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Energy levels, EPR parameters and magnetic properties of the $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ semimagnetic semiconductor

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Abstract. The fine-structure energy levels of the ground state, EPR parameters, specific heat and magnetization in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ are studied by a double spin-orbit model. The results are in good agreement with the recent experiments and a significant charge-transfer effect is found to exist in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$.

1. Introduction

Semimagnetic semiconductors (SMSCs) or diluted magnetic semiconductors (DMSCs) are II–V, II–VI, III–V, or IV–VI compounds, where some nonmagnetic cations are substituted by magnetic ions of the transition-metal or rare-earth-metal elements [1, 2]. Mn and Co SMSCs exhibit typical Brillouin-type paramagnetic behaviour [3, 4] resulting from the single multiplet ground state of the ion, and Fe SMSCs show Van Vleck-type paramagnetism [5–7] due to the singlet ground state of Fe^{2+} . A great interest has been recently devoted to the new group of Cr-based SMSCs which reveal an intermediate type of magnetic behaviour different from all the other SMSCs (see, e.g., [8–12]). In Cr SMSCs a strong static Jahn–Teller (JT) effect is present in the lowest states and leads to a change in symmetry, i.e., a static tetragonal JT distortion, from tetrahedral (T_d) to tetragonal (D_{2d}) symmetry [13, 14], therefore, the ground state is a doublet followed by another closely lying doublet and a singlet, which leads to a pronounced anisotropy of the energy structure [13, 14] and the magnetic properties [8–12].

By a simple crystal-field (CF) approximation a series of studies [8–11] successfully dealt with the energy levels and the magnetic properties of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$, which first fitted the theoretical predictions to the fine-structure experimental data [13, 14] and obtained the corresponding values of the CF and spin-orbit (SO) parameters, and then calculated, e.g., the specific heat and magnetization using these parameters. However, the value of SO parameter $\zeta \cong 340 \text{ cm}^{-1}$ of $\text{Cr}^{2+}(3d^4)$ ion used in [8, 10, 11] seems unreasonably large. From the CF theory, in the semiconductors, i.e., covalent crystals, the Racah (B , C), CF (B_k^q) and SO (ζ) parameters can be written as [15, 16]

$$B = K^2 B_0 \quad C = K^2 C_0 \quad B_k^q = K B_{k0}^q \quad \zeta = K \zeta_0$$

where $K (\leq 1)$ is the covalently reduced constant, and subsymbol 0 corresponds to the free-ion situation. The free-ion SO parameter ζ_0 is only 230–260 cm^{-1} for the Cr^{2+} ion [15–17]. It is well known that in the study of the electronic structure of the transition-metal ions in semiconductors one should consider the SO coupling associated with not only the

central transition-metal ions but also the ligands, because, usually, the SO coupling within the ligands in the semiconductors is much stronger than that within the transition-metal ions. Recently a work [7] has shown the important ligand SO contribution in Fe SMSCs. Too large a value of SO parameter for the Cr^{2+} ion used in [8, 10, 11] may be due to ignoring the ligand SO mechanism for the optical and magnetic properties of the Cr SMSCs.

2. Theoretical model

Considering the SO coupling within the ligands, the orbitals of the double SO model are the linear combinations of the d orbitals of Cr^{2+} and the outermost s and p orbitals of Se in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ as given by [7, 13, 18, 19]

$$\begin{aligned}\Psi_\alpha &= N_E^{-1/2}(\phi_{d\alpha} - \sqrt{3}\lambda_{p_\pi}\chi_{p_\pi\alpha}) \\ \Psi_\beta &= N_{T_2}^{-1/2}(\phi_{d\beta} - \lambda_s\chi_{s\beta} - \lambda_{p_\sigma}\chi_{p_\sigma\beta} - \lambda_{p_\pi}\chi_{p_\pi\beta})\end{aligned}\quad (1)$$

with the normalization constants

$$\begin{aligned}N_E &= 1 + 3\lambda_{p_\pi}^2 - 2\lambda_{p_\pi}S_{p_\pi} \\ N_{T_2} &= 1 + \lambda_s^2 + \lambda_{p_\sigma}^2 + \lambda_{p_\pi}^2 - 2\lambda_sS_s - 2\lambda_{p_\sigma}S_{p_\sigma} - 2\lambda_{p_\pi}S_{p_\pi}\end{aligned}\quad (2)$$

where (in terms of the cubic field representations $\theta, \varepsilon, \xi, \eta, \zeta$) α stands for the symbols θ and ε and β for ξ, η , and ζ . The wave functions $\phi_{d\alpha}$ and $\phi_{d\beta}$ represent the d orbitals of the transition-metal ion (Cr^{2+}), whereas $\chi_{p_\pi\alpha}, \chi_{s\beta}, \chi_{p_\sigma\beta}$ and $\chi_{p_\pi\beta}$ are the appropriate symmetry combinations of the outermost s, p_σ , and p_π orbitals of the ligands (Se). $\lambda_s, \lambda_{p_\sigma}$, and λ_{p_π} are the admixture coefficients, and S_s, S_{p_σ} , and S_{p_π} are the two-centre overlap integrals between central ion and ligands defined as

$$S_s = \langle \phi_{d\xi} | \chi_{s\xi} \rangle \quad S_{p_\sigma} = \langle \phi_{d\xi} | \chi_{p_\sigma\xi} \rangle \quad S_{p_\pi} = \langle \phi_{d\xi} | \chi_{p_\pi\xi} \rangle. \quad (3)$$

The Hamiltonian for the ground ${}^5\text{D}$ multiplet of the $\text{Cr}^{2+}(3d^4)$ ion in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ is taken as [11, 15, 16]

$$H = H_{CF} + H_{SO} + H_{Ze} \quad (4)$$

where H_{Ze} is the Zeeman interaction, H_{CF} the tetragonal crystal potential due to the JT distortion and H_{SO} the SO coupling. One should note that there are two (rather than one, ζ) parameters for the SO coupling within the double SO orbitals (1):

$$\begin{aligned}\zeta_1 &= N_{T_2}^{-1} \left[\zeta_d + \left(\sqrt{2}\lambda_{p_\sigma}\lambda_{p_\pi} - \frac{1}{2}\lambda_{p_\pi}^2 - \sqrt{2}\lambda_s\lambda_{p_\pi}A \right) \zeta_p \right] \\ \zeta_2 &= (N_E N_{T_2})^{-1/2} \left[\zeta_d + \left(\frac{1}{\sqrt{2}}\lambda_{p_\sigma}\lambda_{p_\pi} + \frac{1}{2}\lambda_{p_\pi}^2 - \frac{1}{\sqrt{2}}\lambda_s\lambda_{p_\pi}A \right) \zeta_p \right]\end{aligned}\quad (5)$$

with the overlap integral

$$A = R \left\langle \chi_{p_y} \left| \frac{\partial}{\partial y} \right| \chi_s \right\rangle \quad (6)$$

where R is the distance between central ion and ligands, and ζ_d and ζ_p are the SO coupling constants associated with the d electron of the central transition-metal ion (Cr^{2+}) and p electrons of ligands (Se), respectively. The 25×25 matrices of (4) for the orbitals

(1) have been calculated within the 5D state ($L = S = 2$, and the degeneracy is then $(2L + 1)(2S + 1) = 25$) as

$$\begin{pmatrix} M(\Gamma_1) & B(\Gamma_1, \Gamma_2) & B(\Gamma_1, \Gamma_3) & B(\Gamma_1, \Gamma_4) & B(\Gamma_1, \Gamma_5^-) & B(\Gamma_1, \Gamma_5^+) \\ & M(\Gamma_2) & B(\Gamma_2, \Gamma_3) & B(\Gamma_2, \Gamma_4) & B(\Gamma_2, \Gamma_5^-) & B(\Gamma_2, \Gamma_5^+) \\ & & M(\Gamma_3) & B(\Gamma_3, \Gamma_4) & B(\Gamma_3, \Gamma_5^-) & B(\Gamma_3, \Gamma_5^+) \\ & & & M(\Gamma_4) & B(\Gamma_4, \Gamma_5^-) & B(\Gamma_4, \Gamma_5^+) \\ & & & & M(\Gamma_5^-) & B(\Gamma_5^-, \Gamma_5^+) \\ & & & & & M(\Gamma_5^+) \end{pmatrix} \quad (7)$$

where $M(\Gamma_i)$ ($i = 1, 2, 3, 4, 5$; $M(\Gamma_5^-) = M(\Gamma_5^+)$) are the block matrices resulting from the tetragonal CF and the SO interactions and Γ_i the irreducible representations of the tetragonal symmetry, whereas the $B(\Gamma_i, \Gamma_j)$ represent the block matrices accounting for the mixing of the Γ_i and Γ_j states by the Zeeman H_{Ze} . The Hamiltonian matrix is of Hermite symmetry, and only the blocks on and above the diagonal are shown in (7). Obviously, the matrices in (7) are the functions of the CF (B_k^q) and SO (ζ_1 and ζ_2) parameters and the magnetic field (B_x , B_y , and B_z). It should be pointed out that this matrix is also suitable for the $3d^6$ ion with reverse signs of the CF (B_k^q) and SO (ζ_d) parameters. The energy levels and the magnetic properties of $Zn_{1-x}Cr_xSe$ can be studied by using these matrices as long as the values of not only B_k^q and $\zeta_d(\text{Cr}^{2+})$ but also $\xi_p(\text{Se})$, λ_s , λ_{p_σ} , λ_{p_π} , S_s , S_{p_σ} , S_{p_π} , and A caused by the introduction of the ligand SO mechanism are known.

3. Energy levels and EPR parameters

In this work, the values of the CF parameters $Dq = -494.25$ and $B_4^0 = \frac{1}{5}B_2^0 = -17.14$ (cm^{-1}) used in [11] are adopted, and the values of $\xi_d(\text{Cr}^{2+}) = 240$ cm^{-1} [17], $\xi_p(\text{Se}) = 1659$ cm^{-1} [20] and $R(\text{Cr-Se}) = 2.45$ \AA [21] are used. The values of the overlap integrals $A = 1.7191$, $S_s = 0.0295$, $S_{p_\sigma} = 0.0607$, and $S_{p_\pi} = 0.0173$ can be obtained from a Slater-type orbital [22, 23]. There remain the values of the admixture coefficients λ_s , λ_{p_σ} , and λ_{p_π} unknown, and the present work adopts the procedure [18, 19] of fitting the fine-structure experimental data using λ_s , λ_{p_σ} , and λ_{p_π} . The set of values of the admixture coefficients that explain best the experimental data are $\lambda_s = 0.08$, $\lambda_{p_\sigma} = 0.58$, and $\lambda_{p_\pi} = 0.26$ (see table 1).

Table 1. The fine-structure energy levels and EPR parameters of $Zn_{1-x}Cr_xSe$ (in cm^{-1} , except g_{\parallel} and g_{\perp} , dimensionless).

	ZFS ^a	FIR ^a	JT ^a	ZPL ^a	g_{\parallel}	g_{\perp}	b_2^0	b_4^0	b_4^4
Calc.	0.14	7.61	1650.55	4974.77	1.887	1.930	-2.52	0.0335	0.3400
Expt.	0.14 [14]	7.43 [14]	1650 [14]	4975 [14]	1.961 [14]	1.980 [14]	-2.48 [14]		0.06 [26]

^a ZFS and JT are the zero-field and the Jahn–Teller splitting, respectively, FIR the first transition, ZPL the zero-phonon line.

At the same time, the EPR parameters g_i and b_k^q are obtained (see table 1) by using the formulas, shown in [14] and [24] and [25], respectively, with the necessary values from the matrix diagonalization. The values of g_{\parallel} , g_{\perp} and b_2^0 are in good agreement with the experiments [13, 14]. One may note that the present value of $b_4^4 = 0.34$ is much larger than the previous one $b_4^4 = 0.06$ in ZnSe:Cr^{2+} [26], but quite close to those of $b_4^4 = 0.35$ in ZnS:Cr^{2+} and 0.48 (cm^{-1}) in ZnTe:Cr^{2+} [14], which necessitates further checking of such

a large difference of the b_4^4 measured between in ZnSe and in ZnS and ZnTe because ZnS, ZnSe and ZnTe have similar zinc-blende structures (space group $F\bar{4}3m(216)$) [21, 27]. It should be pointed out that the calculated $g_{\perp} = 1.930$ ($<g_0 = 2.0023$, the free-ion g factor) removes the difficulty that the previously calculated $g_{\perp} = 2.013$ [14] being larger than g_0 is quite contrary to the measured $g_{\perp} = 1.98$ less than g_0 [14]. The above difficulty in [14] seems to be due to some approximations, such as the rough expressions of ζ_1 and ζ_2 as well as K_1 and K_2 that are functions of admixture coefficients λ and overlap integrals S and A , and are necessary for calculation of g , the used values of λ_s , $\lambda_{p\sigma}$, and $\lambda_{p\pi}$ obtained by estimating MnO_4^- and so on.

The large values of λ in Cr-based ZnSe indicate that the contribution of the outermost s , p_{σ} , and p_{π} orbitals of the ligands to the orbitals (1) is important; in other words, the ligand SO contribution to the fine-structure energy levels of the ground state and the EPR parameters is important. These values of λ can be used in the first-order approximation to deduce the charge-transfer covalencies, by means of the expressions [18, 19]

$$\lambda_i = S_i + \gamma_i \quad (i = s, p_{\sigma} \text{ and } p_{\pi}) \quad (8)$$

where S_s , $S_{p_{\sigma}}$, and $S_{p_{\pi}}$ have been defined by (3) and γ are the corresponding charge-transfer covalency parameters. The bonding orbitals can be formed by combining the central-ion d orbitals with the orbitals of the ligands by means of the charge-transfer covalency parameters γ . The calculated values of the parameters γ_s , $\gamma_{p_{\sigma}}$, and $\gamma_{p_{\pi}}$ turn out to be 0.05, 0.51, and 0.24, respectively. This shows clearly the significant charge-transfer effect in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$. It is of interest to note that in this work the SO parameters $\zeta_1 \cong 334 \text{ cm}^{-1}$ and $\zeta_2 \cong 338 \text{ cm}^{-1}$ are quite near to the $\zeta \cong 340 \text{ cm}^{-1}$ used in [8, 10, 11], this is why only $\zeta \cong 340 \text{ cm}^{-1}$, being much larger than expected, may be suitable for the studies [8, 10, 11] in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$, i.e., one may understand that ζ in these works takes approximately the places of ζ_1 and ζ_2 in the present paper. However, this simple approximation [8, 10, 11] ignores the significant charge-transfer effect in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$.

4. Magnetic properties

Using the above values of the CF and SO parameters as well as the admixture coefficients, the specific heat of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ ($x = 0.004$) is plotted in figure 1, whereas the magnetization of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ ($x = 0.002$) is plotted in figures 2 and 3. The methods in [11] for the calculation of the specific heat and the magnetization are used. The specific heat C_m and the magnetization M_m can be written in the form [11]

$$C_m = \frac{K_B x N_{AV}}{(K_B T)^2} (\langle E^2 \rangle - \langle E \rangle^2) \quad (9)$$

$$M_m = \frac{\mu_B x N_{AV}}{m_{mole}} \langle M \rangle \quad (10)$$

where N_{AV} is the Avogadro number, m_{mole} the mass of the $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ molecule, $\langle M \rangle$ the average magnetic moment per isolated Cr^{2+} , and $\langle E^n \rangle$ the expectation value of the n th power of energy Hamiltonian (4). It should be noted that the present paper considers only the contribution to the magnetization from an isolated Cr^{2+} ion; the contribution from an isolated ion has been shown [6, 7] to be much larger than those from, e.g., the nearest-neighbour pair, the JT effect, and so on in Fe-based SMSCs.

From figure 1, in which the curves 1, 2, and 3 correspond to magnetic field $B = 2.8$, 1.0 and 0 T, respectively, one can see easily that the application of a magnetic field results in a

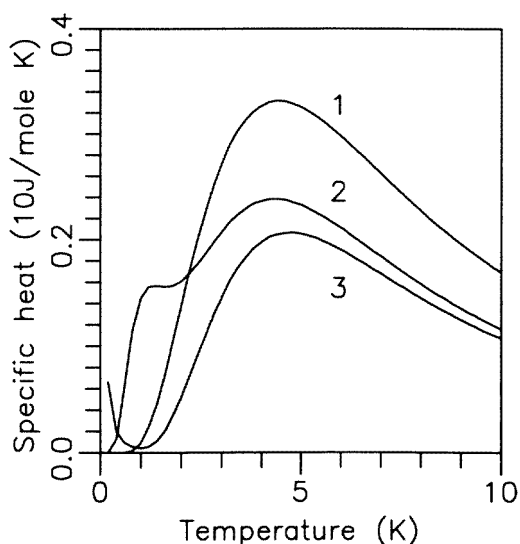


Figure 1. Magnetic specific heat of $Zn_{1-x}Cr_xSe$ ($x = 0.004$) for $B \parallel [111]$. Curves 1, 2, and 3 correspond to $B = 2.8, 1.0$ and 0 T, respectively.

strong increase of specific heat, similar to Mn- and Co-based SMSCs [3,4], but in contrast with Fe-SMSCs [5, 6]. This is due to the ground state being a multiplet since a split multiplet provides a series of levels that can be thermally populated, thereby giving rise to an increase of the specific heat.

Figure 2 shows representative results for magnetic field $B \parallel [100]$ at the temperatures $T = 2, 4.2, 10, 20, 30,$ and 40 K corresponding to the curves 1, 2, 3, 4, 5, and 6, respectively. At the lowest temperatures the magnetization varies strongly with B , which is in contrast with the cases of Mn and Co SMSCs [3,4], whereas a strong variation of the magnetization with temperature is also in contrast to Fe SMSCs whose magnetization is temperature independent at low T [5–7]. This is due to the excited states close to the ground state.

Figure 3 shows the magnetic anisotropy at $T = 2$ K where the curves 1, 2, and 3 correspond to $B \parallel [100], [110],$ and $[111]$, respectively. This figure reveals an intermediate situation as compared with those in Mn- and Co- [3,4] and Fe- [5–7] based SMSCs. The magnetization is isotropic and varies linearly with B at low magnetic field ($B < 1$ T), whereas at higher fields it deviates from linearity leading to the appearance of magnetic anisotropy above $B = 1$ T. Figure 3 indicates the highest magnetization for $B \parallel [100]$ and the lowest for $B \parallel [111]$, and the difference of the magnetization is large between $[100]$ and $[110]$, and small between $[110]$ and $[111]$ directions.

The magnetic susceptibility of $Zn_{1-x}Cr_xSe$ ($x = 0.002$ and 0.006) is also plotted in figure 4 following the method in [28,29]; it is different from those in Mn- [1,2] and Fe- [5,28–30] based SMSCs. The detailed variations for the magnetic susceptibility of $Zn_{1-x}Cr_xSe$ have not been studied in literature. The present results may be useful in future experiments.

It should be pointed out that the results shown in figures 1, 2 and 3 are in good agreement with those measured recently [11], thus provide a further check of the present values of the CF and SO parameters as well as the admixture coefficients. This shows again the charge-transfer effect in $Zn_{1-x}Cr_xSe$.

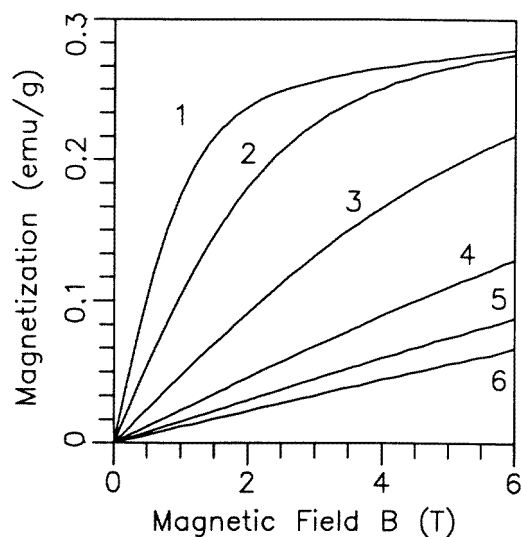


Figure 2. Magnetization of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ ($x = 0.002$) as a function of magnetic field $B \parallel [100]$ at various temperatures. Curves 1, 2, 3, 4, 5, and 6 correspond to $T = 2, 4.2, 10, 20, 30,$ and 40 K, respectively.

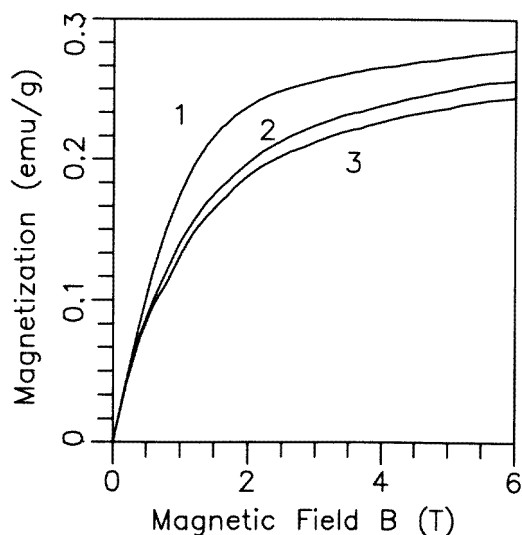


Figure 3. Anisotropy magnetization of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ ($x = 0.002$) at $T = 2$ K. Curves 1, 2, and 3 correspond to $B \parallel [100]$, $B \parallel [110]$, and $B \parallel [111]$, respectively.

5. Conclusions

A Hamiltonian matrix has been constructed for the ground ^5D multiplet of 3d^4 and 3d^6 ions, including the tetragonal crystal-field and Zeeman interactions, and the spin-orbit coupling within not only the central 3d^4 and 3d^6 ions but also the ligands. The matrix has been used to

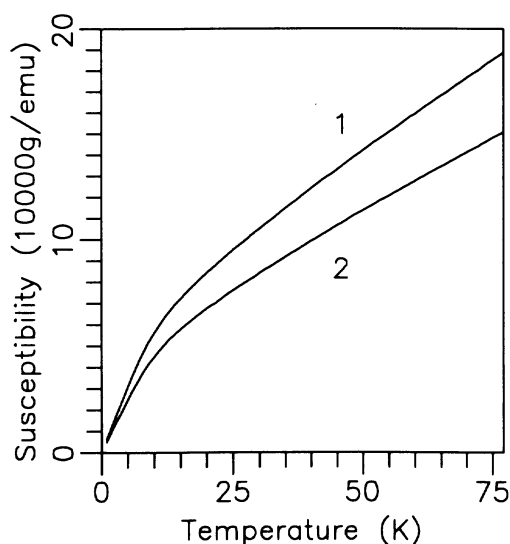


Figure 4. Inverse magnetic susceptibility of $Zn_{1-x}Cr_xSe$ as a function of temperature. Curves 1 and 2 correspond to $x = 0.002$ and 0.006 , respectively.

study the optical and magnetic properties of Cr^{2+} ions in semimagnetic semiconductor ZnSe. The values of the crystal-field and spin-orbit parameters as well as the admixture coefficients that explain best the experimental data of the fine-structure energy levels of the ground state and the EPR parameters are obtained. The contribution of the spin-orbit coupling within ligands to the EPR parameters and energy levels is found to be important, and a significant charge-transfer effect is found to be present in this system. Using these parameter values, the magnetic specific heat, the magnetization, and the magnetic susceptibility are studied. The theoretical results show clearly the intermediate type of magnetic behaviour in Cr based semimagnetic semiconductor different from all the other ones. The agreement between the presently revealed magnetic properties and the experiments shows again the charge-transfer effect in $Zn_{1-x}Cr_xSe$. The estimation of the magnetic susceptibility in $Zn_{1-x}Cr_xSe$ may be useful in future experiments.

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