Superlinearität der Lumineszenz ist die Temperaturabhängigkeit durch die Temperaturabhängigkeit des Quotienten $n(a):\delta$ bestimmt. Da δ mit wachsender Temperatur steil zunimmt, n im Bereich der Superlinearität aber mit wachsender Temperatur rasch abnimmt, sinkt die Lumineszenz mit der Temperatur sehr steil ab.

Eine ausführlichere Betrachtung über die Gültigkeitsgrenzen dieses Modells soll in einer folgenden Arbeit publiziert werden.

Für anregende Diskussionen danken wir Herrn Dr. S. Oberländer, für die Ausführung der numerischen Rechnungen Frau W. Leuschner.

The Relationship of Phosphor Properties to Preparative Methods in some ZnS:Cu/Cl Phosphors[1]

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Dedicated to Prof. N. Riehl *on his sixtieth birthday*

A series of ZnS : Cu/Cl phosphors were prepared of various Cu and Cl concentrations and using different methods of introducing Cu. These were investigated with respect to luminescent and electrical properties. Some effects on these properties of preparative methods and impurity concentrations are presented.

Since this publication is in honor of Professor Riehl's sixtieth birthday it is appropriate that we take the opportunity to report on our attempts to relate phosphor properties to preparative methods. It was Professor Riehl who introduced us to this subject by his extensive work in the field as well as by his kindness in personal discussions.

Several series of ZnS phosphors were prepared and measured in this laboratory, in which activators, coactivators, firing temperatures, atmospheres and cooling rates were varied. An important point of the investigation was that many different phosphor properties were determined for each phosphor as described in Section III.

In each case samples without activator but containing coactivator were also prepared. Various concentrations of activator were later permitted to diffuse into these samples at a relatively low temperature[3]. The results obtained with one series of ZnS : Cu/Cl phosphors are herein reported.

1. Preparation

Precipitated, non-luminescent ZnS was used as starting material. Analysis showed that the impurity content is low enough for phosphor use[4]. Solutions of $CuSO_4$ and NaCl were dried onto the grains while stirring. The samples were placed in quartz test tubes which were put, open end first, into second quartz test tubes of slightly larger diameter. The sample tubes were stacked in a quartz closed-end tube, 4″ ID × 39″ long, so that they would lie in the flat zone of the furnace. The tube is fitted with a Corning type flange. It is closed with a cap fitted with three ground glass joints. These permit the insertion of the controlling thermocouple, the quartz gas inlet tube which extends to the far end of the large tube and a gas exit tube. A gas tight seal is effected by a neoprene O-ring.

The furnace used is a horizontal tube furnace using six Kanthal elements and having a flat zone of approximately 12″. It is provided with a control system which allows a preset heating rate, soak time, soak temperature, and cooling rate.

In the present case prepurified N_2 was passed through the system at a rate of $3.5\ ft^3/min$ for one half hour, then at $0.3\ ft^3/min$ during the firing cycle. The samples were fired at 1150 °C for two hours. They were cooled to 700° in the first hour and then linearly to room temperature during a further nine hours. After removal from the furnace the phosphor powders were washed with KCN solution and prepared for measurement.

Appropriate quantities of $CuSO_4$ solution were dried onto portions of the activator-free samples produced

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[1] The support of this investigation by the Office of Ordnance Research under contract DA 30-069-ORD 2635 is gratefully acknowledged.

[2] On leave from the Labor für Technische Physik, Technische Hochschule, Munich, German Federal Republic.

[3] N. Riehl and H. Ortmann, On the Production of Zinc Sulfide Phosphors, Verlag Chemie, Weinheim, Germany, 1957.

[4] i. e., $Cu < 10^{-4}\%$; $Ag < 10^{-5}\%$.

above and reheated under conditions similar to those described above except that the soak temperature was reduced to 450° and the soak time shortened to one hour. These samples were allowed to cool in N_2, were washed with KCN solution and prepared for measurement.

One sample of precipitated ZnS grains, coated with $CuSO_4$ and NaCl, was divided into two portions. One portion was fired with the other samples as described above; the second was sealed into a quartz tube under 15 mm of prepurified N_2 and fired for two hours in a vertical tube furnace. At the end of the firing time the tube was allowed to fall into a container of ice water. The shock broke the tube and the rapidly cooled phosphor was removed by filtration, washed with KCN solution and prepared for measurement.

In order to see whether some high temperature equilibria were frozen into the rapidly cooled phosphor, a portion of it was reheated at 450 °C for several hours and measured. The resulting phosphor was compared to that derived from the same starting material but cooled slowly.

2. Description of Measurements

The following phosphor properties were investigated: emission spectra, glow curves, deficiency areas, equilibrium intensities at room- and liquid nitrogen temperature, I.R. stimulation and quenching, electroluminescence, photoconductivity and electron paramagnetic resonance. Homogeneous samples of equal thickness were used in each type of measurement described below. The data are presented in the next section.

Emission spectra were measured with a Bausch & Lomb grating monochromator and a 1P21 photomultiplier. The samples were excited with the wavelength region around 3660 Å obtained from an appropriately filtered mercury lamp. The intensity was approximately 50 μw/cm². The spectra obtained were corrected for photomultiplier sensitivity and normalized so that the areas under the curves presented in the next section are proportional to the equilibrium fluorescence intensities. These were measured with a photomultiplier provided with a filter combination giving constant sensitivity over the wavelength range from 4200 Å to more than 6000 Å[5].

Glow curves were measured with the photomultiplier system described above and under a linear heating rate of approximately 12 °C/min.

Before luminescence rise curves were taken each phosphor was deexcited at 150 °C in the dark for a period of several minutes; this was found to deexcite all the phosphors adequately. The samples were cooled to either room or liquid nitrogen temperature and excitation begun. The exciting wavelength was in the 3660 Å region and had an intensity of 5 μw/cm².

Infrared stimulation and quenching effects were measured during ultraviolet excitation at room and liquid nitrogen temperatures. The two I.R. wavelength regions to which phosphors are known to be sensitive were used in each case, 0.7 μ and 1.3 μ. The intensities were approximately 200 μw/cm² and 2000 μw/cm² respectively.

Photoconductivity was measured with the a.c. method as a change in capacitance and dissipation factor[6]. Samples were prepared on conductive glass plates. The plates were attached to pieces of flanged pipe by means of an 0 ring. The second electrode was provided by a 2 cm column of mercury poured on to the sample. Excitation was with the 3660 Å region at an intensity of approximately 500 μw/cm².

Electroluminescence was evaluated at 60 cycles and a field strength of 1200 V/mm. The photomultiplier system of constant sensitivity was used. The samples were sandwiched between two conductive plates in a castor wax binder.

Samples of each phosphor were checked in an electron paramagnetic resonance spectrometer for any u.v. sensitive absorption at room and liquid nitrogen temperature.

3. Experimental Results

Fig. 1 presents the normalized (see previous section) emission spectra at liquid nitrogen temperature of phosphors fired with activator and $10^{-3}\%$ Cl at 1150 °C. Fig. 2 gives the emission spectra of these phosphors at room temperature.

Fig. 3 and 4 present the emission spectra of phosphors similarly prepared but with $10^{-1}\%$ Cl. The rapidly cooled phosphor ($5 \cdot 10^{-3}\%$ Cu, $10^{-1}\%$ Cl) is included for comparison. When the rapidly cooled phosphor was heated in N_2 at 450 °C for several hours its emission spectrum became identical to that of the more slowly cooled phosphor of the same concentrations of activator and coactivator.

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[5] K. Luchner, Z. Instrumentenkde. **12** [1958].

[6] H. Kallmann, Kramer and Perlmutter, Phys. Rev. **89**, 700 [1953].

Figs. 5 to 8 give the emission spectra at room and liquid nitrogen temperatures of the phosphors prepared by allowing Cu to diffuse into the 0% Cu phosphors shown in Fig. 1 to 4. The intensity axes of all the emission spectra are in the same arbitrary units.

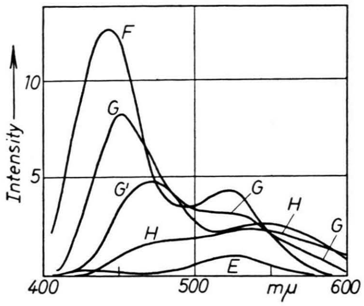

Fig. 1. Low temperature emission spectra of phosphors fired with Cu and 10^{-3}% Cl. E: 0% Cu; F: $5 \cdot 10^{-3}$% Cu; G: $5 \cdot 10^{-2}$% Cu; G′: 10^{-1}% Cu; H: 1% Cu.

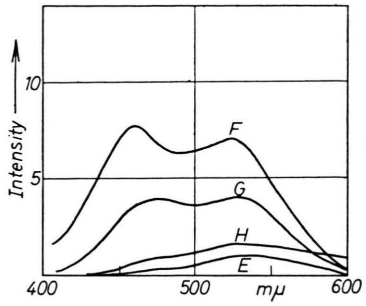

Fig. 2. Room temperature emission spectra of phosphors fired with Cu and 10^{-3}% Cl. E: 0% Cu; F: $5 \cdot 10^{-3}$% Cu; G: $5 \cdot 10^{-2}$% Cu; H: 1% Cu.

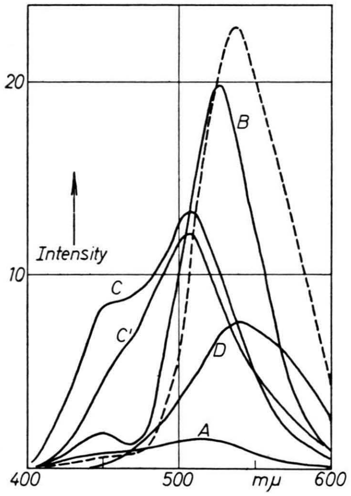

Fig. 3. Low temperature emission spectra of phosphors fired with Cu and 10^{-1}% Cl. A: 0% Cu; B: $5 \cdot 10^{-3}$% Cu; – – –: $5 \cdot 10^{-3}$% Cu, cooled rapidly; C: $5 \cdot 10^{-2}$% Cu; C′: 10^{-1}% Cu; D: 1% Cu.

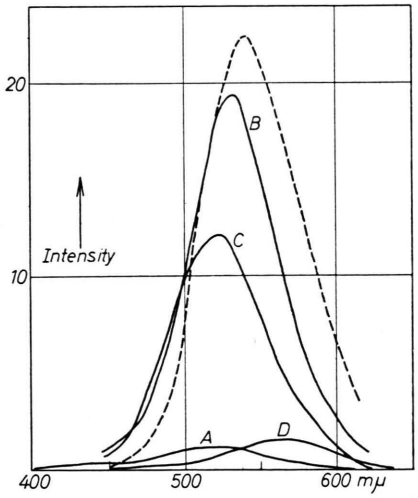

Fig. 4. Room temperature emission spectra of phosphors fired with Cu and 10^{-3}% Cl. A: 0% Cu; B: $5 \cdot 10^{-3}$% Cu; – – –: $5 \cdot 10^{-3}$% Cu, cooled rapidly; C: $5 \cdot 10^{-2}$% Cu; D: 1% Cu.

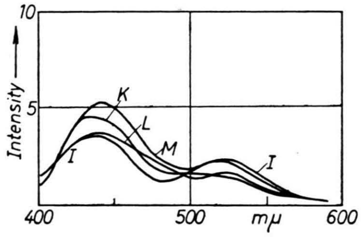

Fig. 5. Low temperature emission spectra of phosphors prepared by Cu diffusion, 10^{-3}% Cl. I: $5 \cdot 10^{-3}$% Cu; K: $5 \cdot 10^{-2}$% Cu; L: $5 \cdot 10^{-1}$% Cu; M: 1% Cu.

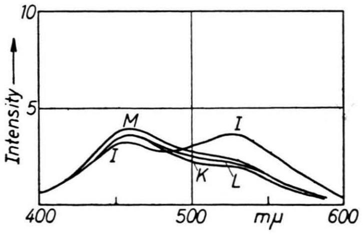

Fig. 6. Room temperature emission spectra of phosphors fired with Cu and 10^{-3}% Cl. I: $5 \cdot 10^{-3}$% Cu; K: $5 \cdot 10^{-2}$% Cu; L: $5 \cdot 10^{-1}$% Cu; M: 1% Cu.

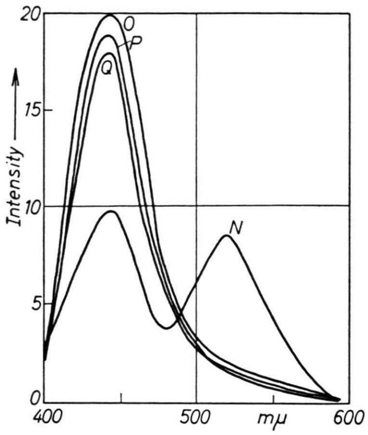

Fig. 7. Low temperature emission spectra of phosphors prepared by Cu diffusion, 10^{-1} % Cl. N: $5 \cdot 10^{-3}$ % Cu; O: $5 \cdot 10^{-2}$ % Cu; P: $5 \cdot 10^{-1}$ % Cu; Q: 1% Cu.

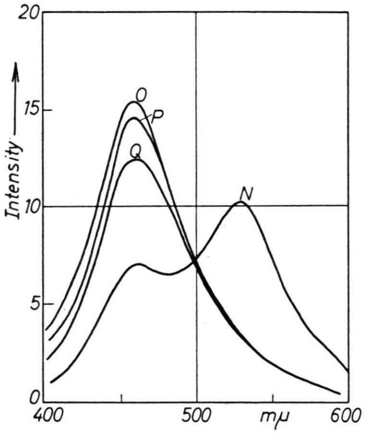

Fig. 8. Room temperature emission spectra of phosphors fired with Cu and 10^{-3} % Cl. N: $5 \cdot 10^{-3}$ % Cu; O: $5 \cdot 10^{-2}$ % Cu; P: $5 \cdot 10^{-1}$ % Cu; Q: 1% Cu.

Figs. 9 to 12 present the glow curves of the phosphors described above. The intensity axes of all the glow curves are in the same arbitrary units.

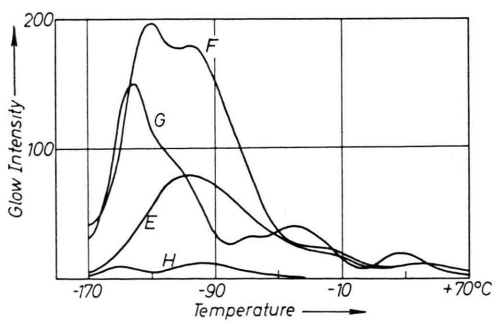

Fig. 9. Glow curves of phosphors fired with Cu and 10^{-3}% Cl. E: 0% Cu; F: $5 \cdot 10^{-3}$ % Cu; G: $5 \cdot 10^{-2}$ % Cu; H: 1% Cu.

Only the self activated and lowest Cu concentration phosphors gave a detectable, lightsensitive EPR signal.

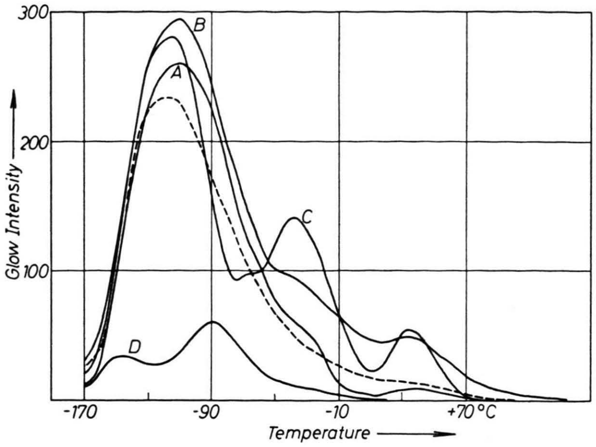

Fig. 10. Glow curves of phosphors fired with Cu and 10^{-1}% Cl. A: 0% Cu; B: $5 \cdot 10^{-3}$ % Cu; – – – : $5 \cdot 10^{-3}$ % Cu, cooled rapidly; C: $5 \cdot 10^{-2}$ % Cu; D: 1% Cu.

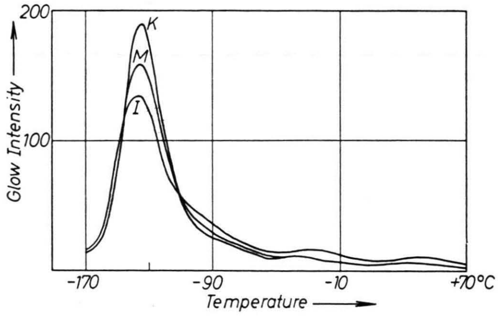

Fig. 11. Glow curves of phosphors prepared by Cu diffusion, 10^{-3} % Cl. I: $5 \cdot 10^{-3}$ % Cu; K: $5 \cdot 10^{-2}$ % Cu; M: 1% Cu.

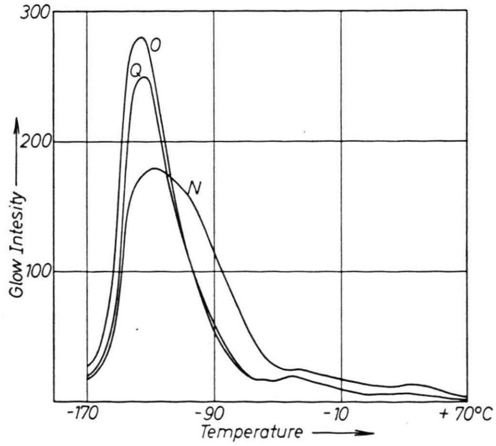

Fig. 12. Glow curves of phosphors prepared by Cu diffusion, 10^{-1} % Cl. N: $5 \cdot 10^{-3}$ % Cu; O: $5 \cdot 10^{-2}$ % Cu; Q: 1% Cu.

4. Discussion

While it is not possible to draw general conclusions based on this limited number of phosphors, it seems worth while to point out some features of interest.

All the spectra (Figs. 1 – 8) show that at the low temperature the blue portion of the emission is more pronounced that at room temperature. It appears that at room temperature the lower lying ionized activators which give rise to the blue luminescence, are thermally neutralized before they can take part in radiative recombinations. A comparison of Figs. 1 and 5, and 3 and 7 shows that the emission spectra of the phosphors into which Cu was allowed to diffuse after firing are much less sensitive to Cu concentration than those of the phosphors fired with Cu. An exception is curve N of Fig. 7 which depicts the only phosphor in which the Cu concentration added by diffusion is much smaller than the Cl concentration present. The intensity of the blue emission (Figs. 1 and 3) seems to depend as usual on whether more or less Cu is present than Cl [7].

The glow and deficiency areas (number of filled traps at liquid nitrogen temperature) are generally larger for the phosphors with the higher coactivator concentration (Tables 1 and 2). Those of the diffused in Cu phosphors do not vary with Cu concentration and approach those of the respective self-activated phosphors. It may be that diffusing Cu into a self-activated phosphor, while resulting in new activator levels, does not result in the formation of new traps.

The shape of the glow curves is relatively unaffected by the Cu concentration in the case of diffused in Cu (Figs. 11 and 12), except once again in the case of Curve N of Fig. 12, the phosphor with much higher Cl than Cu concentration. In the case of fired Cu, however, the shape of the glow curves is strongly affected by the Cu concentration. The glow maximum corresponding to the shallowest traps in the phosphors fired with Cu, which is the only significant one seen in the phosphors with Cu diffused in, is most pronounced in the phosphors having a large excess of Cu over Cl (Figs. 9 and 10). At high fired Cu concentrations low glow areas and glow curves are obtained. This can be partially ascribed to temperature quenching discussed below.

The low temperature luminescence is quite low for both the self-activated phosphors and rises sharply with $5 \cdot 10^{-3}\%$ fired Cu. The luminescence drops again as the Cu concentration rises above the Cl concentration (Tables 1 and 2). In each case the decrease is greater at room temperature than at liquid nitrogen temperature, showing that temperature quenching occurs in addition to the quenching

	Cu %	Rel. Equilibrium Fluorescence		Relative Deficiency Area[a] at Liquid N Temp.	Relative Glow Area[a]	IR Stimulation Max. Intensity [b] Liquid N Temperature		IR Quenching Min. Intensity [b] Liquid N Temperature		Relative Electroluminescence [c] Room Temp.	Relative Photoconductivity Room Temp.
		Room Temp.	Liquid Nitrogen Temp.			0.7 μ	1.3 μ	0.7 μ	1.3 μ		
A	0	16 [d]	14.5 [d]	3000	3910	30	79	11.5	14.5	0	16
	$5 \cdot 10^{-3}$	200	210	8100	7960	231	1260	42	105	0	8.6
	$5 \cdot 10^{-2}$	105	127	4250	4950	165	507	38	63		
	$1 \cdot 10^{-1}$	~60	100				~300			75	2.2
	1	36	61	1140	600	88	67	49	55		
B	$5 \cdot 10^{-3}$	58	58	3900	3900	170	700	17	37	1	
	$5 \cdot 10^{-2}$	44	47	2900	3800	160	590	14	19		
	$5 \cdot 10^{-1}$	47	52							35	
	1	50	58	2420	3550						

a) Deficiency and glow areas are in the same units.
b) Quenched and stimulated intensities are in same units as equilibrium fluorescence; the stimulated intensity given is the total transient intensity.
c) 100 = Electroluminescent intensity of a standard commercial electroluminescent phosphor.
d) Corrected for equivalent absorption.

Table 1. $10^{-3}\%$ Cl, A. Fired with Cu; B. Cu diffused in at 450 °C.

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[7] W. VAN GOOL, Thesis, University of Amsterdam, 1961.

	Cu %	Rel. Equilibrium Fluorescence		Relative Deficiency Area[a] at Liquid N Temp.	Relative Glow Area[a]	IR Stimulation Max. Intensity[b] Liquid N Temperature		IR Quenching Min. Intensity[b] Liquid N Temperature		Relative Electroluminescence[c] Room Temp.	Relative Photoconductivity Room Temp.
		Room Temp.	Liquid Nitrogen Temp.			0.7 μ	1.3 μ	0.7 μ	1.3 μ		
A	0	45[d]	60[d]	5400	10200	240	1230	30	30		23
	$5 \cdot 10^{-3}$	290	245	12000	15500	735	1445	122	245	0	25
	$5 \cdot 10^{-3}$ rapidly cooled	215	205	10000	10600	430		100			
	$5 \cdot 10^{-2}$	190	238	7300	13100	528	1338	119	215		
	10^{-1}	~100	200				~600			2	11
	1	26	140	3250	2320	420	175	100	140		
B	$5 \cdot 10^{-3}$	165	142	5750	6500	340	2300	71	142	0	
	$5 \cdot 10^{-2}$	155	170	7300	7350	510	3100	85	102		
	$5 \cdot 10^{-1}$	144	160							4	
	1	135	148	6000	6100	400	2100	52	74		

a)—d) see Table 1!

Table 2. 10^{-1} % Cl, A. Fired with Cu; B. Cu diffused in at 450 °C.

apparently introduced by the Cu excess. The temperature quenching at higher Cu concentration can also be seen in the glow curves and glow areas.

The intensities at low temperature of the phosphors prepared by Cu diffusion remain relatively constant with changes in Cu concentration. Their intensities correspond to those of the most quenched fired Cu phosphors of the respective Cl concentration. No temperature quenching is observed.

In general stimulation goes parallel to the glow area in these phosphors. The exception is the self-activated phosphor with 10^{-3} % Cl (Table 1). It can be seen from the glow curve of this phosphor (Curve E, Fig. 9) that it has very few shallow traps compared to the others. Since the number of conduction electrons at low temperature chiefly depends on the most shallow occupied traps, this result is consistent with the idea that stimulation is the induction of a faster recombination between conduction electrons and ionized activators[8].

The room temperature photoconductivity goes parallel to the room temperature luminescence intensity except for the self-activated phosphors. This is probably due to more homogeneous absorption in the latter cases which results in a lower recombination rate between conduction and ionized activators. The decrease of photoconductivity with Cu concentration is probably due to the same non-radiative loss of conduction electrons which causes the luminescence intensity to decrease.

It is particularly interesting that no EPR absorption was observed in so many of these phosphors, excited or unexcited. It is hoped that investigations of further groups of phosphors will help to clear up this problem.

Acknowledgements

The authors wish to express their thanks to Lois Eckert Fink for her assistance in the preparation of the phosphors and to James W. Powell, Shirley Aronson and Jean Gallagher for their assistance in the measurements.

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[8] H. Kallmann and K. Luchner, Phys. Rev., in press.