Anomalous magnetocaloric effect in YbAs associated with the giant quadrupolar interaction

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We report a theoretical investigation that predicts the existence of anomalous magnetocaloric effect in the YbAs compound. The YbAs cool upon magnetizing and warm upon demagnetizing, in the temperature range between 33 and 84 K for external magnetic field change from 0 to 23.5 T. The anomalous effect can be observed on the negative part of magnetic entropy changes, upon variation of the external magnetic field, in an isothermic process. This study was carried out using a model Hamiltonian, which takes into account the crystalline electrical field and the quadrupolar interactions within the molecular-field approximation.

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I. INTRODUCTION

The magnetocaloric effect is the ability of some magnetic materials to heat up when they are magnetized, and cool down when removed from the magnetic field in a thermodynamic cycle.[1] The two thermodynamic quantities that characterize the magnetocaloric potential are ΔS_{mag} (the isothermal magnetic entropy change) and ΔT_{ad} (the adiabatic temperature change) which are observed upon changes in an external magnetic field.

Before the Brown report,[2] the magnetocaloric effect was mainly investigated in order to reach ultralow temperature values by nuclear adiabatic demagnetization technique. Recently, Pecharsky and Gschneidner[3] discovered, experimentally, a new material, namely $Gd_5(Si_2Ge_2)$, which exhibits the giant magnetocaloric effect at the critical Curie temperature of ~275 K. The effect was associated to the strong first-order magnetic and structural transitions. This material has some potential applications such as effective working substances for magnetic refrigeration in the room-temperature range. Also, a fairly large number of theoretical works have been carried out in order to understand the microscopic physical mechanisms that govern the magnetocaloric effects, mainly in rare-earth intermetallics materials.[4–7]

The magnetic system YbAs studied in this work is of particular interest since it is a heavy fermion compound characterized by competition between magnetic interaction and Kondo hybridization.[8] Early studies, using the Mössbauer effect, predicted a first-order paramagnetic-antiferromagnetic phase transition at $T_N = 0.58$ K in YbAs.[9] Later, neutron-diffraction investigations in YbAs single crystal proved the existence of long-range antiferromagnetic order, and the mean-field calculation indicated that the magnetic moments are stabilized by quadrupolar interactions.[10] More recently, investigations in YbAs, using nuclear magnetic resonance,[11] showed the existence of a weak antiferromagnetic order below $T_N \sim 0.4$ K. This critical temperature is in good agreement with previous specific-heat measurements, which showed a narrow peak at about $T_N = 0.49$ K.[12,13]

The crystalline electrical field (CEF) in this compound presents cubic symmetry as determined by inelastic neutron scattering that yield the following CEF-level scheme: Γ_6 (doublet), Γ_8 (quartet), and Γ_7 (doublet).[14] Unexpectedly, the Γ_8 quartet was found to be split into two components, which has been interpreted in terms of a bound state involving a phonon and the $\Gamma_6 \rightarrow \Gamma_8$ crystal-field excitation.[15,16] Later, the neutron-scattering experiments point out the existence of a giant quadrupolar interaction.[14] Using a theoretical model in which the CEF and quadrupolar interactions are considered, we have observed the splitting of the Γ_8 level and obtained an anomalous magnetocaloric effect, i.e., the YbAs cool upon magnetizing and warm upon demagnetizing in the temperature range between 33 and 84 K. Curves for $-\Delta S_{\mathrm{mag}}$ versus temperature showed a negative region for external magnetic field changing from zero to 2, 5, and 10 T, analyzed in this work. In addition, the critical magnetical field for the disappearance of the anomalous effect was theoretically predicted and estimated to be equal to $h_C = 23.5$ T.

II. THEORY

The Hamiltonian that describes the crystal-field and quadrupolar interactions for the YbAs compound is given by

$$H = H_{\mathrm{CF}} + H_Q - g\mu_B \vec{h}\cdot\vec{J}, \tag{1}$$

$$\text{where} \quad H_{\mathrm{CF}} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) \tag{2}$$

$$\text{and} \quad H_Q = -\lambda_Q \langle O_2^0 \rangle O_2^0. \tag{3}$$

Relation (2) is the single-ion CEF Hamiltonian, where the O_n^m are the Stevens' equivalent operators.[17] The parameters B_4 and B_6 determine the splitting of the $2J+1$ degenerate Hund's ground state. Relation (3) gives the quadrupolar interaction, where λ_Q is the quadrupolar parameter associated to the quadrupolar order $\langle O_2^0 \rangle = Q = \langle (J_i^z)^2 - J(J+1) \rangle$. The last term in the Hamiltonian (1) represents Zeeman interaction, where h is the external magnetic field. In our theoretical model, the bilinear exchange interaction was neglected since the antiferromagnetic order temperature is very low and, in molecular-field approximation, this interaction term vanishes for $T > T_N = 0.4$ K.

The magnetic entropy can be obtained from the fundamental thermodynamic relation

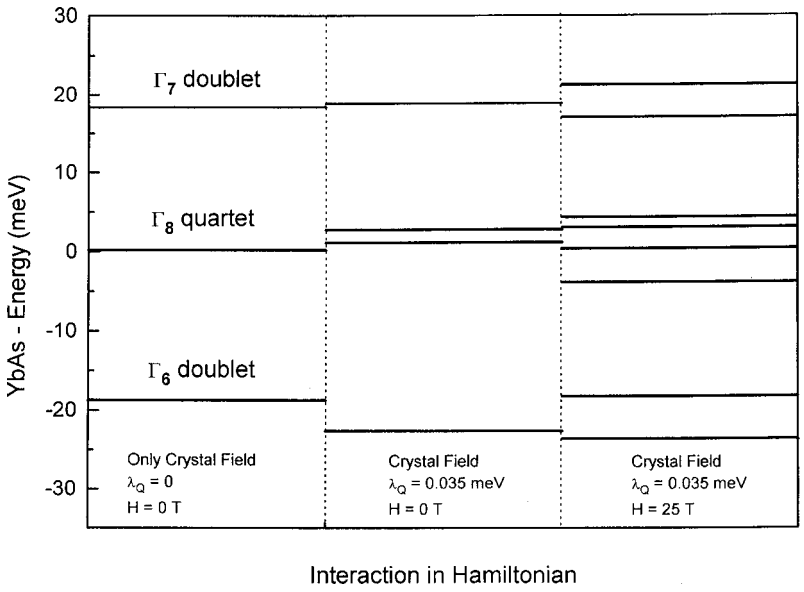

FIG. 1. Energy states obtained from the model Hamiltonian using Furrer parameters for YbAs (Ref. 14).

$$S(T,h)=\left(\frac{1}{T}\right)\frac{\sum_{k=1}^{2J+1} E_k \exp(-E_k/kT)}{\sum_{k=1}^{2J+1} \exp(-E_k/kT)} + k\ln\left(\sum_{k=1}^{2J+1} \exp(-E_k/kT)\right). \quad (4)$$

The temperature dependence of the above magnetic entropy is not trivial, since for a given pair (T, h), the $Q=Q(T,h,Q)$ must be determined self-consistently in order to obtain the proper energy eigeinvalues E_k to update relation (4).

We are interested in the isothermal magnetic entropy changes $-\Delta S_{\mathrm{mag}}$ that occur for changes in the external magnetic field. This quantity is obtained from relation (4):

$$-\Delta S_{\mathrm{mag}}(T,h)=S(T,h)-S(T,h=0). \quad (5)$$

III. RESULTS AND DISCUSSIONS

The crystalline electrical-field and quadrupolar parameters used in this work was obtained from adjusting the energy spectra of neutrons scattered from single-crystal YbAs.[14] They are: $B_4=-0.0187$ meV, $B_6=0.000\,12$ meV, and $\lambda_Q=0.035$ meV. Using these model parameters we have constructed the energy diagram showed in Fig. 1. The crystalline electrical-field interaction partialy splits the ninefold degenerated Hund's magnetic state, the quadrupolar interaction splits the Γ_8 (quartet) into two double and finally the external magnetic field removes all degenerated states. Note that the above parameters lead to a doublet as the ground state in YbAs.

Figure 2 shows the temperature dependence of the quadrupolar order which disappears at $T_Q=84$ K. This quadrupolar phase transition can be correlated to the observed nonlinear relation between the Knight shift and magnetic susceptibility in this temperature range, leading to the change in the hyperfine coupling parameter.[11]

In Fig. 3 is displayed the temperature dependence of magnetic entropy for different magnetic fields, applied in the ⟨100⟩ crystalographic direction. We can note that for $h=0$ T, in the limit $T\rightarrow 0$ K, we got the value $R\cdot\ln(2)$ for magnetic entropy, where R is the universal gas constant. This result is expected since the ground state is the Γ_6 doublet. As a small magnetic field is applied, the Γ_6 doublet level splits and we obtain the proper limit: $\lim_{T\rightarrow 0} S_{\mathrm{mag}}=0$. In the high-temperature limit, we get $S_{\mathrm{mag}}=R\cdot\ln(2J+1)=R\ln(8)\sim 17.2$ J/mol K, since the Yb element has $J=\frac{7}{2}$ as total angular moment. From Fig. 3, it is evident that the entropy associated to the quadrupolar order ($h=0$ T), at critical temperature $T_Q=84$ K, releases about 57% (9.8 J/mol K) of the total magnetic entropy available, the remaining entropy belonging to the crystalline electrical field, as a Schottky effect.

As shown in Fig. 3, the magnetic entropy decrease with the intensity of the applied external magnetic field in low-temperature region ($T<30$ K) as expected, since the mag-

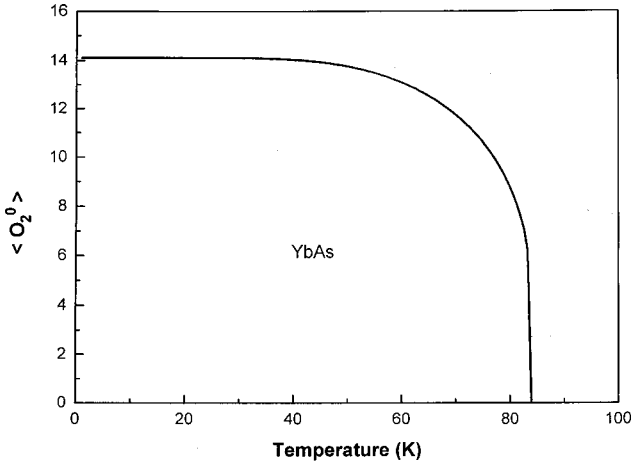

FIG. 2. Temperature dependence of the quadrupolar order for YbAs.

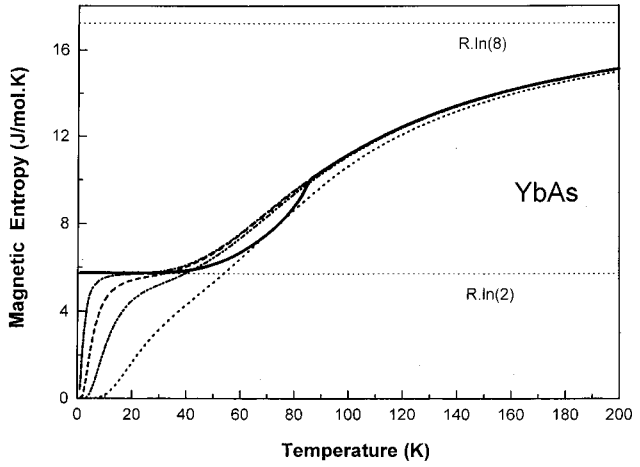

FIG. 3. Magnetic entropy versus temperature in YbAs for different values of magnetic field. $h=0$ (solid line), $h=2$ T $(-\cdot-\cdot-\cdot-)$, $h=5$ T $(- - -)$, $h=10$ T $(\cdots)$, and $h_C=23.5$ $(\cdots)$.

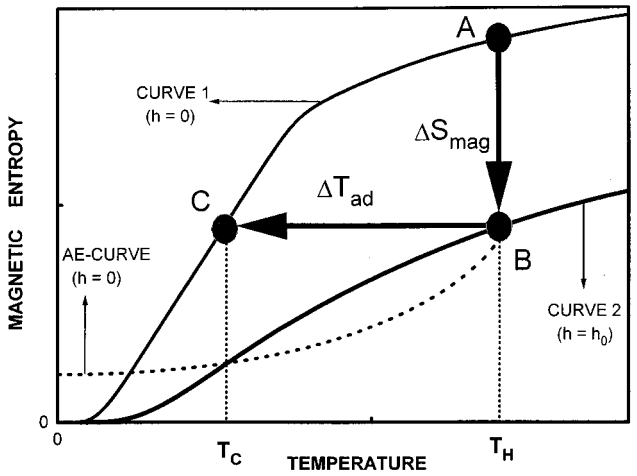

FIG. 5. Scheme of temperature dependence of magnetic entropy. Curves 1 and 2 represent the normal magnetic behaviors with zero field, and with applied magnetic field, respectively. The dotted curve shows the anomalous entropy (AE).

netic field is responsible for the alignment of magnetic moments, reducing the magnetic disorder. On the other hand, for temperature interval $(30<T<84\,\mathrm{K})$ an anomalous behavior in the magnetic entropy is theoreticaly predicted in YbAs, the entropy increasing with external magnetic field. This picture is more clearealy observed in Fig. 4, which shows the magnetocaloric potential $-\Delta S_{\mathrm{mag}}(T,h)$ vs T, obtained from relation (5). The negative $-\Delta S_{\mathrm{mag}}(T,h)$ values exhibit the anomalous magnetocaloric effect, where the magnetic system loses heat when magnetic field is removed or reduced. The temperature interval, where the $-\Delta S_{\mathrm{mag}}(T,h)$ assumes negative value, is reduced as the intensity of the magnetic field is increased. For a magnetic field higher than the critical value, $h_C=23.5\,\mathrm{T}$, the $-\Delta S_{\mathrm{mag}}(T,h)$ vs T curves no longer present negative values, i.e., the anomalous magnetocaloric effect desapears. The predicted anomaly in magnetocaloric effect disappears if the quadrupolar interaction is not considered in YbAs. This can be observed by taking the quadrupolar parameter $\lambda_Q=0$ in the model Hamiltonian, which leads to positive values for $-\Delta S_{\mathrm{mag}}(T,h)$ vs T in all temperature range.

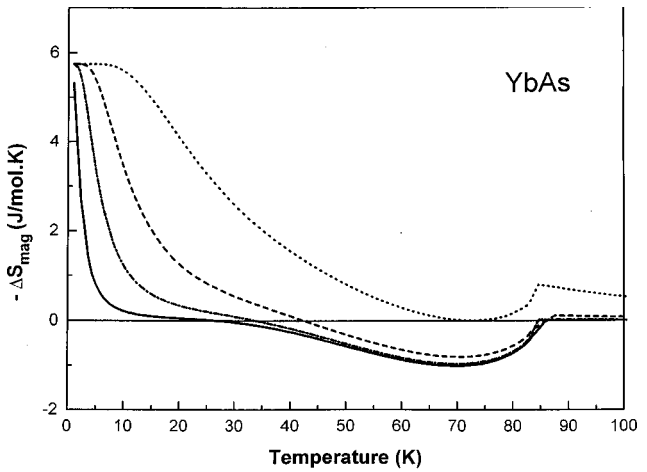

FIG. 4. The temperature dependence of $-\Delta S_{\mathrm{mag}}$ in YbAs for magnetic-field changes: $h:0\rightarrow 2$ T (solid line); $h:0\rightarrow 5$ T $(-\cdot-\cdot-\cdot-)$; $h:0\rightarrow 10$ T $(- - -)$: and $h:0\rightarrow h_C=23.5$ $(\cdots)$.

For the sake of illustration, Fig. 5 shows a normal (solid lines) and the anomalous (dotted line) behavior of magnetic entropy vs temperature for $h=0$ and $h\neq 0$. The arrows ΔS_{mag} and ΔT_{ad} indicate the isothermal magnetic entropy changes and the adiabatic temperature change for external magnetic field changes from $0\rightarrow h_0\rightarrow 0$, in a typical magnetization demagnetization process $(A\rightarrow B\rightarrow C)$. In a reversible Carnnot cycle, the isothermal heat absortion Q_C and expulsion Q_H at constant reservoir temperatures T_C and T_H, respectively, are directly related to the refrigerant capacity $Q_H-Q_C=T_H\Delta S_{\mathrm{mag}}-T_C\Delta S_{\mathrm{mag}}=\Delta T_{\mathrm{ad}}\Delta S_{\mathrm{mag}}$. The concept of refrigerant capacity is well developed and used to provide a general analysis of magnetic refrigeration efficiency in Ref. 18.

Consider now (in Fig. 5) only the curve 2, which represents the magnetic entropy for $h=h_0$ and the anomalous entropy curve (the magnetic entropy in zero field) associated with anomalous behavior. It can be observed that, in the temperature region $T_C<T<T_H$, the effect of applying an external magnetic field is to increase the magnetic entropy. Therefore, if an external magnetical field is isothermically applied, in this anomalous temperature region, and then adiabically removed, the temperature will not be reduced anymore, as in a normal temperature region. On the contrary, it will increase.

The main advantages in the present approach for the temperature dependence of ΔS_{mag} (the isothermal magnetic entropy change with external magnetic field) is the fact that it is not necessary to know information about the electronic and lattice contributions to the total entropy, since these contributions depend only on temperature. Therefore the total entropy changes is equal to the magnetic entropy changes. In

this way, the magnetic model Hamiltonian used in this work is a good theoretical framework.

IV. FINAL COMMENTS

It is out belief that the magnetocaloric experimental data in YbAs can put an end to the controversy in the origin of the observed splitting of the excited Γ_8 quartet state, which has been a puzzle for a long time. Also, we showed theoretically the existence of an anomalous magnetocaloric effect in YbAs compound associated with the quadrupolar interaction. This is still to be verified experimentally. The investigations in magnetic systems which present quadrupolar interaction may have an impact on experimental investigation in order to design new materials presenting large magnetocaloric effect.[19]

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