Ferromagnetic Interactions in EuS and EuSe Studied by Neutron Diffraction at Pressures up to 20.5 GPa

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Using neutron diffraction at very high pressures (up to 20.5 GPa), we studied magnetic interactions in the model system EuX (X = S, Se, Te) in a wide range of lattice constants. Surprisingly, when interatomic distances decrease, the Curie temperatures increase very rapidly and in a different way for each compound. The results were used to test models of an indirect f-d exchange in magnetic semiconductors. The observed behavior cannot be explained by considering only the overlap between Eu^{2+} d orbitals, pointing out a strong influence of the $2p$ shells, neglected before, on the first neighbor magnetic interaction. [S0031-9007(97)05156-9]

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From the early 1960s, europium monochalcogenides EuX (X = O, S, Se, Te) have been a model system to study different phenomena [1], starting from the basic problem of magnetic interactions in Heisenberg ferromagnets and antiferromagnets up to charge order and giant magnetoresistance [2]. They are semiconductors with a simple NaCl-type structure and a lattice parameter increasing when X changes from O to Te. Eu^{2+} ions carry well-localized spin only magnetic moments of 7 μ_B which order in antiferromagnetic (EuTe, EuSe), ferrimagnetic (EuSe), or ferromagnetic (EuS, EuO) structures. The system permits one to test different models of indirect and superexchange [3], since the small radius of $4f$ orbitals prevents any direct exchange and there are no free electrons to mediate Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. In these models, interactions are transmitted through $5d$ or $6s$ orbitals of the cations (indirect f-d or f-s exchange) or by $2p$ orbitals of the anions (superexchange). In most approaches, indirect exchange mediates the ferromagnetic first neighbor interaction J_1, whereas superexchange contributes to the antiferromagnetic interaction J_2 between second neighbors. The sensitivity of J_1 and J_2 to interatomic distances is the crucial point for testing theories. This sensitivity was used to explain the change of order from antiferromagnetic to ferromagnetic and the increase of Curie temperature when X varies from Te to O. Nevertheless, comparing different members of the family does not allow one to study separately the effects of interatomic distances and the chemical nature of the anion. Therefore, completely different models still permit one to explain ambient pressure data in EuX [3,4]. Experiments under applied pressures are the most direct way to test theoretical descriptions. Up to now, the available pressure range (only 0.5–2 GPa for the ordering temperatures in EuS and EuSe [5,6], see also Ref. [7]) yielded much smaller variations of the lattice constant than the chemical substitution. Very recently, studies at very high pressures were performed in EuTe by neutron diffraction [8] (up to 17 GPa) and magnetic measurements [9] (up to 11.7 GPa). The results show the same sequence of transitions as in the EuX series when X varies from Te to O, as expected in the above models. Moreover, we compared ordering temperatures in EuTe at pressures above 10 GPa with data for EuSe in the pressure range 0–1.3 GPa [6], which correspond to the same range of the lattice constant. Surprisingly, we found that both J_1 and J_2 cannot be described by single curves through the EuX family [8].

We report here a neutron diffraction study of the magnetic order in EuS and EuSe at pressures up to 20.5 and 14.8 GPa, respectively, covering the whole range of stability of NaCl-type phases (the initial structure transforms to CsCl-like above 21 and 14.5 GPa, respectively [10]). Together with the previous data for EuTe, our new results permit one to analyze magnetic interactions in a wide range of the lattice constant.

We used isotopically enriched samples ^{153}EuS and ^{153}EuSe. The lattice parameters, magnetic structures, and ordering temperatures measured at ambient pressures are in good agreement with previous studies [1]. Powdered samples with volume only 0.01–0.3 mm^3 were placed in a compact high pressure cell with sapphire or diamond anvils [11]. Changes of pressure were performed at ambient temperature and measured by a standard ruby-fluorescence technique. Measurements of the pressure distribution in the sample volume yield typical pressure inhomogeneities of ±5%. The pressure stability during cooling is expected to be better than ±0.4 GPa. Neutron diffraction experiments were performed on the G6.1 spectrometer of the Laboratoire Léon Brillouin, with an incident wavelength of 4.74 Å. We used a specific version of the spectrometer adapted to studies of very small samples with focusing systems to increase the flux at the sample place and a special environment to achieve a very low background level [11]. At each pressure we measured the temperature dependencies of the magnetic Bragg peaks. The positions of the magnetic and structural peaks were used to determine

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the lattice constant, and therefore the pressure-volume dependence. The counting time for each temperature varied from 2 to 12 hours.

As expected, the NaCl-type crystal structure persists in the studied pressure ranges. The pressure dependencies of the unit cell volumes are in good agreement with x-ray data [10] (Fig. 1). We did not observe any anomaly of the lattice constant in the measured temperature range besides the usual variation due to the linear thermal expansion of about 10^{-5} K^{-1}. The higher compressibility and abnormal temperature dependence found in earlier work [12] should be attributed to experimental artifacts.

Typical neutron diffraction spectra of EuS and EuSe at high pressures are shown in Fig. 2, together with the temperature dependencies of the integrated intensities of the 111 diffraction peak. In both compounds we observed a strong, nonlinear increase of the Curie temperatures T_C with increasing pressure P (Fig. 3). Ordering temperatures are shown in Fig. 4 versus lattice constant. In addition to the present paper, we show the results of our previous study of EuTe [8] and low pressure data ($P = 0.5$ GPa) for EuSe [6]. Clearly, the ordering temperatures do not follow any common dependence, valid within the whole EuX family.

The increase of T_C in each EuX compound is much stronger than expected by comparing members of the family at ambient pressure. Obviously, the influence of the anion substitution is not simply related to a variation of the lattice constant. Our results give a new basis for theoretical interpretations, which should take into account the particular features of the electronic structure of each compound. In order to compare with microscopic models, we derive the exchange constants J_1 from our data. In a molecular field approach, T_C is related to the exchange constant J_1 and J_2 through the following expression: $kT_C = \rho(12J_1 + 6J_2)$, where $\rho = 2S(S+1)/3 = 10.5$. In EuX at ambient pressure, J_1 and J_2 were measured directly by inelastic neutron scattering and spin wave resonance [13]. The sensitivity of J_2 to the lattice constant a can be studied by measuring the Néel temperature T_N at high pressure when the order is antiferromagnetic, since, in the same approach, $kT_N = -6\rho J_2$. From our results for EuTe (as well as from Refs. [9,14]) and the low pressure data of EuSe [6], we expect that, for each compound, J_2 is almost independent of a (even though it changes substantially with anion substitution). The insensitivity of T_N to the interatomic distances could be explained by a competition between the antiferromagnetic and some additional ferromagnetic contributions to J_2 (Ref. [3]). Independently of the nature of this phenomena, we can calculate $J_1(a)$ by assuming for J_2 the same value at high pressure as at ambient pressure (-0.18, -0.08, and -0.12 K for EuTe, EuS, and EuSe, respectively). The results are shown in Fig. 5. The dashed line, which fits the data for different compounds at ambient pressure, was used before to study the influence of the lattice constant [1,3,4]. Clearly, it does not correspond to the real lattice constant dependence of J_1 of any EuX compound.

In EuX compounds, the $4f$ level is placed between the empty conduction band and the valence band. The conduction band is formed by the overlap of the $5d$ orbitals of the cations, split by crystal fields into low energy t_g

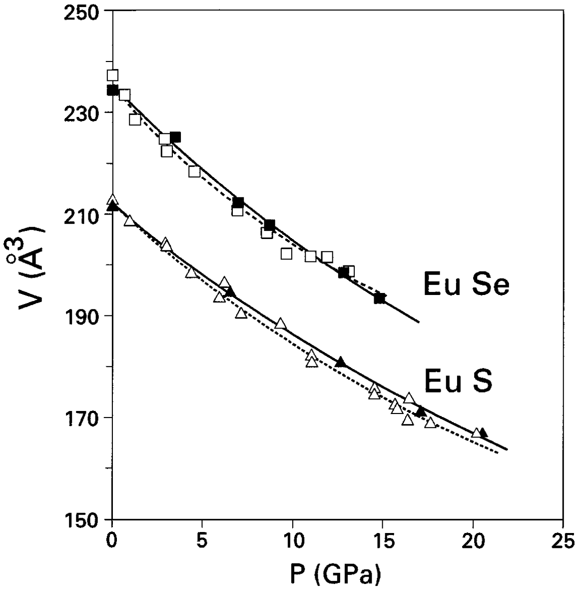

FIG. 1. Volume of the unit cell versus pressure in EuSe and EuS. Filled and open symbols correspond to our data and the x-ray data of Ref. [6], respectively. The solid (dashed) lines are fits by the Birch equation of our data (Ref. [6] data), yielding a bulk modulus and its derivative $B_0 = 67.5$ (52) GPa, $B_1 = 1.3$ (4.0) for EuSe and $B_0 = 71.8$ (61) GPa, $B_1 = 1.3$ (2.0) for EuS.

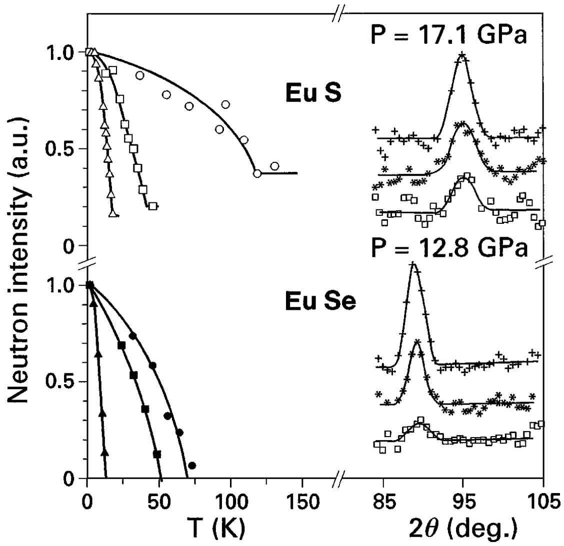

FIG. 2. Integrated intensity of the 111 diffraction peak in EuSe and EuS versus temperature at different pressures. △, □, ○ (▲, ■, ●) correspond to pressures of 0, 6.5, and 17.1 GPa (3.5, 12.8, and 14.8 GPa) in EuS (EuSe). On the right are the neutron diffraction patterns of the 111 peak. The symbols +, $*$, and □ correspond to temperatures of 1.3, 101.5, and 130.5 K (1.3, 31.8, and 47.7 K) in EuS (EuSe).

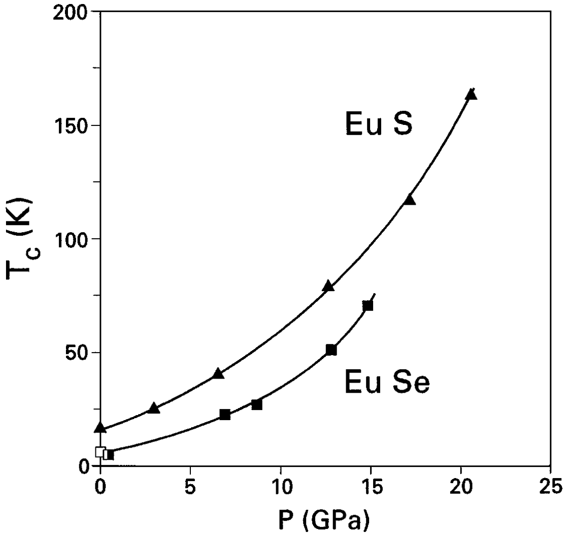

FIG. 3. Pressure dependence of the Curie temperature T_C in EuSe and EuS (our data ▲, ■). In EuSe, (□) is the Néel temperature at ambient pressure (our data), and (◨) is the triple point of the paramagnetism, ferromagnetism, and antiferromagnetism (from Ref. [6]). Solid lines are guides to the eye.

and high energy e_g levels (inset, Fig. 5). The $6s$ levels also contribute to the conduction band, but are believed to play a less important role in the exchange interactions. The valence band is formed by the filled $2p$ orbitals of the anions. In the model of f-d exchange between the half-filled f band and empty d band [3], J_1 is derived in the third order perturbation theory from the overlap of d orbitals and the energy gap E_g, separating f and d levels. Namely, $J_1 = Ab^2/E_g^2$, where A is a constant and b is the overlap of d orbitals [1]. This expression neglects the influence of the symmetry of f and d functions to the strength of the f-d exchange, the k dependence of the magnetic interactions, and the contribution from the formation of a magnetic polaron. More detailed analysis can be found in Ref. [3]. We note that they keep about the same expression for J_1, even though the effective gap might not coincide exactly with the real one (as derived from optical properties, for instance).

Both b and E_g are related to the cation orbitals and do not involve explicitly any contribution from the chemical nature of the anion. This is why the influence of the anion substitution on J_1 was usually considered only through the variation of the lattice constant. However, we notice that E_g could still be affected by the $2p$ shell of the anion through crystal field effects. The crystal field decreases E_g by lowering the energy of the t_{2g} level. The decrease in energy comes from an interaction between charge distributions on the $5d$ and $2p$ orbitals, which favor t_{2g} orbitals, directed to the next cation, with respect to e_g, directed toward the anion (and repelled by the negative charges on the $2p$ shell). This effect becomes stronger with decreasing Eu-X distance. In fact, the crystal field should be independent of the nature of X only if the $2p$ shell had a spherical symmetry, which is not the case. Therefore, by replacing X with an anion of a larger size, we could partly compensate the increase of the Eu-X distance by extending the negative clouds of the p shell towards the cation. Consequently, a chemical pressure will decrease E_g less than applied pressure. The influence of an applied pressure on E_g was studied by optical absorption at low pressures [15] and recently confirmed by measurements of fluorescence [16]. Because

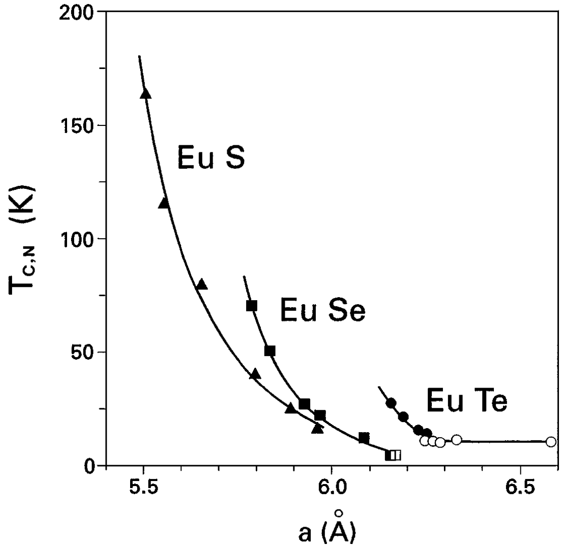

FIG. 4. Ordering temperatures versus lattice constant in EuTe (Ref. [4]), EuSe, and EuS (this paper). Open (filled) symbols correspond to Néel (Curie) temperatures. (◧) corresponds to the triple point of the paramagnetism, ferromagnetism, and antiferromagnetism (from Ref. [6]). Solid lines are derived from the fits of J_1 (see text).

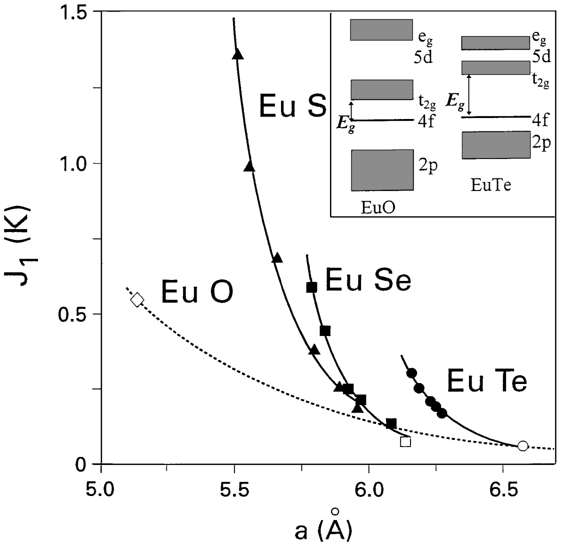

FIG. 5. First neighbor exchange interaction J_1 versus lattice constant a. Filled symbols are derived from our data of T_C. Open symbols correspond to J_1 values at ambient pressure [1,13]. The solid lines are fits as described in the text. Inset: Schematic view of the electronic structure in EuX.

of the lack of reliable compressibility data, the results of Ref. [15] were erroneously interpreted by concluding that a chemical pressure has the same effect as a real one. Using more recent compressibility data (Ref. [10] and this work) and the slopes dE_g/dP from Ref. [14], we derived experimental values of dE_g/da between -2 and -2.8 meV/A for the members of the EuX family. The corresponding value of dE_g/da when a is varied by chemical pressure is only -0.6 meV/A.

Now we fit our data within the model of f-d indirect exchange but assuming that E_g could vary in a different way for each compound. Using a linear dependence for $E_g(a)$ we rewrite E_g and J_1 as follows:

$$E_g = E_g^0(a - a_2)/(a_0 - a_2)\,,$$
$$J_1 = Ab^2/E_g^2 = C(a_0 - a_2)^2b^2/(a - a_2)^2,$$

where $C = A/(E_g^0)^2$. Here E_g^0 and a_0 are the values of E_g and a at ambient pressure, and a_2 is the value of a where the gap closes. These three quantities differ in each compound. To describe the overlap b we used two types of formulas, either an exponential fit of the numerical data derived from Hartree-Fock calculations in EuX family $b \sim \exp(-a/a_1)$ (as done in Ref. [3]) or an analytical formula for the overlap of d orbitals $b \sim 1/r^5$ (as proposed in Ref. [17]). Both fits coincide with a precision of $\pm 4\%$. Because of the ambiguity in the definition the "effective gap," we fitted the parameters C and a_2. We obtained good fits of $J_1(a)$, as shown in Fig. 5 (using the exponential fit $b(a)$, $a_1 = 1.4$ Å for the whole family). The fitted values of a_2 (5.7, 5.5, and 5.1 Å for EuTe, EuSe, and EuS, respectively) are in reasonable agreement with those deduced from the experimental values of dE_g/da (5.7, 5.4, and 5.3 Å, respectively).

In conclusion, our study at very high pressures shows that, in EuX compounds, the ferromagnetic interaction depends more strongly on interatomic distances than assumed for a long time by comparing different members of the family at $P = 0$. In contrast to the single dependence suggested before, our results show a more complex behavior. Therefore, they yield additional constraints to any proposed theory of indirect exchange in EuX. Using the model of indirect f-d exchange to calculate the ferromagnetic interaction between first neighbors, we have shown that our results could be interpreted by assuming a contribution of the anion to the gap between the $4f$ magnetic level and the $5d$ conduction band. Nevertheless, we point out the importance of further experimental studies of the electronic structure at very high pressures ($P > 10$ GPa). Combined with the neutron data, they will give a more precise basis to new theoretical investigations. Such investigations could involve contributions of the electronic correlations and longer range interactions, neglected in the previous models.

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