stress.

In spite of the various interesting open questions, we trust that this Letter has clarified the basic aspects of a very intriguing problem, and will contribute to a better understanding of Si surfaces.

We thank Hartwig Thomas for image processing, F. Himpsel for hints concerning sample preparation, and K. C. Pandey and K. H. Rieder for illuminating discussions on surface problems.

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Electronic and Magnetic Properties of Europium-Intercalated Graphite

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(Received 28 September 1982)

Stage-1 Eu-intercalated graphite EuC_6 was studied by Mössbauer and L-edge spectroscopy. Isomer shift and L_{III}-edge position results indicate the divalent state for Eu. Below 40 K, EuC_6 orders antiferromagnetically with the Eu spins oriented perpendicular to $\vec{c}$ and a magnetic hyperfine field saturating at -10.7 T. The large electric field gradient at the Eu site (-1.4×10^{18} V/cm^2), with axis parallel to $\vec{c}$, is consistent with the structure of EuC_6 and a partial charge transfer from Eu to the C planes.

PACS numbers: 75.30.Kz, 76.80.+y, 78.70.Dm

The highly anisotropic magnetic properties of graphite intercalation compounds (GIC) are of considerable current interest.[1,2] By increasing the number of graphite layers separating the two-dimensional arrays of magnetic intercalants studies of the transition from three-dimensional to more and more two-dimensional magnetic behavior are feasible.[3] Most of the relevant work so far has dealt with transition-metal chlorides as magnetic intercalants, and substantial changes in the magnetic properties relative to those of the pure intercalants were observed.[1-3] With the demonstration of the feasibility of vapor-phase intercalation of Eu,[4] a magnetic intercalation system with bare magnetic ions became available, since Eu is expected to intercalate in its $4f^7$-divalent magnetic state.[5] Higher-stage Eu GIC's should constitute prototypes for two-dimensional arrays of magnetic ions with almost isotropic exchange. Up to now only the results of magnetization measurements[5] and Raman studies[6] have been published for EuC_6.

The present paper reports on a ^{151}Eu Mössbauer study of EuC_6 as well as on L-edge x-ray absorption and magnetic measurements. From the observed Mössbauer isomer shift and the position of the L_{III} edge Eu is shown to be intercalated in its divalent state. The magnitude, negative sign, and orientation of the axially symmetric electric-field gradient (EFG) tensor at the Eu site are in quantitative agreement with the crystallographic structure of EuC_6.[4] Below 40 K the Mössbauer

spectra exhibit a combined magnetic–electric-quadrupole hyperfine interaction due to long-range magnetic order, with the Eu spins oriented in the basal plane of graphite. Magnetization measurements, which are in accord with recently published work,[5] reveal antiferromagnetic order.

The Mössbauer experiments were performed in transmission geometry with a $^{151}SmF_3$ source. For the L_{III}-edge measurements an x-ray absorption spectrometer based on a focusing monochromator and a 2-kW x-ray source was employed.[7] Magnetic data were taken with a vibrating-sample magnetometer. The EuC_6 samples were prepared by vapor-phase intercalation in sealed Mo or quartz containers from natural graphite flakes or highly oriented pyrolytic graphite (HOPG) and 99.99%-pure Eu metal. The samples were intercalated up to 20 d at 520 °C. X-ray analysis revealed the dominant presence of stage-1 EuC_6 with a c-axis periodicity of 4.87 Å, in addition to pristine graphite. The Eu GIC's were handled in purified inert-gas atmosphere.

Figure 1 shows a Mössbauer spectrum and an L_{III}-edge spectrum, taken from Eu-intercalated natural graphite flakes at 300 K (sample EuC_6 No. 2). The Mössbauer spectrum, which is characterized by a pure Eu^{2+} signal of the 21.6-keV $\frac{5}{2} \rightarrow \frac{7}{2}$ γ transition, was least-squares fitted (solid line) by a superposition of an electric-quadrupole-split subspectrum (dashed curve, composed of eight individual lines) and a single absorption line (dotted curve). The main subspectrum originates from EuC_6 and is described by an isomer shift $S = -11.7 \pm 0.1$ mm/s and an axially symmetric EFG tensor $V_{zz} = -(1.4 \pm 0.1) \times 10^{18}$ V/cm^2 [corresponding to $eV_{zz}Q(\frac{5}{2}) = -389$ MHz]. The weaker, dotted subspectrum ($\cong 25\%$ intensity) is described by a single Lorentzian at $S = -11.3 \pm 0.2$ mm/s and is due to EuO and Eu-carbide (EuC_x) impurity phases (see below). From the relative intensities of the eight components of the electric-quadrupole-split EuC_6 subspectrum there follows a strong texture of the absorber with the graphite c axis oriented predominantly perpendicular to the absorber plane. Therefore, a Mössbauer spectrum taken with the same absorber tilted by 45° relative to the γ-ray direction (not shown here) revealed that the axis of the EFG tensor is directed parallel to $\vec{c}$. This is expected from the structure of EuC_6, since for an s-state ion like Eu^{2+} the EFG is caused only by the lattice, providing a direct measure of the crystalline anisotropy.

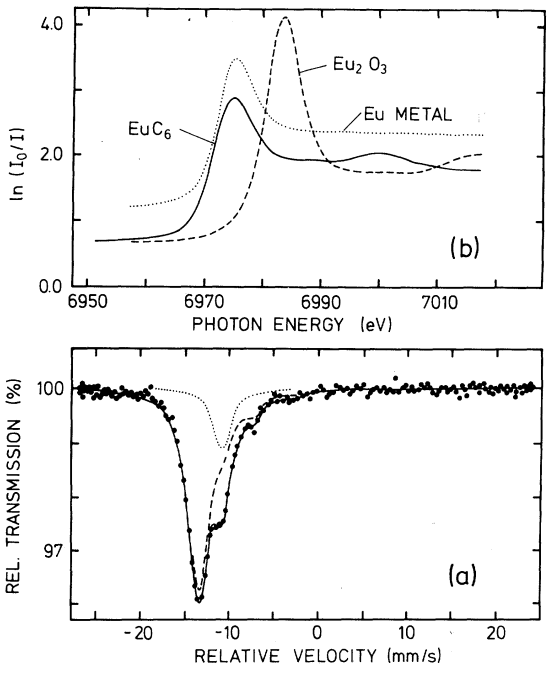

FIG. 1. (a) ^{151}Eu Mössbauer spectrum and (b) L_{III}-edge spectrum (solid curve) of EuC_6 (sample No. 2) at 300 K. The solid line in (a) represents the result of a least-squares fit (see text). In (b) the L_{III} edges of typical Eu^{2+} and Eu^{3+} solids are also shown.

In Fig. 1(b) the L_{III}-edge spectra of divalent Eu metal (dotted curve) and of trivalent Eu_2O_3 (dashed curve) are shown in addition to the one of EuC_6. The L_{III} edges are characterized by an intense peak at the absorption threshold ("white line") due to transitions from a $2p$ initial state to empty $5d$ states at E_F. The L_{III}-edge position is mainly determined by the $4f$ occupation number, reflecting the difference of $\cong 8$ eV in $2p$ binding energies between the $4f^7$ and $4f^6$ configurations of Eu.[8] Chemical effects are expected to vary the L_{III}-edge position by less than 1 eV. Therefore, the L_{III}-edge position confirms the divalent character of EuC_6.

Low-temperature Mössbauer spectra taken from the same sample are shown in Fig. 2. The 77-K resonance curve is essentially identical to the 300-K spectrum of Fig. 1(a), while those taken at 30 K and below are dominated (dashed EuC_6 subspectrum) by a combined electric-quadrupole–magnetic-dipole hyperfine interaction with a small hyperfine field B_{eff} (−10.7 T at 4.2 K). The weak, dotted subspectrum from EuC_x and EuO impurity phases can be described by a pure magnetic hyperfine interaction with a large field $B_{eff} = -(29.5 \pm 1)$ T and $S = -11.3$ mm/s. In the least-squares-fit analysis the angle θ

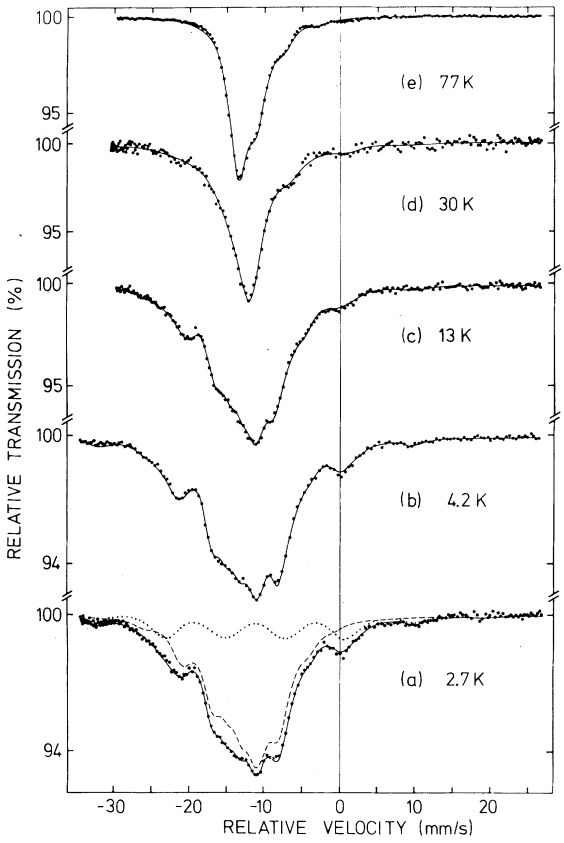

FIG. 2. Mössbauer spectra of EuC_6 (sample No. 2) at various temperatures. The solid lines are fit results. The dashed subspectrum in (a) stems from EuC_6, and the dotted one from EuC_x and EuO impurity phases.

between the axis of the EFG tensor and B_{eff} in EuC_6 was treated as a free parameter, resulting in $\theta = (90 \pm 5)°$. This means that the *Eu spins are oriented in the basal plane of graphite in the magnetically ordered phase of* EuC_6. A paramagnetic state with slow spin-lattice relaxation can be ruled out for the following reasons: (i) the small magnitude and the low-temperature saturation behavior of B_{eff} and (ii) the nonisotropic orientation of B_{eff} with respect to the EFG axis.

We have taken 300-K spectra of five and low-temperature spectra of two separately prepared EuC_6 samples (No. 2 and No. 9) with consistent results. Only the relative intensity of the impurity-phase subspectrum varied slightly among samples. In order to identify better the chemical nature of the weak impurity phase we have studied Eu carbide samples prepared from the elements in closed Mo crucibles at 900 and 1200 °C, respectively. The tetragonal EuC_2 [9] obtained at 1200 °C orders ferromagnetically at $\cong$ 22 K, while the carbide prepared at 900 °C was found to

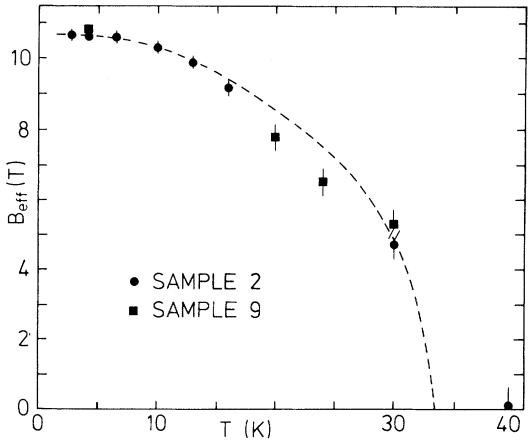

FIG. 3. Temperature dependence of the magnetic hyperfine field at ^{151}Eu in EuC_6, together with a Brillouin ($S = \frac{7}{2}$) fit (dashed curve).

order at $\cong$ 13 K. The 4.2-K Mössbauer spectra of both carbides are practically identical, with $B_{eff} = -30.5 \pm 1$ T, $S = -(11.3 \pm 0.2)$ mm/s, and a small positive EFG. These hyperfine parameters are very similar to those of EuO,[10] and are compatible with the spectral parameters for the impurity phase in our EuC_6 samples. In the magnetization measurements (not shown here) steps at 69 K (due to EuO), 22 K, and 13 K (due to EuC_x impurities) were clearly observed in the samples prepared from natural graphite flakes (No. 2 and No. 9); no EuO, however, could be found in an EuC_6 sample prepared from HOPG. The EuC_x and EuO impurities can be distinguished in the Mössbauer spectra by their rather different magnetic ordering temperatures. This resulted for the EuC_6 sample No. 2 in an EuC_x (EuO) content of $\cong$ 12% ($\cong$ 13%), in agreement with our magnetization measurements.

The results for the temperature dependence of B_{eff} obtained from two different samples are plotted in Fig. 3. B_{eff} is expected to be proportional to the local magnetization at the Eu site. The dashed line represents a fit with a three-dimensional molecular-field Brillouin ($S = \frac{7}{2}$) curve, resulting in a magnetic ordering temperature of $\cong$ 34 K, which has to be considered as a lower limit. In Ref. 5 a value of $T_N = 40$ K was given on the basis of magnetization measurements.

The magnetization measurements of Ref. 5 as well as our own show that EuC_6 orders antiferromagnetically. In addition, we learned in the present work that the Eu spins are oriented within the intercalant planes. There is strong indication from the metamagnetic transitions observed

in external fields up to 35 T (Ref. 5) that the long-range antiferromagnetic order exists *within the Eu planes*. We can therefore describe EuC_6 as a quasi-isotropic layered Heisenberg antiferromagnet,[11] where a small anisotropy in the magnetic exchange may be due to dipolar and crystalline-electric fields; in addition, a weak interlayer exchange has to be expected. As can be seen in Fig. 3, B_{eff} falls off more rapidly with temperature than described by the Brillouin curve. This is actually expected for such a layered magnetic system because of a higher density of low-energy magnons as compared with the isotropic three-dimensional case.[11]

The isomer shift of EuC_6 is the most negative one observed for any metallic Eu^{2+} system.[10] It reflects the relatively small s-like conduction-electron density at Eu due to partial charge transfer to the C planes and strong hybridization of the intercalant-layer conduction bands.[12] A strong hybridization can also be inferred from the shape of the Eu L_I edge in EuC_6,[7] which depends on the local p density of empty conduction-band states.

Both the electronic and the lattice structures of EuC_6 are reflected in the EFG tensor. The magnitude of V_{zz}, which does not change with temperature, is the largest one observed for any Eu^{2+} compound,[13] reflecting the strong lattice anisotropy of EuC_6. It is mainly caused by the positively charged in-plane Eu neighbors and was reproduced quantitatively by a point-charge calculation based on the structure of EuC_6 using a lattice Sternheimer factor of -72.[14]

Finally we discuss the saturation value of $B_{eff}(T \to 0) = -10.7 \pm 0.2$ T. The sign was deduced from the observed decrease in the total magnetic splitting in strong external fields up to 6 T. In Eu^{2+} compounds the size of the Eu moment cannot be inferred from B_{eff} because of large contributions from conduction-electron polarization by the $4f$ moment itself (B_s) and from transferred hyperfine fields (B_t), in addition to a rather chemically indifferent core-polarization field, $B_c = -(34 \pm 2)$ T.[15] In order to explain the relatively small magnitude of B_{eff} for EuC_6, we have to assume large positive contributions from B_s and B_t. In other magnetically ordered metallic Eu systems B_s was found to vary between +5 and +19 T, and large positive B_t contributions were found for compounds like $EuPt_2$ and $EuPd_2$.[15] A quantitative analysis of B_{eff} must wait for detailed results on the spin structure of EuC_6.

The authors wish to thank Dr. B. Perscheid, Professor I. Nowik, P. Schmidt, and G. Wisny for various contributions, as well as Dr. A. W. Moore of Union Carbide for the HOPG material. The work was supported by the Sonderforschungsbereich-161 of the Deutsche Forschungsgemeinschaft.

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