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MATERIALS
AND SUPERCONDUCTORS

Substitutions in the Nd/Ba Cation Subsystem in Thin Films of the $NdBa_2Cu_3O_y$ High-Temperature Superconductor

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Abstract—Thin films of the $Nd_{1+x}Ba_{2-x}Cu_3O_y$ high-T_c superconductor (NBCO) with different neodymium/barium ratios have been obtained by laser ablative cosputtering of targets with different elemental compositions. The films with excess neodymium ($x > 0$) had a low surface particle density and were rough, but their critical temperature decreased with increasing x. On the contrary, barium-rich films ($x < 0$) exhibited independence of the superconducting properties of the film composition, with an appreciable amount of particles observed on the surface. Substitution of Ba for Nd in NBCO thin films is apparently impeded, so that excess barium precipitates in the form of $(Ba,Cu)O_z$ particles. The structure and superconducting properties of NBCO reveal a strong dependence on the conditions of film saturation by oxygen. *© 2000 MAIK "Nauka/Interperiodica".*

$NdBa_2Cu_3O_x$ (NBCO) is a metal-oxide high-temperature superconductor (HTSC) with a $ReBa_2Cu_3O_x$ structure (ReBCO), where Re stands for a rare-earth element. This material has recently become a subject of intensive studies as a substitute for the most-widespread compound of this structure, $YBa_2Cu_3O_x$ (YBCO). The critical temperature of NBCO is the highest recorded among materials of the ReBCO structure and is 98 K [1], with a value of 94 K having been reached in thin films [2].

An essential role in the formation of the structure in ReBCO materials is played by the ionic radius of the rare-earth element, whose magnitude determines the probability of Ba being replaced (ionic radius 0.142 nm) by a rare-earth element with the formation of a $Re_{1+x}Ba_{2-x}Cu_3O_y$ solid solution or the exchange of Ba and Re atoms giving rise to disorder in the Re/Ba cation subsystem [3]. The yttrium ion, which has a relatively small ionic radius (0.089 nm), does not form a solid solution, and disorder in the cation subsystem becomes manifest only at high temperatures [4]. The neodymium ion has the largest ionic radius among the rare-earth elements forming ReBCO superconducting compounds (0.0995 nm), which makes possible the solid-solution formation up to $x = 0.7$ [3].

Substitutions in the Nd/Ba cation subsystem have been intensively studied from the time of the report on the NBCO preparation [5–10]. Incorporation of a Nd^{3+} ion into the Ba^{2+} site results in the appearance in the Cu–O chain plane of an additional oxygen ion, the destruction of the chain order around it, and the formation of the tetragonal modification with the attendant increase in the lattice constant c. The increase in the number of oxygen ions per unit cell reduces the hole concentration and lowers the critical temperature. These phenomena were observed to occur both in Nd substitution for Ba [5–8] and in mutual rearrangement (disorder) in the Nd/Ba cation subsystem [8–10]. Optimization of the conditions of preparation of Nd-rich films ($x > 0$) permitted, however, reaching a critical temperature close to that obtained in films with $x = 0$ [11]. The NBCO films had a remarkably smooth surface, which is accounted for by the smaller effect of deviations from stoichiometry, with the excess material becoming incorporated in the solid solution rather than precipitating in the form of foreign-phase particles. The crystal structure of the films obtained also revealed an extremely high quality, which is due to the layer-by-layer growth persisting up to thicknesses above 200 nm [11]. The effect of increasing the barium content in NBCO thin films was studied [6–8], but the results obtained were contradictory. This can apparently be attributed to these studies not having been systematic enough; in particular, no independent optimization of the deposition parameters for films of different elemental composition was carried out.

The purpose of this work was to investigate the effect of substitutions in the Nd/Ba cation subsystem on the properties of films with different neodymium and barium contents obtained by laser ablation sputtering.

1. TECHNIQUES

Thin $Nd_{1+x}Ba_{2-x}Cu_3O_y$ films ($x = -0.15, \ldots, 0.15$) were prepared by pulsed laser ablation cosputtering (a KrF excimer laser, the energy density at the target 1.7 J/cm^2) of two ceramic targets of different elemental composition [12]. The targets were mounted on a rotating holder, and a laser pulse was directed on the target to be sputtered by a computer-controlled synchronizing system. The numbers of sputtering pulses directed on each target were in an integer ratio. The relative amounts of the elements in the films thus prepared were found from the compositions of the sputtered targets using the measurements made with an x-ray microprobe analyzer.

The material was sputtered on $LaAlO_3$(001) and $SrTiO_3$(001) substrates, and on sapphire(1102) with a 250-Å thick CeO_2(001) buffer layer, which were heated to a high temperature T_D (about 800°C) [13]. Silver paste was used to improve the thermal contact of the substrate with the heater. The pressure during the deposition was 0.3–1.0 mbar. After the deposition, the films were saturated by oxygen, a procedure including rapid cooling to a temperature T_a, admission of oxygen to atmospheric pressure, and cooling at a rate r_a during a time t_a (inset in Fig. 2). Some samples were maintained after the completion of deposition at the deposition temperature and pressure for a time t_h. The parameters of this procedure were typically $t_h = 0$, $T_a = 450$°C, $r_a = 0$°C/min, and $t_a = 1$ h.

The superconducting properties (the critical transition temperature T_c and the transition width ΔT_c) were derived from the measured dependences of the magnetic susceptibility of films on temperature. The crystal structure parameters of the films were determined by x-ray θ/2θscanning. The lattice parameters were calculated with due account of all diffraction peaks of the (*h*00), (0*k*0), and (00*l*) families observed [14], and the stresses in the films were estimated from the dependence of peak broadening on diffraction angle [15]. The volume ratios of the domains with *a*, *b*, and *c* orientation were estimated from integrated-intensity ratios of the (200), (020), and (006) peaks, respectively, taking into account the standard intensities obtained by θ/2θ scanning of powder samples and available from the literature. The particle density on the surface was determined from photomicrographs made with an optical microscope, which permitted one to take into account particles greater than 0.3 μm in size. The surface roughness R_a was calculated automatically during surface profile measurements with an AlfaStep profilometer as the arithmetic mean of the deviation from the mean height of the relief. The needle advance velocity was 2 μm/s, the measurement frequency 50 Hz, the vertical resolution better than 5 Å, and the measured trace length 50 μm. The substrate surface roughness measured in these conditions before the film deposition was 10–15 Å.

2. RESULTS AND DISCUSSION

The superconducting properties of the NBCO films with $x \approx 0$ depended strongly on the deposition regime, and for films obtained on $LaAlO_3$ substrates were T_c = 85–86 K and ΔT_c was less than 2 K. Such films were oriented with the *c* axis perpendicular to the substrate plane (*c*-oriented films), the lattice parameter *c* varied from 11.74 to 11.755 Å and the stresses in the films did not exceed 0.15%. The lattice parameters of the films saturated by oxygen by the standard procedure are listed in Table 1, and typical diffraction patterns of the NBCO films are presented in Fig. 1. In some films, besides the *c*-oriented, *a*- and *b*-oriented domains were also present (Figs. 1a and 1b). The lattice constants *a* and *b* estimated from the θ/2θ x-ray scans of such films were 3.864–3.876 and 3.905–3.907 Å, respectively. The *a* or *b* domain orientation perpendicular to the substrate plane depended on the material of the substrate. On $LaAlO_3$ and the CeO_2 buffer layer, one observed the formation of *a*-oriented parts of NBCO films; however, the films on $SrTiO_3$ always contained domains oriented with the *b* axis perpendicular to the substrate plane, irrespective of the deposition conditions. This orientation is not typical of the ReBCO-family materials, although when NBCO films were deposited by laser sputtering on a $SrTiO_3$ film, one also observed [16] the growth of a *b*-oriented film (peak *3* in the inset to Fig. 2 in [16]). This could be due to the parameter of the $SrTiO_3$ cubic lattice (3.905 Å) being close to the *b* parameter of the NBCO films. The x-ray diffraction peaks of a *b*-oriented NBCO film and of a $SrTiO_3$ film practically coincide, which required the deconvolution of the observed diffraction peak into the constituent peaks (see inset to Fig. 1b). Lowering the deposition temperature to 740°C produced films predominantly of the *a* orientation with the lattice constants $c^* = 11.83$–11.85 Å, and $a^* = 3.91 \pm 0.001$ Å. Such films were not superconducting, which, besides the lattice constants, implies the formation of a tetragonal NBCO structure.

The oxygen saturation regime strongly affected the structure and properties of $NdBa_2Cu_3O_y$ films. Increasing T_a and t_a compared to the standard procedure resulted in an increase of the lattice constant *c* to 11.77–11.81 Å and a decrease of T_c (Fig. 2). These phenomena are probably associated with the disorder in the Nd/Ba cation subsystem which sets in during oxygen saturation at a high temperature [9, 10]. It was shown [9, 17] that maintaining NBCO at a high temperature (800–900°C) and low oxygen pressure favors ordering in the Nd/Ba subsystem. Subsequent saturation with oxygen at a low temperature (340°C) does not bring about a substantial disorder and degradation of the superconducting properties [17]. The saturation of NBCO films with oxygen in accordance with these recommendations allowed us to reach T_c and ΔT_c on the level of the best parameters attained with the standard oxygen-saturation procedure (curve *1* in Fig. 2).

In order to systematically investigate the effect of the composition of films on their properties, the oxygen pressure during the sputtering, in accordance with the literature data [2], was chosen equal to 0.3 mbar, and the films were deposited on $LaAlO_3$(001) substrates.

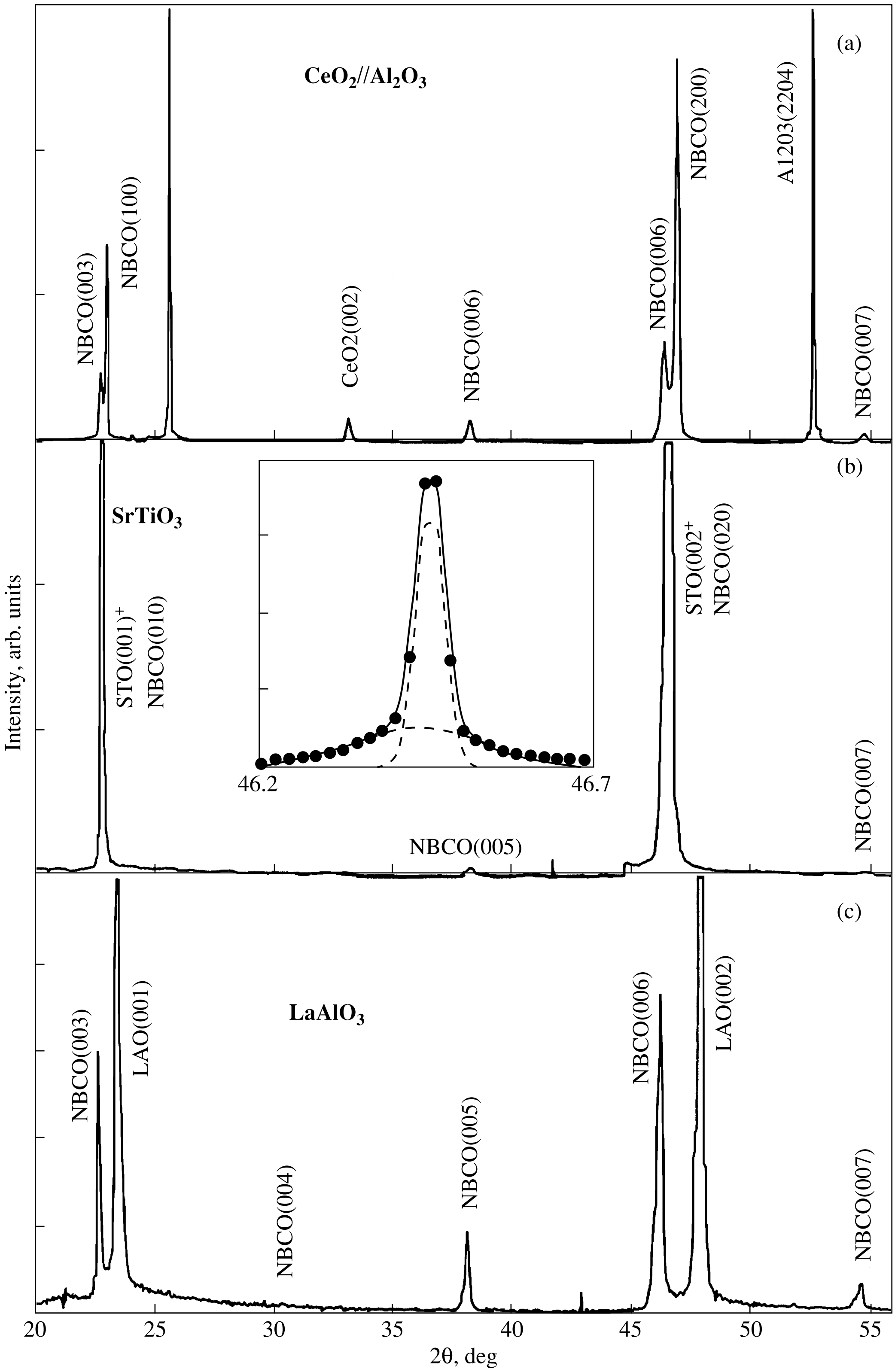

Fig. 1. X-ray θ/2θ diffractograms of $Nd_1Ba_2Cu_3O_y$ films (a) of the mixed *a* and *c* orientations on (001)//Al_2O_3(1$\underline{1}$02) substrate, (b) of the mixed *b* and c orientations on $SrTiO_3$(001) substrate, and (c) of the *c* orientation on $LaAlO_3$(001) substrate. Inset to (b): decomposition of the x-ray diffraction peak into the constituent peaks due to $SrTiO_3$(002) (46.457°, half-width 0.058°) and NBCO(020) (46.44°, half-width 0.235°); dashed lines show calculated peaks and the solid line is their sum.

Table 1. Lattice parameters of $NdBa_2Cu_3O_y$ films deposited by laser ablation sputtering

Substrate	p_{02}, mbar	T_D, °C	*c* orientation			*a*(*b*) orientation		
			Fraction, %	Lattice constant, Å	Stresses, %	Fraction, %	Lattice constant, Å	Stresses, %
$LaAlO_3$ $CeO_2//Al_2O_3$	0.6–1.0	770–790	100	$c = 11.74 – 11.755$	0.13–0.5	0	Not determined	Not determined
$SrTiO_3$	0.75–1.0	760–830	37–54	$c = 11.74 – 11.77$	0.11–0.17	46–63	$b = 3.906$	Same
$CeO_2//Al_2O_3$	0.4–0.6	780	17–50	$c = 11.725 – 11.76$	0.4–0.9	50–83	$a = 3.867 – 3.876$	0.5–1.0
$SrTiO_3$	0.3–0.6	750–770	2–6	$c = 11.76 – 11.765$	Not determined	94–98	$b = 3.906$	0.34–0.74
$LaAlO_3$, $SrTiO_3$	0.4–0.75	680–730	<1	$c = 11.83 – 11.85$	Same	100	$a = 3.91$	0.36–0.42
$LaAlO_3^*$	1.0	750–790	65–100	$c = 11.77 – 11.78$	0.47–0.6	0–38	$a = 3.872$; $b = 3.907$	2.7–3.0
$LaAlO_3^{**}$	0.3–1.0	780	1–2	$c = 11.80 – 11.805$	0.8	98–99	$a = 3.89 – 3.91$	0.55

Notes: * oxygen admitted at a high temperature.
** prolonged oxidation.

Table 2. Properties of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ films with different elemental compositions deposited on $LaAlO_3(001)$ substrates at a pressure of 0.3 mbar

x	Deposition temperature providing the highest T_c, °C	Critical temperature T_c, K	Surface roughness, Å	Surface particle density, 10^6 cm^{-2}
0.14	795	73	14	2
0.06	800	81	12	3
0	810	85.95	11	2
–0.06	No optimization		16	2.5
–0.08	810	85.5	52	20
–0.13	810	86.2	360	30
–0.14	No optimization		600	70

For each elemental composition of NBCO films, the deposition temperature providing the highest T_c was determined. The film parameters obtained at these temperatures are listed in Table 2. The dependence of T_c on the relative content of barium and neodymium is plotted in Fig. 3. A decrease of the barium content below two atoms per unit cell reduces the attainable critical temperature, which agrees with the literature. At the same time, an increase in the barium content does not entail a further increase or decrease of T_c within the range covered. The film surface morphology also underwent changes as one crossed over from barium-deficient to barium-rich films (Fig. 3). The former had a smooth surface with a low particle density (less than 10^6 cm^{-2}) and a roughness comparable with that of the original substrates (10–20 Å). An increase in the barium content above the stoichiometric level produced a fast growth of both the particle density on the film surface and the film roughness (Table 2). A similar effect was observed in [6–8] for $x < –0.10$. X-ray diffractometric measurements allowed one to identify the forming particles as BaO and Ba_2CuO_3 [6, 7]. In contrast to the dependences of T_c on the composition of the films under study obtained by us, a maximum in T_c was observed at $x = –0.03$ in [6, 7] and at $x = 0$ in [8]. This is possibly due to the fact that in none of the works cited above did one optimize the deposition conditions for each elemental composition studied.

The observed behavior of T_c and of the film morphology under variation of the elemental composition can be attributed to a different character of substitutions in the Ba/Nd subsystem. The neodymium ion apparently enters the barium site quite easily, and the deficiency of barium in a film is compensated by neodymium. This results in the formation of a smooth film with a high lattice perfection, but T_c of such a film decreases with an increasing Nd content. The corresponding chemical reaction can be written as $(1 + x)NdO_{1.5} + (2 – x)BaO + 3CuO \longrightarrow Nd_{1+x}Cu_3O_y$ for $x > 0$. By contrast, the excess barium is only incorporated into the lattice in small amounts and precipitates

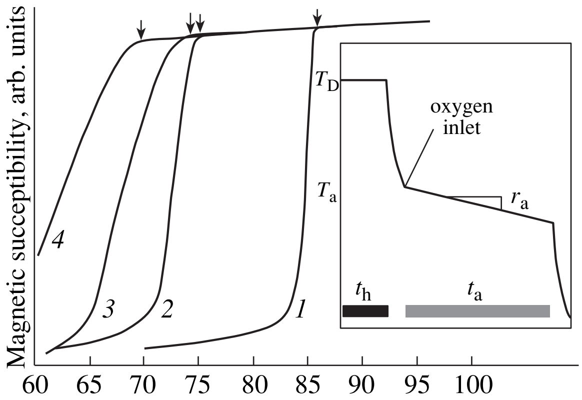

Fig. 2. Dependence of the magnetic susceptibility on temperature for $NdBa_2Cu_3O_y$ films deposited on a $LaAlO_3(001)$ substrate at 780°C and subjected to various oxygen saturation procedures: (*1*) t_h = 15 min, T_a = 350°C, r_a = 0, t_a = 1 h; (*2*) t_h = 0, T_a = 450°C, r_a = 0, t_a = 1 h; (*3*) t_h = 0, T_a = 750°C, r_a = 10°C/min, t_a = 1 h; and (*4*) t_h = 0, T_a = 450°C, r_a = 0, t_a = 25 h. The critical temperatures are identified by arrows. Inset: schematic of oxygen saturation procedure. See text for explanation of the notation.

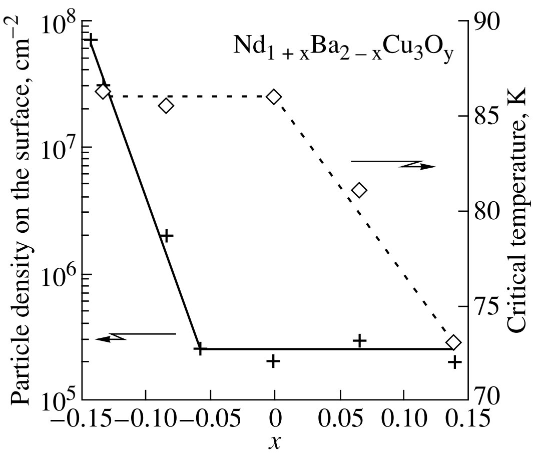

Fig. 3. Dependence of the critical temperature and particle density on the surface of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ films on a $LaAlO_3(001)$ substrate on their elemental composition. The deposition temperature was optimized for each elemental composition (see Table 2). The lines are drawn to aid the eye.

in the form of foreign phases. Therefore, the NBCO film has a close-to-stoichiometric composition ($x = 0$) and exhibits the corresponding superconducting properties, but particles appear on its surface. The reaction of NBCO formation assumes the form $(1 + x)NdO_{1.5} + (2 - x)BaO + 3CuO \longrightarrow (1 + x)Nd_1Ba_2Cu_3Cu_3O_y + (-3x)(Ba,Cu)O_z$ for $x < 0$. The proposed mechanism finds support in the observation that the optimum film deposition temperature remains constant with increasing barium content, whereas when *x* decreases, the optimum deposition temperature decreases (Table 2). The optimum temperatures of the formation of phases with excess neodymium are known to decrease with an increasing Nd content [11].

The relatively low critical temperature of 86 K, reached in the optimization of the deposition process, may be due to one of two possible reasons. First, the critical temperature of the films thus prepared can decrease as a result of the destruction of the chain order in the Cu–O sheets due to the disorder in the Nd/Ba subsystem. However, an increase of disorder results in an increase of the lattice parameter *c*, while the values measured by us agree with those for standard films with $T_c > 90$ K. A more probable reason is the presence of impurities in the sputtered target; indeed, the high sensitivity of NBCO to impurities [18, 19] can bring about a sharp drop of T_c even at a very low impurity concentration.

It should be pointed out that some of the authors ([16, 20–23]), despite a comprehensive optimization of the deposition conditions, did not succeed in reaching critical temperatures in NBCO films above 86–88.5 K, whereas others ([6–8, 11]) report repeatedly obtaining critical temperatures above 91 K. In both groups, the same techniques and similar deposition parameters were used. This discrepancy suggests the existence of some overlooked factor, which results in a T_c drop by 5–8 K. There is a report [20] of the formation of a "high-temperature" NBCO phase with T_c = 95 K, which the authors did not, however, succeed in isolating from the "low-temperature" (T_c < 90 K) one.

Thus, we have studied the effect of substitutions in the Nd/Ba cation subsystem on the properties of $Nd_{1+x}Ba_{2-x}CuO_y$ films obtained by laser ablation sputtering. NBCO films prepared on $SrTiO_3(001)$ substrates exhibited the orientation of a substantial part of the film with the *b* axis perpendicular to the substrate plane. The structure and superconducting properties of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ reveal a strong dependence on the conditions of film saturation with oxygen, which is probably associated with disorder setting in the Nd/Ba subsystem during the film saturation with oxygen. The investigation of the deposition of NBCO films with different barium and neodymium contents indicates the incorporation of the excess neodymium into the barium sites on the superconductor lattice, whereas excess barium precipitates in the form of particles observed on the film surface.

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SPELL: cosputtering, AlfaStep, succeptibility