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Magnetic properties and the crystal field problem for tetragonal $HoBa_2Cu_3O_x$

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Abstract

Magnetic susceptibilities of the first and third orders as well as the magnetization of the singlet paramagnet $HoBa_2Cu_3O_x$ ($x \approx 6.0$) at low temperatures are studied experimentally using a SQUID magnetometer and compared with theoretical calculations. The magnetic behaviour of single-crystal $HoBa_2Cu_3O_x$ at low temperature is found not to follow the one calculated on the basis of the known crystal field parameters. Different effects which may change the magnetic properties are analysed and discussed: low symmetry components of the crystal field due to some disorder in the oxygen subsystem, a noncompensated effective field from the ordered Cu subsystem acting on the Ho^{3+} ions, and others.

1. Introduction

In $RBa_2Cu_3O_x$ compounds (R is a rare-earth, RE, ion or yttrium), the rare-earth and superconducting subsystems are known to weakly interact, which is evidenced by independent magnetic ordering in the rare-earth subsystem observed both in superconducting and in non-superconducting samples at low temperatures. However, rare-earth ions are arranged in the structure sufficiently close to CuO_2 'superconducting planes' and can act as ideal probes sensitive to the local symmetry of their environment and charge density distribution, whose changes affect the crystal field (CF) forming the electron structure of the RE ion. There are a number of papers dealing with the inelastic neutron scattering in $RBa_2Cu_3O_x$ and the variation of the crystal field parameters of different orders with the oxygen content [1–3]. These experiments show that for some copper superconductors, spectral lines of a RE ion corresponding to transitions between the levels of the ground multiplet split in a crystal field, are split additionally into individual components, whose spectral density is related to the level of

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doping. Neutron data have to be completed by studies of magnetic properties for single crystals in weak and high magnetic fields which allow one also to explore the electron structure of RE ions and to derive/improve the crystal field interactions. Our experiments on crystals from the $RBa_2Cu_3O_x$ (R123) family have shown that without these data the R^{3+} electron structure determined may be ambiguous or even incorrect.

One of the most interesting objects from the R123 family is a singlet paramagnet $HoBa_2Cu_3O_x$ which reveals coupled electron–nuclear ordering at very low temperature [4]. Calculations of the Zeeman effect in the compounds $HoBa_2Cu_3O_x$ with the crystal field parameters determined in neutron scattering experiments predict crossover of the energy levels of Ho^{3+} ions for magnetic field $H \parallel [001]$, the crossover field $H_c = 42$ kOe being in the range convenient for experimental investigation [5, 6].

In this work, experimental studies of the magnetic properties of a $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystal in weak and high magnetic fields are performed. Numerical calculations of the corresponding properties are carried out in order to improve the determination of the low lying energy levels and their connection with the peculiarities of the magnetic behaviour of the compound investigated: the value and sign of the magnetic anisotropy, the change of the easy anisotropy axis when the temperature or magnetic field varies, a manifestation of the energy level crossing effect in high magnetic field etc.

2. Formalism

The complete Hamiltonian for a single 4f ion includes the Hamiltonian of the crystal field, H_{CF}, and the Zeeman, H_Z, and bilinear, H_B, terms, which describe the interaction of the 4f magnetic moment $\mathbf{J}$ with the external, $\mathbf{H}$, and exchange, $\mathbf{H}_B$, fields:

$$H = H_{CF} + H_Z + H_B. \tag{1}$$

Using the operator equivalent method and the molecular field approximation for the pair bilinear interactions, we can write these terms in the form

$$H_{CF} = \alpha_J B_2^0 O_2^0 + \beta_J (B_4^0 O_4^0 + B_4^4 O_4^4) + \gamma_J (B_6^0 O_6^0 + B_6^4 O_6^4), \tag{2}$$

$$H_Z = -g_J \mu_B \mathbf{H} \cdot \mathbf{J}, \tag{3}$$

$$H_B = -g_J \mu_B \mathbf{H}_B \cdot \mathbf{J}, \qquad \mathbf{H}_B = n g_J \mu_B \langle \mathbf{J} \rangle. \tag{4}$$

Here O_n^m and α_J, β_J, γ_J are the Stevens operator and Stevens parameters, respectively, B_n^m the crystal field parameters; g_J and μ_B are the Landé factor and the Bohr magneton, n the bilinear exchange parameter. The molecular field, $\mathbf{H}_B$, is determined by the parameter $n_i = \theta_i / C$ ($i = \parallel, \perp$), where θ_i is the Curie paramagnetic temperature, $C = N\mu_{eff}^2 / 3k_B$ is the Curie constant. Small dipole–dipole and exchange interactions in this compound give rise to a spontaneous antiferromagnetic ordering at $T_N = 0.03$ K [4]. The coefficients of isotropic bilinear interactions $\theta_i = -0.37$ K were estimated from the Néel temperature $T_N = 0.8$ K of the neighbour tetragonal compound $DyBa_2Cu_3O_6$. Bilinear interactions of this value are found not to change noticeably the magnetic properties of the $HoBa_2Cu_3O_x$ crystal investigated above 2 K.

To describe the anomalous magnetic properties at low temperatures we have to introduce low symmetry components of the crystal field due to some disorder in the oxygen sublattice as well as an additional effective field at the Ho^{3+} sites from the ordered Cu^{2+} subsystem, H_{Cu}, perpendicular to the tetragonal axis. The latter term can appear in a high magnetic field for a magnetic structure with canted Cu^{2+} magnetic moments. Note that for a simple collinear magnetic structure, according to symmetry arguments the effective fields from the two Cu sublattices cancel each other at the Ho^{3+} sites [7–9].

Table 1. Different sets of CF parameters B_n^m (in K) for $HoBa_2Cu_3O_x$ and other Ho oxide compounds used in the analysis of magnetic data.

Compound		B_2^0	B_2^2	B_4^0	B_4^2	B_4^4	B_6^0	B_6^2	B_6^4	B_6^6	Reference
$HoBa_2Cu_3O_6$	Set 1	240.5		−331.2		1499	39.6		1296		[10]
$HoBa_2Cu_3O_7$	Set 1o	241	104	−317	22	1465	40	−25	1211	−17	[11]
$HoBa_2Cu_3O_6$	Set 2	40.7		−298		1643	39.6		1296		
$HoBa_2Cu_3O_6$	Set 3	40.7		−49.1		2043	2.7		952		[12]
$HoPO_4$	—	265		4		956	−60		54		[13]
Ho^{3+}:$Y_3Al_5O_{12}$	—	−278	358	−437	293	1553	60	−177	1141	−134	[14]

The crystal field parameters for the tetragonal and orthorhombic $HoBa_2Cu_3O_x$ compounds are known from inelastic neutron scattering [10–12]. Various sets of crystal field parameters for the tetragonal compound $HoBa_2Cu_3O_6$ used in the calculation are presented in table 1 together with the crystal field parameters of other Ho compounds with local tetragonal ($HoPO_4$ [13]) and orthorhombic (Ho^{3+}:$Y_3Al_5O_{12}$ [14]) symmetries. The eigenvalues and eigenfunctions of the Ho^{3+} ion, which are necessary for the calculations of thermodynamic properties, were determined by the numerical diagonalization of the complete Hamiltonian (1). Magnetic susceptibilities of the first and third orders were calculated for the known electron structure according to the well known formulae (see e.g. [15]).

3. Samples and experimental techniques

Single crystals of $HoBa_2Cu_3O_x$ were obtained by the flux method. The $0.007Ho_2O_3$ –$0.287BaO_2$–0.706 CuO mixture was heated in an aluminium crucible in air to 990 °C, held for 20 h and then cooled at a rate of 7 °C/day to 920 °C. After decanting the liquid within the furnace the crystals were cooled to room temperature at a rate of 25 °C h^{-1}. Chemical and microprobe analyses showed that the ratio of Ho:Ba:Cu cations in the crystals is 1:2:3 within the determination accuracy. The mass fraction of the Al impurity entering the melt due to the interaction with the crucible is about 0.5%. The crystal composition was determined as $HoBa_2Cu_{2.9}Al_{0.1}O_x$.

The measurements were carried out on crystals of thin plate shape having the length of about 1.5–2 mm in the plane perpendicular to the tetragonal axis. The as grown Ho123 crystals (space group $P4/mmm$; lattice parameters $a = 3.8688$ Å and $c = 11.765$ Å) had the superconducting transition temperature $T_c \sim 40$ K. Magnetic properties of the Ho^{3+} subsystem manifest themselves properly in the tetragonal $HoBa_2Cu_3O_6$ for which there is no superconducting contribution. The crystals were annealed at temperature ∼900 °C for 10 h and quenched quickly in air to room temperature in order to reduce the oxygen content to $x \approx 6.0$ and convert the samples in the tetragonal phase.

The magnetization measurements were performed using a SQUID and an extraction-type magnetometer in steady magnetic fields up to 5 and 10 T, respectively, and in the temperature range 2.0–300 K. Temperature was regulated within a ±0.1 K range and the accuracy on the magnetization was around 0.05 μ_B for our samples. The isothermal magnetization curves were collected along the [001], [100] and [110] directions. The first- and third-order magnetic susceptibility values were then deduced from the zero-field extrapolation and the initial slope of the $M/H(H^2)$ plots, respectively. Sequences of measurements on four different samples gave inverse susceptibility values differing within 10% at high temperatures; only the sequence giving the largest susceptibility will be considered in the following.

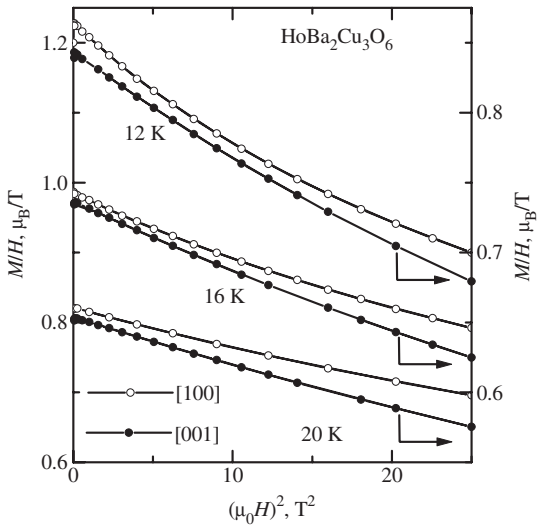

Figure 1. Curves for M/H versus H^2 for the $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystal along the symmetry axis [100] (open points, left axis) and [001] (closed points, right axis) at different temperatures.

4. Experimental data

4.1. Magnetic susceptibilities of the first and third orders

The fit of our magnetic data to M/H versus H^2 curves for different temperatures is presented in figure 1. Magnetic susceptibilities of the first and third orders deduced from these plots are then used to test different sets of the CF parameters. The magnetic susceptibility of the tetragonal $HoBa_2Cu_3O_x$ crystal exhibits a noticeable anisotropy along and perpendicular to the tetragonal axis in the low temperature range, the tetragonal axis being the hard axis (inset in figure 2). Within the experimental accuracy, the magnetic susceptibility is isotropic in the basal plane as expected for the tetragonal symmetry. A characteristic feature is that the curves $\chi_c(T)$, $\chi_a(T)$ come to a constant value at low temperature. This evidences a singlet ground state of the Ho^{3+} ion. Above 70 K the susceptibility anisotropy is small, and therefore various factors which may influence the result (an anisotropy of the sample shape, correct consideration of the background signal, contribution from the Cu subsystem, diamagnetic contribution etc) have to be taken into account and analysed in order to determine it correctly. According to our studies in the room temperature range the susceptibility anisotropy, $\Delta\chi/\chi = 2(\chi_c - \chi_a)(\chi_c + \chi_a)$, is about 0.05, and the tetragonal axis becomes the easy axis. The orientation of the easy magnetization axis changes near about 70 K for the tetragonal Ho compound.

The experimental susceptibility of $HoBa_2Cu_3O_x$ is compared with the calculated one for two sets of CF parameters in figure 2. The value and sign of the magnetic anisotropy at high temperatures determined mainly by the second-order CF parameter prove the small value of $B_2^0 = 28\ \mathrm{cm}^{-1}$ from [12]. For the easy axis [100], at low temperatures the calculated curves $\chi_a(T)$ are close to the experimental one and depend weakly on the CF parameters. Along the hard axis the experimental curve $\chi_c(T)$ at low temperatures is not in accordance with that calculated on the basis of the known CF parameters from [11] (calculated curves 1). The main distinction is in the pronounced susceptibility decrease when temperature decreases below 10 K which is not observed in the experimental curve. This behaviour is typical for a singlet system;

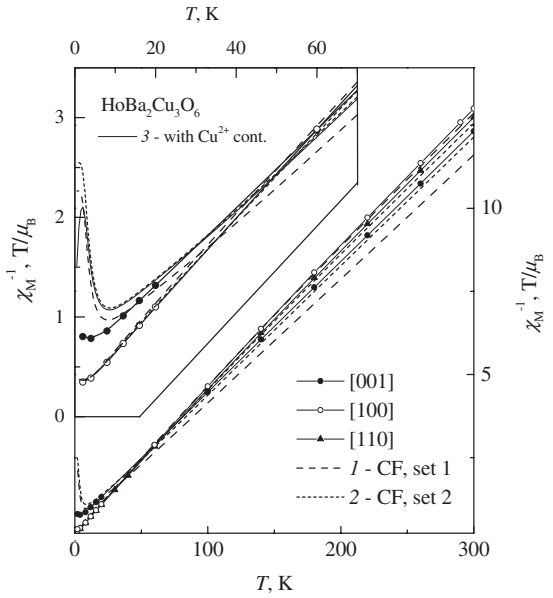

Figure 2. Inverse first-order magnetic susceptibility of the $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystal along the symmetry axis [100], [110] and [001]. Theoretical curves are calculated for two sets of CF parameters (lines 1—set 1, lines 2—set 2). The inset shows the low temperature part on a larger scale (line 3—set 2 with a paramagnetic Cu^{2+} contribution).

see for example experimental data for $HoVO_4$ [16] and $TmPO_4$ [17]. A small, within $\pm 20\%$, variation of the CF parameters from [11] does not allow us to obtain the monotonic behaviour of $\chi_c(T)$. Characteristic features of the experimental magnetic susceptibility at low temperatures especially along the hard axis provide valuable information about the low lying part of the Ho^{3+} energy spectrum. We tried to describe our magnetic data on the basis of other sets of the CF parameters ('model set' 2, calculated curves 2) derived from magnetic data and the energy levels in the window (0–160 K). Our magnetic data are not very sensitive to higher lying energy levels and 'model set' 2 does not describe the energy levels in the window (650–900 K).

The contribution to the magnetic properties from the ordered Cu^{2+} subsystem characterized by strong AF interactions and a Néel temperature of about 500 K does not exceed 0.1% at low temperature [8]. An increase of the oxygen content over $x \approx 6.0$ is known to lead to the appearance of paramagnetic Cu^{2+} ions in the oxygen deficient B layers and a pronounced paramagnetic contribution at low temperatures. Our estimation shows that this contribution for a concentration of Cu^{2+} paramagnetic centres yielding about $0.2\ \mu_B$/f.u. is essential only below 2 K (compare calculated curves 2 and 3 in the inset).

The third-order magnetic susceptibility $\chi_M^{(3)}(T)$ of a tetragonal $HoBa_2Cu_3O_x$ crystal is also anisotropic along and perpendicular to the tetragonal axis at low temperatures (figure 3) and follows the Curie–Weiss law, whereby $|\chi_M^{(3)}|^{-1/3} \propto T$, above 20 K (inset in figure 3). It should be noted that bilinear interactions with $\theta = -0.37$ K do not lead to any significant renormalization of $\chi_M(T)$ and $\chi_M^{(3)}(T)$ in $HoBa_2Cu_3O_x$. The calculated curves of $\chi_M^{(3)}(T)$ for the two symmetry axes [100] and [110] in the basal plane are very close to the experimental ones. In contrast, for the $\chi_M^{(3)}$ curve along the tetragonal axis the calculations predict a change of the sign and a positive value below ~7–8 K with a characteristic maximum near 4 K. This behaviour is a precursor of the energy level crossing and was observed earlier for the singlet

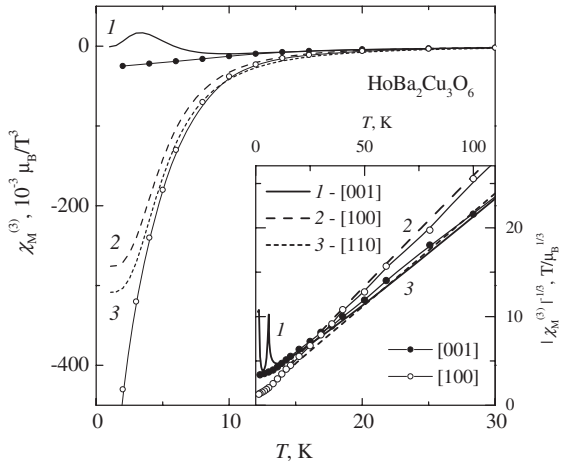

Figure 3. Third-order magnetic susceptibility of the $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystal along the symmetry axes [100], [110] and [001]. Theoretical curves 1, 2, 3 are calculated for set 2 of the CF parameters. The inset shows the temperature dependences of the inverse third-order magnetic susceptibility $|\chi_M^{(3)}(T)|^{-1/3}$ in the high temperature range.

paramagnets $HoVO_4$ [16] and $TmPO_4$ [17]. In experiment only a small negative value of $\chi_M^{(3)}$ is observed for this case.

4.2. Magnetization curves

Experimental magnetization curves $M(H)$ for a $HoBa_2Cu_3O_x$ crystal at 2.0 K along three symmetry axes are depicted in figure 4 together with theoretical curves calculated for the set 2 of the CF parameters. Along the two axes [100], [110] in the basal plane the experimental magnetization is very close to the theoretical one and varies weakly for two sets of the CF parameters. In contrast, along the hard axis [001] the curve $M(H)$ does not exhibit the jump expected from the calculation. One can observe only a small anomaly in the $dM(H)/dH$ curve which is an order of magnitude less than the calculated one (inset in figure 4). Calculations with various sets of the CF parameters reveal that the smaller the anisotropy of the initial susceptibility at low temperature the less distinct the anomaly in the $dM(H)/dH$ curve. This demonstrates once more that the magnetic behaviour of the tetragonal Ho compound along the hard axis is not in accordance with the simple singlet–doublet scheme.

5. Calculations and discussion

5.1. Problem of the crystal field

Thus the problem of the crystal field and Ho^{3+} electron structure in the layered perovskite $HoBa_2Cu_3O_x$ is found not to be solved completely so far. Today there exist numerous studies of magnetic excitations in the series of layered perovskites $HoBa_2Cu_3O_x$ with different oxygen contents using neutron spectroscopy [10–12]. This technique directly provides one with information on the splitting of the Russell–Saunders ground state multiplet. However, although the neutron spectra are relatively easy to analyse in terms of magnetic dipole matrix elements, the set of the five CF parameters present in tetragonal symmetry is not unique and the knowledge of the actual solution has required an analysis in close connection with the magnetic data.

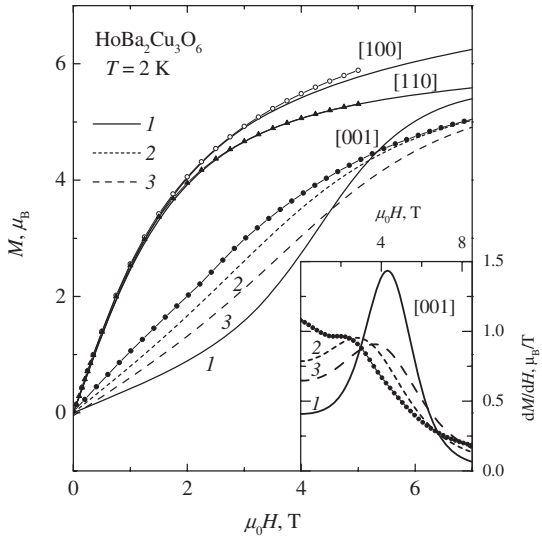

Figure 4. Magnetization curves of the $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystal along the symmetry axis [100], [110] and [001] at $T = 2$ K. Theoretical curves are calculated for set 2 of the CF parameters without (curves 1) and with (curves 2—$B_2^1 = 150$ K, curves 3—$H_{Cu} = 15$ kOe) low symmetry interactions. The inset demonstrates the effect of the low symmetry interactions on the anomaly in the $dM/dH(H)$ curve near the critical field H_c.

Inelastic neutron scattering experiments allowed reconstruction of the structure of the ground multiplet split in the CF and to determine the CF parameters on the basis of the ground multiplet [10, 11] or with consideration of J and L–S mixing [12]. For the operator equivalent formalism, CF parameters determined in the tensor operator formalism have to be renormalized and modified additionally in order to take into account some change of the energy level scheme due to J and L–S mixing. The renormalized set of the CF parameters from [12] (set 3) is found to result in an energy level scheme differing strongly from the experimental one. This is due to the competition of the various terms in the CF Hamiltonian of $HoBa_2Cu_3O_x$ which leads to an essential change of the low lying energy levels caused by small variations of the parameters, for example, to a scheme with a lowest doublet level. In addition, in the case of $HoBa_2Cu_3O_x$ the ground multiplet splitting is large enough and the intermultiplet mixing seems to be essential. We note the essentially different values of the B_2^0 parameter for the sets 1 and 3, its value for the set 3 being in better agreement with the observed magnetic anisotropy value.

A characteristic feature of the crystal field for tetragonal $HoBa_2Cu_3O_x$ is that the ratio of the diagonal and nondiagonal parameters of the fourth (B_4^0/B_4^4) and sixth (B_6^0/B_6^4) orders is close to their values for cubic symmetry, i.e., to $1/5$ and $-1/21$, respectively [10, 11]. Thus, for instance, we have $B_4^0/B_4^4 \sim -0.209$ and $B_6^0/B_6^4 \sim 0.037$ for the tetragonal Ho compound in a crystallographic coordinate system (set 1). So, the distortion in the symmetry of the local environment of a rare-earth ion with respect to the cubic symmetry is related largely to the second-order parameter B_2^0. This regularity indicates a smaller deviation of the symmetry of an oxygen dodecahedron from cubic symmetry in tetragonal and orthorhombic compounds $RBa_2Cu_3O_x$ as compared with garnets, for example, which was discussed for orthorhombic compounds in [18]. For rare-earth zircons and garnets, these ratios are distantly different from those for cubic symmetry (see table 1). A smaller distortion is observed in a low anisotropy of the initial susceptibility at high temperature in compounds $HoBa_2Cu_3O_x$ which becomes practically isotropic when $B_2^0 = 0$.

According to inelastic neutron scattering experiments on tetragonal $HoBa_2Cu_3O_x$ the lower levels are a singlet and an exited doublet at about 13 K. The evolution of the spectrum with oxygen content x demonstrates how the first and second excited singlets in the orthorhombic compound approach and merge into the doublet for $x < 6.4$. The next two excited singlets forming 'a quasidoublet' are separated by a gap of about 45 K. The overall splitting of the ground multiplet $^5I_8$ of the Ho^{3+} ion amounts to about 900 K (74 meV) at $H = 0$ both in the tetragonal and orthorhombic layered perovskite structure. For the CF parameters derived in [11] in the J, J_z representation, the wavefunctions of the lowest levels are $\{0.54|6\rangle - 0.46|2\rangle - 0.46|-2\rangle + 0.54|-6\rangle\}$ and $\{0.64|\pm 7\rangle + 0.72|\pm 3\rangle + \cdots\}$, respectively. Calculations with known CF parameters predict unusual magnetic properties of $HoBa_2Cu_3O_x$ at low temperatures: the nonmonotonic temperature dependences of $\chi_M(T)$ and $\chi_M^{(3)}(T)$ for magnetic field along the [001] axis as well as energy level crossing effects near 4 T. However the observed magnetic behaviour of the $HoBa_2Cu_3O_x$ crystal at low temperatures (see sections 4.1 and 4.2) does not agree with the calculated electron structure of Ho^{3+} ions in the tetragonal crystal field derived in [10–12]. We believe that the energy level scheme and, in particular, low lying energy levels are not disputed, while their wavefunctions should be analysed and revised. Though they describe the transition intensities in the inelastic neutron scattering spectrum adequately, this solution seems not to be unique.

5.2. Energy level crossing and the effect of low symmetry interactions

The specific features of the spectrum and wavefunctions of the Ho^{3+} ion are favourable for the energy level crossing for a magnetic field along the tetragonal axis. The energy of the ground singlet weakly decreases for $H \parallel [001]$, whereas the ground doublet is split strongly. As a result, the lower component of the split doublet with the large component $\langle M_z \rangle$ of the magnetic moment approaches and crosses in a critical field H_c the ground singlet with the smaller component $\langle M_z \rangle$, causing an increase of the magnetic moment. Within the framework of the Hamiltonian used there is no gap between the lowest levels at the crossover for magnetic field strictly along the [001] axis and the gap stays small (<3 K) for a field deviation up to 10°.

This energy level crossing without a gap should be accompanied by distinct magnetic anomalies in the $M(H)$ and $dM(H)/dH$ curves at low temperatures. However our studies on the $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystals did not reveal the expected anomalies. This means that the Ho^{3+} electron structure and CF parameters should be revised and improved, taking into account the magnetic properties. A finite gap near the critical field is known to noticeably smooth magnetic anomalies at the crossover. This gap may appear due to some interactions which mix the wavefunctions of the interacting levels. Taking into account the wavefunction symmetry for the lower levels we can propose possible interactions resulting in the largest effect. They should contain the operators J_x or J_y (or odd powers of these operators) which mix strongly the components $|\pm 6\rangle$ and $|\pm 7\rangle$ as well as $|\pm 2\rangle$ and $|\pm 3\rangle$ of the lowest singlet and first excited doublet.

Among the interactions possessing these symmetry properties one can note two types which may in principle be effective in Ho cuprates. Firstly, lower symmetry components of the CF of accidental character are expected to arise due to some disorder in the oxygen subsystem at $x > 6.0$ and to a lesser degree at $x \approx 6.0$. It is interesting to note that the orthorhombic CF which is described by even powers of J_x and J_y, for example the term $B_2^2 O_2^2$, does not mix the wavefunctions of the singlet and doublet and thus changes only weakly the magnetic properties along the hard axis.

In contrast, the second-order component $B_2^1 O_2^1$ of the monoclinic CF strongly mixes the wavefunctions and decreases the anomaly in the $\chi_c(T)$ curve (curve 2 in figure 5). This term

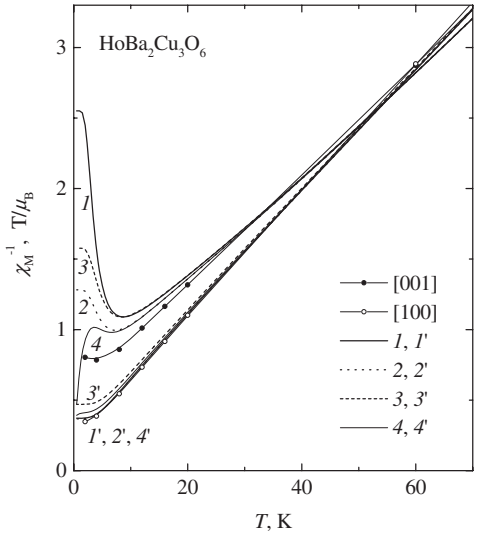

Figure 5. Inverse magnetic susceptibility of the $HoBa_2Cu_3O_x$ ($x \approx 6.0$) crystal along the symmetry axes [100] and [001]. Theoretical curves are calculated for the set 2 of CF parameters without (curves 1, 1′) and with (curves 2, 2′—$B_2^1 = 150$ K, curves 3, 3′—$H_{Cu} = 15$ kOe, curves 4, 4′—$B_2^1 = 150$ K, $H_{Cu} = 10$ kOe) low symmetry interactions.

written as $(J_z J_x + J_x J_z)/2$ in the operator equivalent notation may appear if oxygen atoms in oxygen deficient planes B are not completely ordered. We emphasize that usually the second-order crystal field parameters B_2^0 and B_2^1 receive a noticeable contribution from ions far from the nearest neighbouring ones. This low symmetry field is of an accidental character so that the parameter B_2^1 varies in sign and value from site to site; however an averaging over a crystal results in a non-zero effect for the $\chi_c(T)$ curve. It is important to note that the CF parameter $B_2^1 = 150$ K comparable in value with the second-order one B_2^0 shifts or splits very weakly, within 2–4 K, the energy spacings (except for the doublet at 720 K) but mixes strongly the wavefunctions of the lowest levels and thus changes greatly the magnetic properties of the Ho cuprate at low temperatures. The singlet paramagnet $HoBa_2Cu_3O_x$ is probably very sensitive to the low symmetry crystal field.

The molecular field from the ordered Cu subsystems due to a small exchange coupling J_{R-Cu} if it exists at RE ions results in a similar effect on the magnetic susceptibility $\chi_c(T)$. Our analysis shows that the molecular field $H_{Cu} \sim 15$ kOe changes the curves $\chi_c(T)$ and $dM/dH(T)$ along the hard axis [001] to closer to the experimental ones (curves 3 in figures 5 and 4). However we note that there is no effective field on Ho^{3+} sites for the simple two-sublattice antiferromagnetic structure without defects [7–9]. According to symmetry arguments the effective fields from two sublattices cancel each other for collinear magnetic structure. The effective field can appear for a magnetic structure with canted Cu^{2+} magnetic moments or, as in the case of R_2CuO_4, at the magnetic phase transition accompanied by change of the magnetic structure [19]. In the case of the accidental character of the molecular field H_{Cu} its averaging over a crystal results in a non-zero effect for magnetic properties along the tetragonal axis but the effect in the perpendicular plane, for example the component $M_\perp$, will be cancelled.

The characters of the wavefunction mixing for the two types of interaction discussed above are different so their combined effect is not additive and results in an another $\chi_c(T)$ curve (curve 4 in figure 5), characterized by a sharp decrease at very low temperatures. Along

the easy axis [100], the curves calculated with the same parameters $B_2^1 = 150$ K (curve 2′), $H_{Cu} = 15$ kOe (curve 3′), and $B_2^1 = 150$ K, $H_{Cu} \sim 10$ kOe (curve 4′) are found to be very close to the original unperturbed one calculated without any interactions (curve 1′).

The interactions which mix the wavefunctions of the lowest levels and give rise to a finite gap near H_c also noticeably smooth the anomaly in the $M(H)$ and $dM/dH(H)$ curves. Comparison shows that the effect from the term H_{Cu} is smaller than that from term $B_2^1 O_2^1$ (compare curves 2 and 3 in the inset of figure 4). One can see that both types of interaction increase the initial magnetic susceptibility along the hard axis (and thus decrease the magnetic anisotropy) as well as smoothing the anomaly near the critical field and decreasing the H_c value in accordance with our experimental data. We believe however that the value of the second-order coefficient $B_2^1 \sim 150$ K of the monoclinic field which changes the magnetic properties enough is sufficiently large in comparison with the symmetry allowed coefficient B_2^0. Thus we conclude that the inclusion in the Hamiltonian of these low symmetry terms of reasonable value does not permit one to describe completely available experimental data.

6. Conclusion

The development of methods for determining and refining the crystal field based on experimental data for crystals of tetragonal and lower symmetry is a currently important task. The low temperature magnetic properties are well known to provide essential information about low lying energy levels, which make the major contribution to them. Studies in high magnetic fields prove that the magnetic behaviour of crystals, in particular magnetic anomalies due to the energy level approaching, are determined to a considerable extent by the excited levels, and thus may be highly informative from the standpoint of crystal field interactions.

This work is devoted to experimental study of the effect of the crystal field on magnetic characteristics of the tetragonal compound $HoBa_2Cu_3O_x$ ($x \approx 6.0$). The magnetic behaviour at low temperatures allows us to suppose that the electron structure of the Ho^{3+} ion in the layered perovskite does not agree with the simple singlet–doublet scheme and the tetragonal or orthorhombic crystal field derived in [10–12]. The energy level scheme seems not to be disputed but the wavefunction character for low lying energy levels should be revised. The low symmetry interactions, namely the second-order term of a monoclinic crystal field as well as an exchange field in the basal plane, from the ordered Cu^{2+} subsystem might change the wavefunctions and magnetic properties in the required way. These terms are absent for the ideal crystal and magnetic structures but might arise in principle due to some disorder in the oxygen subsystem or deviation of the Cu^{2+} magnetic moments from the simple collinear structure. Additional studies which provide direct information about the character of low lying energy levels are required to clear up the problem.

Studies of microwave absorption spectra under a high magnetic field at low temperatures allow one to obtain direct information about the low part of a R^{3+} ion spectrum: energy spacings, values and anisotropies of g-factors, matrix elements of corresponding operators, etc. Comparative studies of the Ho^{3+} electron structure and its modification under a high magnetic field in related RE compounds may also be performed. Another effective probe is studies of the magnetic heat capacity $C_{mag}(T)$ under magnetic fields of various orientations. The magnetic field effect on the Schottky anomaly may provide information about low lying exited levels: their degeneracy and energy, the anisotropy of the related g-factor etc.

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