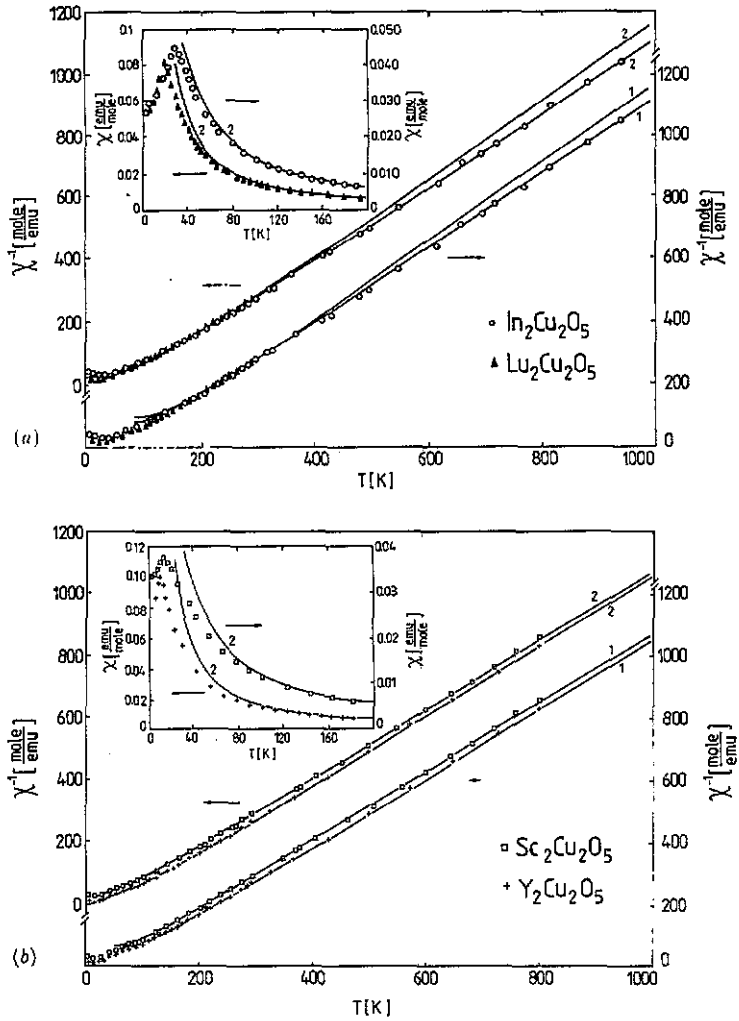

Figure 4. The temperature dependences of the inverse molar susceptibility. The experimental points are shown by circles, squares, triangles and crosses for a given compound, respectively, whereas the full curves 1 and 2 represent the theoretical results obtained on the basis of equations (7) and (3), respectively. Both the insets of parts (*a*) and (*b*) show the molar magnetic susceptibility below 200 K for the compounds indicated. Note a shift of the scales.

We are convinced that the temperature dependence of the magnetic susceptibility of ternary $(In;Sc;Lu;Y)_2Cu_2O_5$ oxides exhibits a pronounced one-dimensional character. The model for the ferromagnetic chains as being antiferromagnetically coupled seems to be a good approximation to the situation existing in the ternary oxide systems considered above.

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