($\sim 0.16\mu_B$) which produces a field increase at Fe nuclei of 16.4 kOe, and give f the value 0.025, so that the moments transferred to $N2$, $N3$, $N4$, and $N5$ should cause additional shifts at Fe of 1.64, 0.82, 0.09, and 0.41 kOe, respectively, about as observed. The $N4$ shift shown in Table I for Co, which was included in computing the spectra, was assigned on the assumption that it approximated the Fe shift.

As discussed above, this interpretation suggests that the Co spectra display mainly the effects of Co impurities on the polarization of delocalized electrons, with an oscillatory behavior having zeros between the first and second shells and at about the fifth shell as shown in Fig. 4. This is not unlike the radial variation about nonmagnetic impurities.[8] Small moment changes could occur on the Co atoms without seriously affecting this conclusion, although such changes would foreshadow the eventual breakdown of the assumed additivity picture.

In summary, two possible schemes are capable of explaining the Fe spectra within the additivity model. One of these, model A above, is similar to that proposed elsewhere,[2,3] although next-nearest-neighbor Co effects are only one-half as large. Both Fe models imply that oscillatory conduction-electron polarization effects exist here similar to those found with nonmagnetic impurities, but they are augmented by local moment changes on Fe atoms near Co impurities. The model A is preferable in that, by simple arguments, it can be correlated with the Co resonance behavior, which appears mainly to be the results of conduction-electron polarization.

I am happy to acknowledge that the experimental data were obtained in collaboration with M. Rubinstein, using samples prepared by M. B. Stearns and G. F. Day.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 9 1 NOVEMBER 1971

Low-Temperature Heat Capacity of the Metamagnet $Ni(NO_3)_2 \cdot 2H_2O$[†]

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The heat capacity C_p of Ni $(No_3)_2 \cdot 2H_2O$ has been measured in the range $1.5\ \mathrm{K} \le T \le 10\ \mathrm{K}$, revealing a sharp λ anomaly characteristic of the transition to a magnetically ordered state at $T_N = 4.105 \pm 0.005$ K. The magnetic contribution to C_p has been separated from the lattice part and the temperature variation of the magnetic entropy has been calculated. The magnetic entropy at T_N is found to be only $0.546R$, suggesting a two-dimensional character to the ordering which is compatible with the picture of this system as an antiferromagnetically coupled array of alternating sheets of ferromagnetically aligned Ni^{++} spins. This interpretation, however, is complicated by the effect of anisotropy on C_p.

INTRODUCTION

Nickel nitrate dihydrate forms monoclinic crystals belonging[1] to the space group $P2_1/c$. The bimolecular unit cell has the dimensions $a = 5.79$ Å, $b = 5.90$ Å, and $c = 8.51$ Å with $\beta = 91.1°$. The crystals are needlelike with the a axis parallel to the needle axis and exhibit good cleavage along the bc plane. Ni^{++} ions at the two nonequivalent sites in the unit cell are surrounded by octahedra composed of four oxygens (from four NO_3^- groups) and two water molecules. Within bc sheets, every Ni^{++} ion is connected by a NO_3^- group to each of four neighboring Ni^{++} ions. Intersheet linkages are presumably rather weak. The path between Ni^{++} ions on adjacent sheets traverses at least two NO_3^- ions.

The magnetic susceptibilities of powdered and single-crystal $Ni(NO_3)_2 \cdot 2H_2O$, measured at low temperatures by Berger and Friedberg,[2] reflect several of its structural features. χ_a exhibits a large spike at ~4.2 K while χ_b and χ_c are nearly equal and pass through a much less pronounced maximum at the same temperature. Between 4 and 20 K, the powder susceptibility obeys a Curie-Weiss law with a ferromagnetic Weiss constant θ. It proved possible to fit these data in the molecular-field approximation with a simplified two-sublattice model in which spins of a given sublattice occupy sites on alternate sheets of Ni^{++} ions. The intrasheet (intrasublattice) exchange coupling is ferromagnetic in sign and given by $2z_2J_2/k = +4.02$ K while the intersheet interaction is antiferromagnetic and much smaller in magnitude, namely, $2z_1J_1/k = -0.61$ K. The approximate uniaxial anisotropy about the a axis (z direction) was incorporated in the model through inclusion of a single-ion term DS_z^2, where $D/k = 6.5$ K and represents an average property of the two inequivalent Ni^{++} ion sites per unit cell.

The fact that the anisotropy energy in $Ni(NO_3)_2 \cdot 2H_2O$ is large in comparison with the exchange energy and that the intrasublattice exchange is of ferromagnetic sign places this antiferromagnet in the metamagnetic category. Thus, it was anticipated that for $T < T_N$ a magnetic field applied along the direction of apparent preferred spin alignment (a axis) exceeding a certain threshold value would cause abrupt switching of alternate sheets of spins to yield a ferromagnetically saturated specimen. This behavior in applied fields has been observed and described in a semiquantitive way with the simplified model by Schmidt and Friedberg.[3]

Neither of the earlier magnetic studies of $Ni(NO_3)_2 \cdot 2H_2O$ located T_N very precisely. This was one of our objectives in carrying out the present measurements. In addition, we were curious to see whether C_p data might reveal evidence of pronounced two-dimensional character in the magnetic ordering which is suggested by the relative magnitudes of inter- and intra-layer spin coupling. This could lead to significant short-range order above T_N which would show up in the temperature variation of the magnetic heat capacity and entropy.

EXPERIMENTS

The specimen of $Ni(NO_3)_2 \cdot 2H_2O$ was prepared by recrystallization from "Baker-Analyzed Reagent Grade" $Ni(NO_3)_2 \cdot 6H_2O$. The starting material was melted at 70 °C and placed in a flask immersed in a water bath kept at 98 °C.[4] Aspirator pumping on this solution led to the formation of pieces of the solid dihydrate composed of many small crystals. Chemical analysis[5] of this material indicated the presence of 26.63 wt% Ni and 17.04 wt% H_2O. The theoretical values for the dihydrate are 26.84 and 16.46%, respectively. The small discrepancy, if significant, appears from x-ray powder analysis[6] not to be associated with the presence of higher hydrates of $Ni(NO_3)_2$.

Details of the experimental procedure have been discussed elsewhere.[7] The 19.7809-g sample was sealed together with a small amount of He^3 gas to assure heat transfer in a copper capsule whose heat capacity had been independently determined. A germanium resistance thermometer attached to the capsule was part of an ac bridge circuit with phase-sensitive detection operated at 38 Hz. We estimate the accuracy of our temperature scale to be ± 0.005 K for $T \leq 4.2$ K and ± 0.01 K above 4.2K.

RESULTS AND DISCUSSION

The measured heat capacity of $Ni(NO_3)_2 \cdot 2H_2O$ below ~10 K is shown in Fig. 1. The tabulated

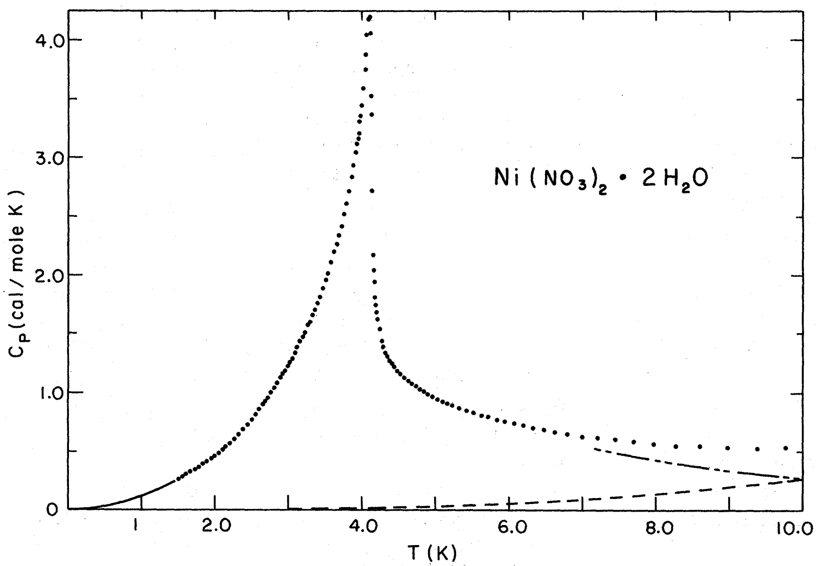

FIG. 1. Measured heat capacity C_p of $Ni(NO_3)_2 \cdot 2H_2O$ as a function of the temperature (dots). Also shown are (a) estimated lattice contribution $2.69 \times 10^{-4}\ T^3$ cal/mole K (dashed line), (b) estimated high-temperature magnetic contribution $27.6T^{-2}$ cal/mole K (broken line), and (c) low-temperature extrapolation $C_p = 0.99R(T/4.105)^2$ (solid line).

TABLE I. Heat capacity of $Ni(NO_3)_2 \cdot 2H_2O$. C_p is given in cal/mole K and T in K.

T	C_p	T	C_p	T	C_p	T	C_p
1.515	0.263	2.692	0.931	4.011	3.476	5.101	0.932
1.538	0.272	2.721	0.962	4.024	3.587	5.170	0.913
1.562	0.287	2.783	1.005	4.035	3.670	5.246	0.894
1.587	0.294	2.814	1.046	4.047	3.746	5.330	0.875
1.612	0.302	2.844	1.085	4.058	3.870	5.421	0.854
1.639	0.317	2.899	1.134	4.070	3.992	5.517	0.833
1.665	0.326	2.931	1.161	4.082	4.055	5.617	0.812
1.693	0.333	2.962	1.188	4.094	4.175	5.723	0.800
1.722	0.344	2.993	1.232	4.106	4.192	5.832	0.774
1.751	0.356	3.025	1.259	4.118	4.055	5.947	0.757
1.780	0.366	3.057	1.288	4.130	3.525	6.069	0.737
1.809	0.378	3.089	1.342	4.141	2.722	6.195	0.720
1.837	0.394	3.122	1.381	4.152	2.170	6.329	0.702
1.867	0.405	3.156	1.436	4.163	1.946	6.470	0.684
1.896	0.420	3.190	1.474	4.175	1.813	6.618	0.670
1.926	0.430	3.225	1.508	4.186	1.745	6.778	0.652
1.957	0.445	3.260	1.578	4.198	1.678	6.764	0.652
1.988	0.459	3.286	1.592	4.209	1.632	6.986	0.629
2.019	0.478	3.322	1.657	4.221	1.605	7.202	0.619
2.050	0.487	3.359	1.704	4.232	1.560	7.436	0.605
				4.244	1.538		
2.080	0.504	3.396	1.754	4.278	1.429	7.694	0.591
2.114	0.516	3.433	1.811	4.290	1.393	7.966	0.569
2.144	0.540	3.471	1.885	4.303	1.378	8.267	0.558
2.175	0.557	3.507	1.956	4.315	1.346	8.600	0.552
2.205	0.572	3.544	2.012	4.332	1.332	8.966	0.538
2.235	0.596	3.581	2.108	4.353	1.312	9.383	0.531
2.265	0.607	3.618	2.198	4.378	1.280	9.761	0.544
2.296	0.629	3.654	2.252	4.408	1.254		
2.326	0.646	3.689	2.333	4.441	1.225		
2.357	0.663	3.723	2.413	4.482	1.194		
2.387	0.686	3.757	2.521	4.532	1.160		
2.418	0.707	3.790	2.609	4.582	1.133		
2.449	0.725	3.821	2.711	4.631	1.105		
2.479	0.747	3.854	2.829	4.682	1.080		
2.510	0.772	3.880	2.929	4.735	1.058		
2.539	0.797	3.941	3.081	4.789	1.035		
2.557	0.811	3.953	3.151	4.844	1.024		
2.582	0.852	3.965	3.206	4.901	0.993		
2.609	0.858	3.976	3.258	4.964	0.970		
2.636	0.872	3.988	3.335	5.033	0.950		
2.663	0.904						

data are presented in Table I. The striking feature is, of course, the sharp λ anomaly which attains a peak value of 4.192 ± 0.01 cal/mole K at $T_{\max} = 4.105 \pm 0.005$ K and marks the cooperative onset of long-range magnetic order below $T_N \approx T_{\max}$. For $T < 2.2$ K, the data are described to within 1% by the simple expression

$$C_p/R = 0.99(T/T_N)^2 .$$

Above T_N, C_p falls rapidly but continuously at first, then continues to fall more slowly with increasing temperature until a minimum is reached very near 10 K.

It is usually possible,[8] in systems of this type, to assume separability of lattice and magnetic contributions to the heat capacity. If T_N is not too high, there is often a temperature interval for $T > T_N$ in which the lattice term varies as T^3, while the magnetic part follows a T^{-2} law. In Fig. 2 we show a plot of C_pT^2 vs T^5 in which those data above ~ 7.5 K fall on a straight line. A least-squares orthogonal polynomial fit of the expression

$$C_pT^2 = a + bT^5$$

to the data yielded $a = 27.6$ cal K/mole and $b = 2.69 \times 10^{-4}$ cal/mole K^4. The coefficient b is compara-

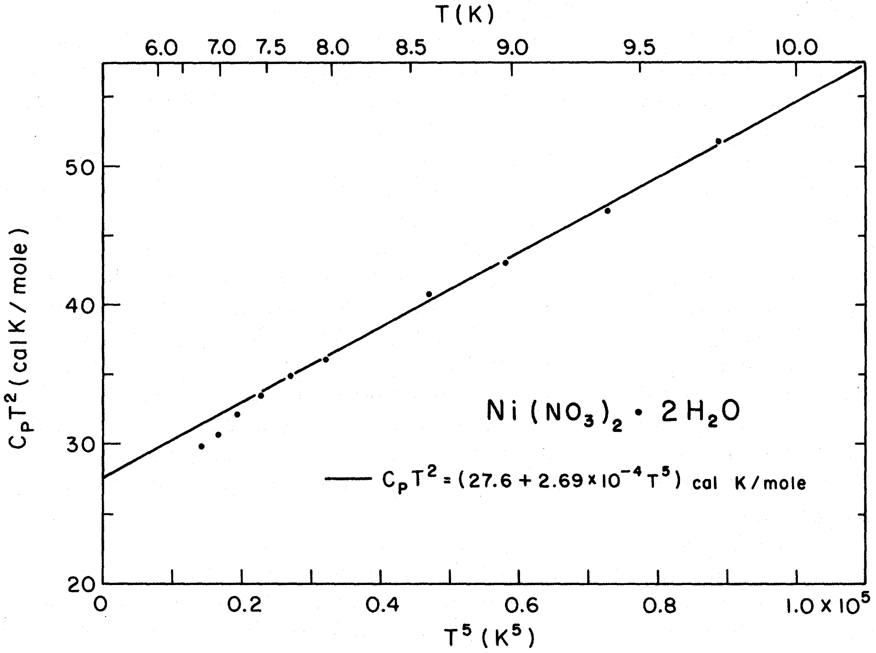

FIG. 2. C_pT^2 vs T^5 for Ni $(NO_3)_2 \cdot 2H_2O$.

ble, for example, to the value 3.59×10^{-4} cal/mole K^4 found[8] in the lattice term of the antiferromagnet $NiCl_2 \cdot 6H_2O$ whose Néel point T_N is 5.34 K.

We shall assume that the lattice contribution in Ni $(NO_3)_2 \cdot 2H_2O$ below ~ 10 K is represented by the fitted expression bT^3, shown as a dashed curve in Fig. 1. Subtracting this quantity from the measured total C_p we obtain an estimate of the magnetic contribution C_{mag}. The magnetic entropy is then given by

$$S_{\text{mag}}(T) = \int_0^T \frac{C_{\text{mag}}}{T}\, dT,$$

where we take $S_{\text{mag}}(0) = 0$. Between 1.515 and 9.761 K this integral has been evaluated numerically using the corrected data. Below 1.515 K, it has been assumed that C_p follows the T^2 relation found to be valid between 2.2 and 1.5 K (see solid line in Fig. 1). C_{mag} has been extrapolated beyond 9.76 K using the fitted expression aT^{-2}, as given above, and has been indicated by a broken line in Fig. 1. $S_{\text{mag}}(T)/R$ is plotted in Fig. 3.

The entropy difference between the fully ordered and disordered states of a system of spins with $S = 1$ should be $\Delta S_{\text{mag}} = R\ln(2S+1) = R\ln 3 = 1.098R$. We note in Fig. 3 that roughly one-half this amount (0.546R) has been realized on warming $Ni(NO_3)_2 \cdot 2H_2O$ to T_N. This "critical entropy" is substantially less than that expected for three-dimensional ordered arrays of spins with $S = 1$. Typical theoretical[9] values are those for the fcc lattices, namely, 0.983R in the Ising limit and 0.810R for the Heisenberg model. It is known theoretically,[9] for Ising models with $S = \frac{1}{2}$, that the critical

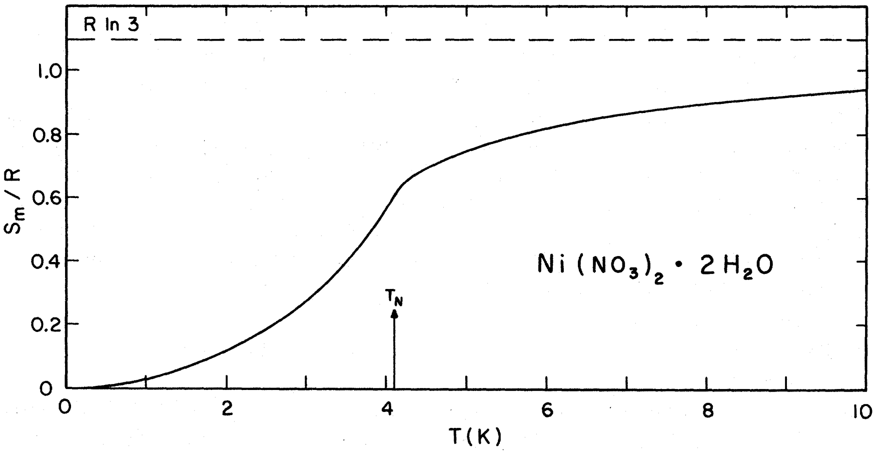

FIG. 3. Magnetic entropy, S_{mag}/R, as a function of temperature for $Ni(NO_3)_2 \cdot 2H_2O$.

entropy is significantly lower for two-dimensional than for three-dimensional spin structures. It is tempting, therefore, to relate the low critical entropy of $Ni(NO_3)_2 \cdot 2H_2O$ to a distinct two-dimensional character in its magnetic ordering. This would be consistent with the conclusion drawn from the magnetic studies that intralayer exchange is much stronger than interlayer spin coupling in this system.

However, the effect of dimensionality may be at least partially obscured by the large single-ion anisotropy also believed to exist in $Ni(NO_3)_2 \cdot 2H_2O$. This is of the form DS_z^2 with $D < 0$. In the absence of external or exchange fields, the Ni^{++} ion ground state ($S = 1$) would thus be split into a lower doublet and an upper singlet, separated by an energy $|D|/k$. If $|D|$ were much larger than the exchange energy, then the Ni^{++} ions would behave during the ordering process as though they had effective spins $S' = \frac{1}{2}$. Note that the critical entropy of the $S = \frac{1}{2}$ Ising model on a three-dimensional simple cubic lattice is $0.560R$, which is close to the value observed in $Ni(NO_3)_2 \cdot 2H_2O$. In our case $D/k \approx -6.5$ K. Thus, $|D|$ is not so large in comparison with $T_N (= 4.1$ K) as to ensure that $S' = \frac{1}{2}$ is a good approximation near or below T_N. $|D|$ is large enough, however, to make it difficult to draw conclusions about dimensionality from a comparison of the data with theoretical predictions for simple models with $S = 1$.

Extrapolating the magnetic entropy to $T = \infty$, assuming C_{mag} to have the temperature dependence inferred above for the interval 7–10 K, one finds a total $\Delta S_{mag} = 1.007R$. This value is close enough to $R \ln 3 = 1.098R$ to indicate that all three components of the Ni^{++} ion ground state are populated during the ordering process. However, about 8% of the theoretical entropy change is not accounted for. It is not likely that this difference can be explained by inadequacy of the extrapolation of C_{mag} below 1.5 K which, if anything, involves an overestimate. We are inclined, rather, to attribute it to the inability of a single term in T^{-2} to describe C_{mag} adequately below ~ 10 K (where we have fitted the coefficient a) due to the effects of short-range order in a layered structure or anisotropy or a mixture of the two. A proper representation of C_{mag} in this region would probably require several terms of the high-temperature series expansion appropriate to this lattice for the particular interactions which are applicable. In view of the comparable magnitudes of single-ion anisotropy and exchange energies in this material, it seems unlikely that either the pure Ising or the pure Heisenberg models would be adequate for the calculation of these terms. In principle, they can be extracted from the data by a suitable curve-fitting procedure. However, when one includes a simultaneous fit of the lattice heat capacity, the number of adjustable parameters becomes large and the results rather unreliable.

The rapidly-grown fine crystals used in these measurements might be expected to exhibit a cooperative heat capacity anomaly distinctly rounded off at its maximum as a result of specimen inhomogeneity through imperfection, strain, or effective particle size. For this reason we have not attempted a detailed study of the temperature dependence of C_p through T_N or the assignment of critical indices above and below T_N. We note, however, that for $3.723 \text{ K} < T < 4.004$ K, C_p varies logarithmically with $(T_N - T)$ if T_N is taken to be slightly higher than $T_{max} = 4.105$ K. This is consistent with observations on other antiferromagnets showing rounding of the λ anomaly in the critical region.[10] The value of T_N is, nevertheless, still smaller than the temperature at which the powder and single-crystal susceptibilities appear to achieve their maximum values,[2] namely, ~ 4.2 K. This is to be expected for a system which, in spite of its strong ferromagnetic intralayer interaction, is basically an antiferromagnet whose Néel point is depressed in an applied magnetic field. In zero field, Fisher's relation[11,12] should apply and $d\chi/dT$, not χ, should have its maximum at T_N.

As noted above, C_p appears to vary as T^2 at the lowest temperatures achieved in the present work (~ 1.5 K). It is not clear that this observation has any simple interpretation. Kubo[13] has shown, on the basis of spin-wave theory, that the specific heat of a two-dimensional Heisenberg antiferromagnet should vary as T^2 at temperatures well below T_N but such that $kT >$ the anisotropy gap in the spin-wave spectrum. Unfortunately, this result seems to have little bearing on the problem of $Ni(NO_3)_2 \cdot 2H_2O$, for which the intralayer coupling is ferromagnetic and the single-ion anisotropy is large in comparison with the exchange energy. An Ising model is thus likely to be more suitable than the Heisenberg model and spin-wave results are inapplicable. The latter objection appears to apply also to Yoshimori's[14] spin-wave model of a metamagnet composed of ferromagnetic layers. In a certain range of temperature for some values of the parameters the specific heat of this model varies as T^2, but again the applicability of spin-wave theory is doubtful. It should be noted that the possible existence of spin canting[2,3] in this system may further complicate the interpretation of the temperature dependence of C_p in this region. We hope, eventually, to extend the present measurements below 1 K to provide a clearer picture of the limiting form of that temperature dependence.

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Path-Integral Approach to the Magnetic-Impurity Problem. I

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The Anderson model is treated using a functional-integral technique. A systematic approach is described which does not resort to expansions in the amplitudes of the oscillating components of the random field, nor in the parameters of the model. The first leg of the program, which selects a given temperature interval, is carried out in detail, and the resulting distribution functions and thermodynamic quantities are calculated. The results are discussed and compared with other approaches to the magnetic-impurity problem.

I. INTRODUCTION

Recently, the problem of a single impurity inside a conduction band was vigorously attacked in a series of articles[1–6] using the path-integral method. This method, which was originally introduced by Stratonovich and Hubbard,[7] consists of replacing the electrostatic interaction of two electrons on the impurity with a time-dependent field (or two fields) acting only on the electrons which are on the impurity site. To obtain the exact partition function of the problem, one must carry out a functional average with a Gaussian weight over the auxiliary fields.[1–5]

The above-mentioned replacement is exact, and the one-particle problem in the presence of the time-dependent fields can be formally solved.[1–5] Nevertheless, concrete results have been obtained only in certain approximations. Most of the approximations to date[1–6] have consisted of treating the oscillating part of the field as a small quantity. In this paper we present an approach which treats each Fourier component of the oscillating field exactly to all orders, but approximates interactions between different oscillating components.

To put our contribution in perspective, we review briefly the approximations that have been used in previous work. The simplest approximation is the "static" one.[1–5] Here, the fields are time independent and all thermodynamic quantities can be fully calculated. In this approximation one obtains exact results in two limiting cases: (i) when there is finite electrostatic repulsion U and vanishing width Γ of the impurity level, and (ii) when $U=0$ and $\Gamma > 0$.[1–4] The first-order corrections (in Γ/U or U/Γ) to these limits do not agree with the static approximation.

The static approximation to the partition function as a function of the time-independent field ξ_0 (before the Gaussian average) develops maxima at