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Ion pairs and spontaneous break of symmetry in the valence-fluctuating compound YbB_{12}

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Electron spin resonance (ESR) from Yb^{3+} ions in a single crystal of fluctuating valence compound YbB_{12} was studied. We have observed two main lines symmetrically displaced from a g value of 2.55 and exhibiting modulation with 5% anisotropy, when the magnetic field was rotated in the (110) plane from the cubic axis to the [110] direction. Experimental results are explained by an existence of Yb-Yb pairs which are coupled by isotropic exchange but interact also with the other pairs by dipole and exchange coupling. A strong temperature dependence of the amplitude of the ESR signals is found and interpreted as a result of capture of electrons by Yb^{3+} ions from electron traps with a binding energy of 18 K. The occurrence of a slight anisotropy in a cubic semiconductor may be the result of a spontaneous break of symmetry specific for the ground state of a Kondo dielectric.

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I. INTRODUCTION

Ytterbium dodecaboride YbB_{12} has been intensely studied in recent years since, besides samarium hexaboride SmB_6, it is a classical representative of semiconductors with fluctuating valence (Kondo dielectrics). The unusual properties of these materials being macroscopic quantum systems have attracted traditionally the attention of investigators. They are partly discussed in reviews (see Refs. 1 and 2).

Though ytterbium dodecaboride was studied by a number of experimental methods (electrical measurements,[1,3] magnetic susceptibility,[1,3] heat capacity,[4] optical conductivity in the far infrared,[5] inelastic neutron scattering,[6,7] photoemission,[8] and NMR[9] spectroscopy), the nature of the ground state in this semiconductor is not well understood. In contrast to samarium hexaboride SmB_6 with an intermediate value of samarium valence 2.6 the valence of ytterbium ions in ytterbium dodecaboride, YbB_{12}, is much closer to integer and is approximately 2.9. Therefore even the classification of YbB_{12} as a material with fluctuating valence is sometimes disputed.[6,7]

The experimental results on the properties of YbB_{12} are usually treated using a model which considers fluctuations of the ytterbium valence between 2+ and 3+ states and implies the existence of a gap in the electronic energy spectrum of this material. According to the experimental data, the width of the gap is 10–25 meV and it opens below 70 K.

However, the origin of the gap differs depending on the particular model. Unusual low-temperature properties of the Kondo insulator were treated mostly in the framework of a model with an f-d hybridization gap partly renormalized by correlation effects.[2] This model could not explain some fine details of the behavior of this material at low temperatures and more elaborate theories were put forward [e.g., the exciton-polaron model developed by Kikoin and Mishchenko[10] and Curnoe and Kikoin[11] and Wigner crystallization or Wigner liquid model (Kasuya[12])].

A full variety of experimental methods can be useful to choose between different models. Electron spin resonance (ESR) can provide information on the existence of the gap in the electronic energy spectrum of the Kondo semiconductor and its temperature dependence. Such a study was realized in SmB_6 for a classical representative of Kondo semiconductors.[13] ESR studies in this material have also revealed both dynamic and static Jahn-Teller effect[14,15] favoring an exciton-polaron model of the ground state of SmB_6. Recently two of the present authors[16] have studied the temperature dependence of the energy gap in YbB_{12}, using ESR from spin markers (Gd^{3+} ions) inserted into the crystal.

In the present work ESR is first studied from Yb^{3+} ions with a stabilized valence in YbB_{12} single crystal. Stabilization of the valence in valence-fluctuating compounds with impurities or defects in the crystal lattice is well known for samarium ions in SmB_6.[17] In Ref. 15 ESR from Sm^{3+} ions was studied, and both static and dynamic Jahn-Teller effects were found. However, as far as we know, stabilization of the valence of Yb^{3+} ions has not been observed up to now.

Our experimental results demonstrate splitting and angular modulation of the ESR line, which should exhibit isotropic behavior in a cubic crystal. The results can be understood assuming the existence of Yb^{3+} ion pairs coupled by isotropic exchange interaction, which also interact with neighboring pairs. A strong temperature dependence of the amplitude of the ESR signals is found and interpreted as a result of the capture of electrons by Yb^{3+} ions from electron traps with a binding energy of 18 K. The occurrence of anisotropy in a cubic semiconductor may be the result of a spontaneous break of symmetry specific for the ground state of a Kondo dielectric.

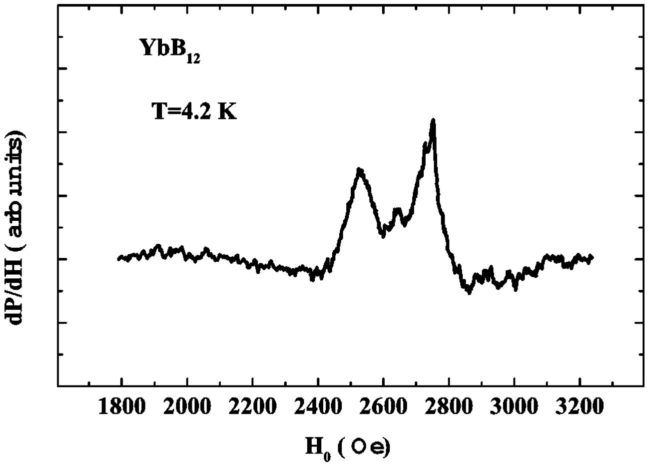

FIG. 1. ESR spectrum at $T=4.2$ K and $\phi=0°$ demonstrating two large lines and a weak in-between line.

II. EXPERIMENT

In this work ESR in a single crystal of YbB_{12} was studied. Single-crystal YbB_{12} was grown by the floating zone method using an image furnace equipped with four Xe lamps.[3] The single crystals obtained by this technology were of purity highest to the state of the art.[3]

The measurements were done at the X band in the temperature range 1.6–4.2 K. YbB_{12} is an intermediate valence compound. These materials have usually the frequency of valence fluctuations on the order of 10^{13}–10^{14} Hz.[18] Therefore, observation of ESR signals at 10^{10} Hz from the ions with a fluctuating valence is impossible. However, we succeeded in observing an ESR signal from the localized Yb^{3+} state ($4f^{13}$, ${}^2F_{7/2}$). The origin of this signal can be attributed to the effect of defects and/or vacancies stabilizing the valence of Yb ions. A similar effect of valence stabilization due to local compensation of charge was previously observed in SmB_6.[15] The concentration of Yb^{3+} ions was estimated by comparing the ESR signals with those from a reference sample and was 0.2–0.5 at. %.

The ESR signal consisted of two intense and one weak line (Fig. 1). The position of the side intense lines of the spectrum depends on the orientation of the crystal in the magnetic fields (on the angle ϕ between the magnetic field and the [001] axis in the (110) crystal plane). The average g factor of the side lines at $T=1.6$ K is 2.55. The central weak line corresponds to a g factor of 2.52 with little anisotropy.

The linewidth ΔH of the side intense lines is 80–90 Oe at the lowest temperature ($T=1.6$ K) which increases to 110–120 Oe at 4.2 K. Such a large linewidth with its fairly weak temperature dependence is characteristic of an inhomogeneous broadening of the ESR lines. We have observed also a slight increase of the g factor of the side lines on the temperature decrease from 2.42 and 2.62 at 4.2 K to 2.45 and 2.65 at 1.6 K. In the same temperature interval the magnetic susceptibility was independent of the temperature within the accuracy of 1%. The decrease of temperature from 4.2 to 1.6 K leads to a sharp enhancement of the intense lines by a factor of 30–40 (Fig. 2). The intensity of the weak line follows approximately the same temperature dependence.

The angular dependence of the position of the ESR lines with the magnetic field rotated in the (110) plane was measured at 4.2 and 1.6 K. This angular dependence did not change with temperature. In Fig. 3, ESR signals are presented for different angles ϕ between the fourfold axis and magnetic field at 1.6 K. The angular dependence of the position of the intense lines is shown in Fig. 4. It can be described by a function $H=2635\pm100(3\cos^3\phi-2\cos\phi)$. As stated above, the weak line had nearly no angular dependence.

At $T=1.6$ K besides the ESR signal from Yb^{3+} ions we have observed seven narrow lines ($\Delta H\sim17$ Oe) at the resonance field of 3300 Oe ($g\sim2.00$) with the intensity by two

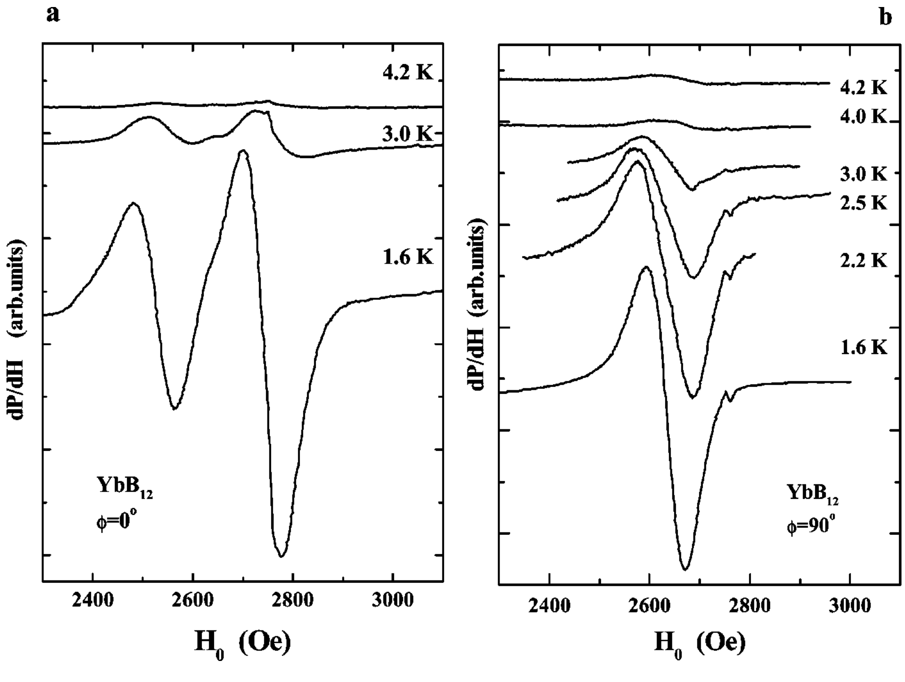

FIG. 2. a. ESR spectra for several temperatures in the 1.6–4.2 K range at $\phi=0°$. b. ESR spectra for several temperatures in the 1.6–4.2 K range at $\phi=90°$.

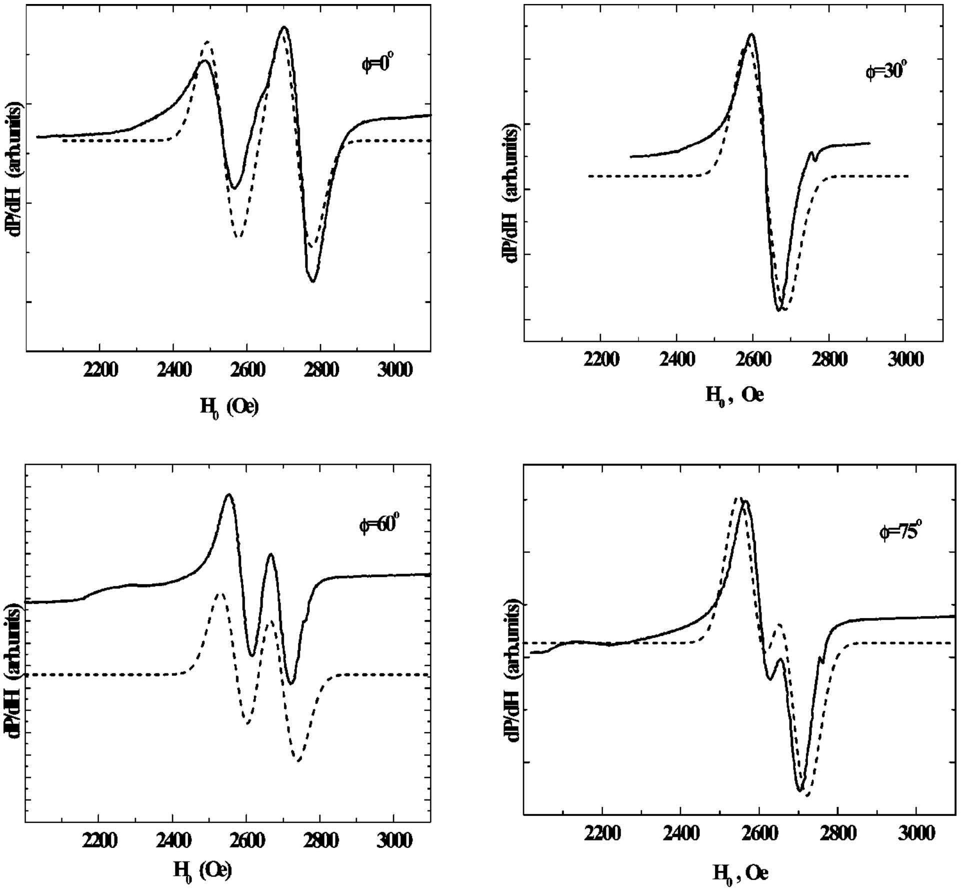

FIG. 3. ESR spectra for four values of the angle ϕ between the magnetic field and [001] direction in the (110) plane. Solid lines are experimental spectra; dashed lines are calculated ones.

orders of magnitude lower than that of ytterbium lines. These lines can be identified as ESR from natural impurity of Gd^{3+} with concentration less than 0.005 at. %.

III. DISCUSSION

As stated in Sec. II, we have observed two main lines symmetrically displaced from $g=(7148\nu)/2635=2.55$ at $T=1.6$ K and exhibiting modulation with 5% anisotropy when magnetic field was rotated in the (110) plane from the cubic axis to the [110] direction.

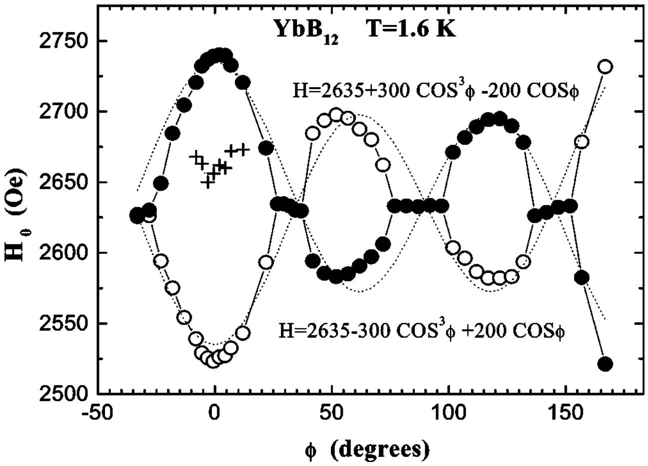

FIG. 4. Angular dependence of the ESR lines position for rotation of the magnetic field in the (110) plane. Additional points at 2650–2675 Oe are due to unpaired Yb^{3+} ions.

The value of the mean g factor should be compared with the results for the Yb^{3+} ion, where $g=2.585$ was obtained by Low and Rubins[19] and $g=2.58$ was found by Martins *et al.*[20] This value and practically isotropic behavior of the g factor suggest the ground state of the Yb^{3+}ion in YbB_{12} to be the Γ_6 state. (The deviation of the Yb^{3+} g factor from a theoretical value of 2.667 was attributed by Low and Rubins to an existence of partially covalent bonding in ytterbium ions.)

In our case the g-factor shift from a theoretical value results from the effect of internal magnetic field, i.e., magnetization caused by Van Vleck paramagnetism of valence fluctuating Yb ions (cf. Ref. 21),

$$\Delta g=\frac{g-1}{g}\,\frac{J\chi}{N\mu^2}, \tag{1}$$

where $g=8/3$ is the Landé factor of the Γ_6 state, J is the exchange integral for the interaction of Yb^{3+} ions and Yb ions with fluctuating valence, χ is the molar magnetic susceptibility, N is the Avogadro number, and μ is the Bohr magneton. Using Eq. (1) and $\chi=3.3\times10^{-3}$ emu/mol we have calculated the exchange integral value, $J=1.8$ meV. The sign of the g-factor shift indicates antiferromagnetic coupling of ‘‘defect’’ and ‘‘normal’’ Yb ions.

The Γ_6 state with a g factor close to 2.667 can be also observed from Nd^{3+} ions (cf. Ref. 22). Its resonance can be distinguished from that of Yb^{3+} ions mainly by hyperfine structure (HFS). Unfortunately we have not observed HFS in our experiments, presumably due to large inhomogeneous broadening of the resonance lines. Therefore, we attribute the ESR spectrum to Yb^{3+} mostly basing on the intensity of its lines. The concentration of Yb^{3+} centers in our sample is 0.2–0.5 at. %, while the residual concentration of Nd in our sample is estimated from chemical analysis data and magnetic susceptibility to be less than 0.025 at. %. The absence of noticeable concentration of the other rare earths in the crystal is corroborated by observation of Gd^{3+} resonance mentioned above which permitted estimation of residual concentration of Gd amounting to less than 0.005 at. %. Besides, in contrast to Nd^{3+} we expect that Yb^{3+} ions will be present even in the purest crystal similarly to Sm^{3+} ions in SmB_6.[15,17] The small concentration of the active spins confirms the concept that the majority of ytterbium ions do not contribute to the ESR. Therefore, the attribution of YbB_{12} to the family of valence-fluctuating compounds is justified.

Though our ESR signal corresponds to a g factor of the Γ_6 state, instead of one isotropic line we observe two lines with resonance frequencies equally displaced against the g factor of the Γ_6 state with opposite signs of the shift. Such a behavior points directly to the presence of two similar interacting oscillators. This situation is well known in the theory of ESR. It corresponds to a pair of identical ions coupled by exchange and/or dipole-dipole interactions.[23] In fact the splitting of the Γ_6 resonance due to formation of pairs of closely spaced Yb^{3+} ions coupled by the dipole-dipole interaction was recently observed in Yb-doped $CsCdBr_3$.[24,25] We should like to stress, however, that our results differ significantly from those in Refs. 24 and 25. $CsCdBr_3$ is an anisotropic D_{6h}^4 crystal, and the existence of Yb-Yb pairs was predicted in advance.[26] In contrast, YbB_{12} is an intermediate valence compound of cubic O_h symmetry. In our experiments the modulation of the resonance was more complicated than the conventional $(3\cos^2\phi-1)$ dependence.[23] In $CsCdBr_3$, Yb ions are located in regularly situated positions; therefore, the inhomogeneous broadening of the resonance is fairly small (the linewidth is ~18 Oe in contrast to 80 Oe in our case) and HFS could be observed in Ref. 24.

The Γ_6 state corresponds to an effective spin 1/2. The spin Hamiltonian of the interacting 1/2 spins has the form (Ref. 23, Sec. 9.5)

$$\left|\begin{array}{c} |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{array}\right| \left|\begin{array}{cccc} +G_z+(1/4)\Im_z & 0 & 0 & (1/4)(\Im_x-\Im_y) \\ 0 & -(1/4)\Im_z & (1/4)(\Im_x+\Im_y) & 0 \\ 0 & (1/4)(\Im_x+\Im_y) & -(1/4)\Im_z & 0 \\ (1/4)(\Im_x-\Im_y) & 0 & 0 & -G_z+(1/4)\Im_z \end{array}\right|,$$

where $G_z=g\mu H_z$ is the Zeeman splitting of the Γ_6 state, and $\Im_x$, $\Im_y$, and $\Im_z$ are the components of the exchange integral tensor for two interacting spins. The exchange interaction of spins forming the pair leads to splitting of the levels and the appearance of two ESR lines on frequencies equally displaced from the mean frequency corresponding to the Γ_6 state: $h\nu=g\mu H_z\pm 3\Im_z'/4$, where $\Im_z'=\Im_z-1/3(\Im_x+\Im_y+\Im_z)$ is the anisotropic part of the exchange integral.

The splitting of one resonance line into two under interaction of two spins of the pair can be observed only if the exchange interaction is anisotropic. In the isotropic case the levels of the pair are split to singlet and triplet, but there is no frequency shift for both transitions between the triplet levels. It should be noted that in the conditions of our experiment we could expect the existence of an anisotropic exchange, but in that case the angular dependence should be $\cos^2\phi$, not $(3\cos^3\phi-2\cos\phi)$. Therefore, the model given by Abraham and Bleaney[23] cannot explain our result directly and should be supplemented by some interaction having the proper symmetry.

If we add to the Hamiltonian in our problem,

$$H=g\mu H_z T_z+(1/2)\Im[T(T+1)-3/2], \tag{2}$$

the term $a(3T_{1z}T_{2z}-\vec{T}_1\vec{T}_2)(\vec{T}_2\vec{H})$, where $\vec{T}=\vec{S}_1+\vec{S}_2$ is the total spin of the pair and T_z is its z projection, it will transform on rotation of the magnetic field as $(3\cos^3\phi-\cos\phi)$ (here we have already dropped the anisotropic part of the exchange). This quantity corresponds to the dipole-dipole interaction of neighbor pairs and still differs slightly from the experimentally observed angular dependence. However, if we add also the exchange interaction of the neighbor pairs which transforms as $\cos^3\phi$, we shall obtain the necessary result with $b=-3a/2$.

The dipole-dipole splitting of the resonance lines permits estimation of the distance between the interacting pairs from the formula

$$\Delta E=0.05h\nu=\frac{(2g\mu)^2}{R^3}. \tag{3}$$

The result is $R=9.1$ Å—i.e., quite reasonable. This estimate gives in fact an averaged interpair distance: we should expect that ion pairs are distributed chaotically with different interpair distances in the crystal, and their interaction energy fluctuates in space contributing to fluctuations of the local crystal field, i.e., to inhomogeneous broadening of the ESR line.

This is the main reason for the large difference between the ESR linewidth in Refs. 24 and 25 and our work.

The special feature of our Hamiltonian is the neglect of the intrapair dipole-dipole interaction. However, if we recollect the large predominance of the exchange coupling over the dipole-dipole one for small distances between the ions forming the pair (Ref. 23, Sec. 1.10), this approximation seems to be more justified.

The formal description of our experimental results achieved with the use of the Hamiltonian discussed above points to the alignment of all ion pairs, i.e., the appearance of a special direction in a formerly cubic crystal. This fact is equivalent to the existence of a sort of phase transition induced by interpair coupling. Though we cannot explain now the nature of this phase transition, we can speculate that it can have much in common with the dipole-dipole ordering of nuclei discussed in Ref. 27.

The intensity of the ESR signal is determined by the derivative of an imaginary part of the high-frequency magnetic susceptibility,

$$\partial\chi''/\partial H \propto \sum_i (B-B_{0i})(\Delta B)^{-2}\exp[-(B-B_{0i})^2/\Delta B^2], \tag{4}$$

where

$$B_{0i}=h\nu/g\mu \pm H(\phi), \quad H(\phi)=b(3\cos^3\phi-2\cos\phi). \tag{5}$$

In Fig. 3 a comparison is done of computer-simulated line shapes with those experimentally measured. In these calculations we did not take account of the hyperfine structure since it was not observed experimentally. The agreement between the experiment and calculations is satisfactory, though there is some difference at the lines wings.

We should like to note that besides the energy level splitting due to the ion pair formation other alternatives to the Yb^{3+} ground state were considered, including, for instance, the possibility of the Γ_8 state. However, only the concept of pair formation in YbB_{12} provided a consistent description of the experiment.

A weak line in the center of the ESR spectrum with a g factor of 2.52 (Figs. 1, 2, and 4) can be assigned to a resonance from single (unpaired) Yb^{3+} ions in the Γ_6 state. According to a crude estimate, the concentration of such centers is more than by an order of magnitude less than that of the pairs.

The temperature decrease from 4.2 to 1.6 K leads to a sharp, by 30–40 times, increase of the ESR signal. We can see from Fig. 2 that the ESR signal was very intense at 1.6 K, but nearly disappears at 4.2 K. This behavior is quite unusual for ESR on Yb^{3+} ions. It is well known that in contrast to other rare-earth ions being not in the S ground state, Yb^{3+} ions have fairly long spin relaxation times, which permit observation of ESR signals up to liquid nitrogen temperatures. However, though our spectra demonstrate only weak temperature dependence of the ESR linewidth indicating inhomogeneous line broadening, the ESR intensity decays sharply with temperature increase.

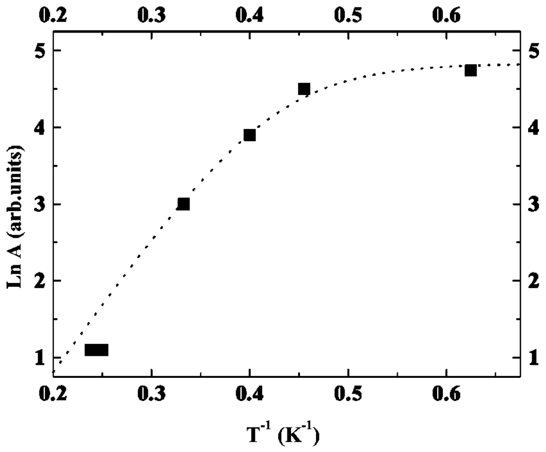

FIG. 5. Temperature dependence of the maximum-to-minimum amplitude of the ESR line for $\phi=90°$. Dotted curve is drawn according to the relation $D/[1+R\exp(-\Delta/T)]$ with $D=125$, $R=2000$, and $\Delta=18$ K.

We could expect that the increase of the ESR intensity observed is connected with a possible ferromagnetic or structure phase transition. However, no indications of either transition in the temperature range studied are found. The measurements of magnetic susceptibility showed nearly no temperature dependence in correspondence with the behavior of the g factor. It was demonstrated also that the angular dependence of the ESR spectrum does not change with temperature; i.e., the local symmetry of the crystalline field remains the same. On these grounds we deduce that the most probable reason for the strong temperature dependence of the ESR signal is the change in the concentration of the Yb^{3+} ions.

The temperature dependence of the ESR amplitude presented in Fig. 5 is close to an exponential increase with a characteristic temperature $\Delta\approx 18$ K. We have described the temperature dependence of the ESR amplitude using the function

$$A\propto D/[1+R\exp(-\Delta/T)]. \tag{6}$$

The results of our simulation are shown in Fig. 5 by dotted curve demonstrating good agreement with the experiment. Equation (6) can be interpreted as a result of capture of electrons from certain traps by Yb^{3+} ions transforming them into ESR inactive ions with fluctuating valence. In this case $\Delta\approx 18$ K is the binding energy of the traps, while the parameter $R=N_i/N_{tr}$ is the ratio of the concentration of "defect" ions N_i to that of the electron traps N_{tr}. Since $N_i\sim 10^{19}\ \mathrm{cm}^{-3}$, the concentration of traps should be of the order of $10^{16}\ \mathrm{cm}^{-3}$. This means that the traps are different from the states where electrons from ytterbium ions are collected when defect Yb^{3+} ions are generated.

Though we have described formally the temperature dependence of the ESR amplitude, we cannot make definite conclusions on the nature of the traps. Their energy level lies below the lower edge of the energy gap by 18 K, i.e., nearly the same characteristic energy as that of the position of additional density of states inside the gap of the valence-fluctuating compound.[16] The intragap states with an energy of 3.5 meV were found in another Kondo dielectric SmB_6 by Sluchanko *et al.*[28] and interpreted as bound states of electrons in *n*-type material dressed by mixed exciton-polaron excitations.[11] However, the bound exciton-polaron states predicted by Curnoe and Kikoin[11] should lie below the upper edge of the energy gap in contradiction to our model. Therefore, we cannot at present identify our electron traps with the bound electron-polaron states, and this point needs additional studies.

It would be interesting if we could propose a specific model of defects compensating the 0.1 change in the valence of the Yb ions. However, our experimental results are too scarce to make definite conclusions on such a model. We can only remark that in the case of valence stabilization in SmB_6, where the symmetry of the ground state of the Sm^{3+} ions was studied using Jahn-Teller effect,[15] it was possible to conclude that the defect stabilizing the valence of Sm ions can be located well remote from this ion.

To clarify the situation with the hyperfine structure we have simulated the ESR spectrum similarly to the procedure used by Malkin *et al.*[24] The results of simulation are shown in Fig. 6. We see that due to a large inhomogeneous linewidth of the resonance, the hyperfine structure should be nearly completely smeared out. Actually the experimental ESR signal contains no contribution from HFS. This fact can be caused by a possible decrease of HFS constant in a material with fluctuating valence which was proposed in Ref. 20.

The most striking and unexpected result is the possibility of a spontaneous break of symmetry in a cubic crystal with fairly low concentration of defect ions. If the appearance of a selected direction in a cubic crystal is not a result of uncontrolled deformation of the sample during growth or preparation, it can be a consequence of a sort of phase transition into an asymmetrical low-temperature state of the Kondo dielectric predicted, in particular, by Kasuya.[12]

IV. CONCLUSIONS

We have observed ESR from Yb^{3+} ions with stabilized valence in a single crystal of valence-fluctuating compound YbB_{12}. The ground state of a Yb^{3+} ion is identified as the Γ_6 state, which should be isotropic in a cubic crystal but is actually modulated and split by a slight anisotropic correction. Experimental results are explained by the existence of Yb-Yb pairs which are coupled by isotropic exchange but interact also with the other pairs by dipole and exchange coupling.

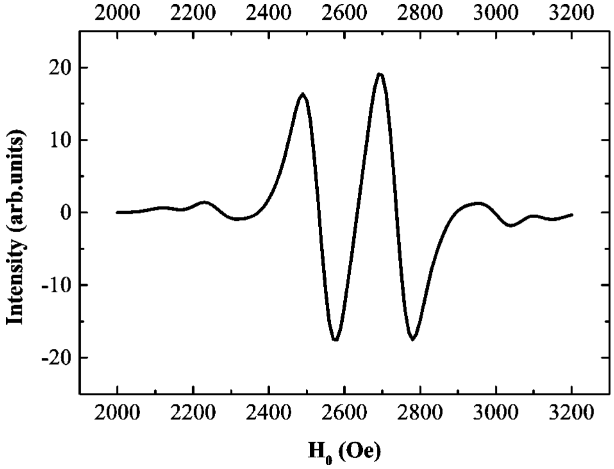

FIG. 6. Computer simulation of the ESR signal for $\phi = 0°$ with hyperfine structure included both for ^{171}Yb and ^{173}Yb isotopes. The linewidth was set to 60 Oe.

A strong, close to exponential, temperature dependence of the amplitude of the ESR signals was found in the interval 1.6–4.2 K. It is attributed to the change in concentration of Yb^{3+} ions with temperature and was interpreted as a result of the capture of electrons from electron traps with a binding energy of 18 K by Yb^{3+} ions.

The occurrence of anisotropy in a cubic semiconductor may be the result of a spontaneous break of symmetry specific for the ground state of a Kondo dielectric.

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