is that zero-field splitting effects are small, implying an isotropic g value close to 2. In high-spin iron(II) compounds, the zero-field effects can be large (comparable in magnitude to the intracluster exchange interactions) resulting in an anisotropic **g** tensor. The dipolar coupling model does not include the zero-field effects directly but incorporates them indirectly in the g value. This may be the reason the g value obtained from the fit ($g = 2.2$) is greater than 2. It was also assumed the intercluster (pair in the present case) exchange was zero. In real systems, the intercluster interactions are operable but are usually considerably weaker than the intracluster interactions justifying the preceding assumption. It is interesting to note that a spin-coupled dimer model has been used in the interpretation of the magnetic data in a recent study of the linear chain polymer $Fe(C_2O_4)\cdot 2H_2O$.[38] In this study, the magnetic susceptibility exhibited a single broad maximum at ~35 K and could be represented accurately by a 1-D Heisenberg model for $T > 25$ K. Below 25 K, the susceptibility dropped sharply, which was interpreted as the onset of 3-D antiferromagnetic ordering. An alternative fit with the Heisenberg–Dirac–Van Vleck dipolar coupling model gave a successful fit of the data for $T > 4.2$ K, perhaps suggesting significant pairwise antiferromagnetic interactions between metal atoms.

More complete theories which incorporate the foregoing interpair interactions are known as the ladder[45] and the alternating chain models.[46] In the former model, the strongest interactions occur *between metal atoms in adjacent polymer chains* with weaker interactions within the chain. The stronger interactions from the "rungs", and the weaker interactions from the "sides" of the ladder. In contrast, in the alternating chain model, the strong intrapair and weaker interpair interactions *alternate throughout* the chain. Both models have been used to explain the magnetic properties of $Cu(NO_3)_2\cdot 2.5H_2O$.[47] The available data are in agreement with the alternating chain model. We tend to reject the ladder model for $Fe(bpy)(NCS)_2$ in view of the proposed structure and analogy to $Co(bpy)Cl_2$. For the latter compound,[12] there are no bonded interactions between parallel chains, and the *closest interchain* Co–Co and Cl–Cl distances are 8.8 and 6.7 Å, respectively; i.e., the rungs are very weak or nonexistent. It does not seem likely that some form of an alternating chain model is most appropriate to represent the magnetic behavior of $Fe(bpy)(NCS)_2$. However, in the final analysis, this can only be judged in the light of an X-ray structure determination. In any event, to our knowledge, theoretical work using the alternating chain model has been done only for $S = {}^1/_2$,[47] and verification of this model in the present case must await advances in the theory of the alternative chain. In subsequent work, we shall report on the antiferromagnetic behavior of $Mn(bpy)(NCS)_2$ and the strong 3-D ferromagnetism of the divalent nickel analogue.

Acknowledgment. We wish to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grants No. DMR-77-12625 and DMR-80-16441.

Registry No. $Fe(bpy)(NCS)_2$, 79803-24-0; $Fe(bpy)_2(NCS)_2$, 37843-42-8.

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Magnetic Properties of α-$Li_2Eu_5O_8$ and β-$Li_2Eu_5O_8$. Evidence for Linear-Chain Heisenberg Ferromagnetic Behavior

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Some magnetic properties of the α and β modifications of $Li_2Eu_5O_8$ have been determined in the temperature range 1.2–50 K. In both materials there occur linear chains of Eu^{II} ions at rather close distances, 3.5 Å, while the interchain distances are much greater, 7.72 Å for the α phase and 8.57 Å for the β phase. Susceptibility data between 4.2 and 50 K can be analyzed in terms of a linear-chain Heisenberg ferromagnetic model for both compounds. Both phases undergo 3-D AF order with $T_N = 2.2$ K for the α phase and 1.9 K for the β phase. Metamagnetic transitions are observed at critical fields of 0.019 T for the α phase and 0.010 T for the β phase. Intra-, J_1, and interchain, J_2, exchange parameters have been derived as follows: α phase $J_1/k = +0.2$ K, $J_2/k = -0.002$ K; β phase $J_1/k = +0.1$ K, $J_2/k = -0.001$ K. The values of J_1 are discussed in light of diffuse-reflectance spectra for both phases and current ideas about exchange in Eu^{2+} compounds.

Introduction

Very few compounds exist whose magnetic behavior is a good approximation to the ferromagnetic linear (1-D) Heisenberg chain. To date the best examples are Cu^{II} ($S = {}^1/_2$) and Ni^{II} ($S = 1$) salts such as $[(CH_3)_4N]NiCl_3$[1] and $[(CH_3)_4N]CuCl_3$.[2] Compounds containing divalent europium, Eu^{II}, seem to have been overlooked as potential candidates. Eu^{II}, ${}^8S_{7/2}$, is an ideal Heisenberg ion, which, given the spin value of ${}^7/_2$, should represent a fair approximation to classical $S = \infty$ behavior. Furthermore, ferromagnetic exchange interactions are commonly found in Eu^{II} compounds with relatively short Eu^{II}–Eu^{II} distances. It is well-known that EuO, with a near neighbor (nn) Eu^{II}–Eu^{II} distance of 3.63 Å, has a ferromagnetic nn interaction, $J_1/k = +0.5$ K.[3]

The magnetic properties of Eu_3O_4 ($Eu^{II}Eu^{III}O_4$) have been determined by Holmes and Schieber.[4] In this compound the

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Table I. Crystal Data of Li$_2$Eu$_5$O$_8$

α-Li$_2$Eu$_5$O$_8$: monoclinic, space group *B*2/*m* (No. 12), 2 formula units/unit cell
β-Li$_2$Eu$_5$O$_8$: orthorhombic, space group *A*2$_1$*am* (No. 36), 4 formula units/unit cell

Lattice Constants (Std Dev in Parentheses)

compd	*a*, Å	*b*, Å	*c*, Å	γ, deg
α-Li$_2$Eu$_5$O$_8$	13.378 (5)	9.666 (3)	3.539 (1)	119.52 (2)
β-Li$_2$Eu$_5$O$_8$	13.152 (4)	17.137 (6)	3.545 (1)	

		x	*y*	*z*	*B*, Å^2
		α-Li$_2$Eu$_5$O$_8$^{a}			
Eu(1)	(Eu^{II})	0.5	0	0	1.39 (3)
Eu(2)	(Eu^{III})	0.61028 (1)	0.43727 (2)	0	0.34 (1)
Eu(3)	(Eu^{III})	0.66361 (1)	0.81358 (2)	0.5	0.36 (1)
Li		0.6913 (9)	0.2622 (14)	0.5	1.4 (2)
O(1)		0.5417 (2)	0.2422 (4)	0.5	0.80 (4)
O(2)		0.7362 (2)	0.6195 (3)	0.5	0.67 (3)
O(3)		0.8148 (3)	0.9360 (4)	0	0.77 (4)
O(4)		0.5819 (2)	0.6556 (3)	0	0.59 (3)
		β-Li$_2$Eu$_5$O$_8$^{b}			
Eu(1)	(Eu^{II})	0.5	−0.01082 (4)	0	0.83 (3)
Eu(2)	(Eu^{III})	0.42717 (7)	0.18837 (4)	0	0.60 (2)
Eu(3)	(Eu^{III})	0.28700 (7)	0.34987 (3)	0.5	0.55 (2)
Eu(4)	(Eu^{III})	0.13822 (7)	0.19850 (3)	0	0.53 (2)
Eu(5)	(Eu^{III})	0.25211 (7)	0.03425 (4)	0.5	0.62 (2)
Li(1)		0.6056 (32)	0.1219 (25)	0.5	2.2 (2)
Li(2)		0.4668 (29)	0.3502 (21)	0	1.8 (2)
O(1)		0.4639 (9)	0.0999 (6)	0.5	0.85 (6)
O(2)		0.4572 (8)	0.2902 (6)	0.5	0.68 (5)
O(3)		0.3659 (8)	0.4299 (6)	0	0.75 (5)
O(4)		0.2857 (10)	0.2709 (6)	0	0.70 (5)
O(5)		0.1123 (8)	0.2910 (6)	0.5	0.64 (5)
O(6)		0.0972 (9)	0.1047 (6)	0.5	0.76 (5)
O(7)		0.1768 (9)	−0.0435 (6)	0	0.93 (6)
O(8)		0.2806 (10)	0.1122 (6)	0	0.79 (5)

^{a} With the exception of Eu(1), which is in the special position 2b, all atoms are in the special position 4i of the space group *B*2/*m* (No. 12). ^{b} All atoms are in the special position 4a of the space group *A*2$_1$*am* (No. 36).

Eu^{II} ions form linear chains, with an intrachain distance of 3.5 Å and an interchain distance of 5.6 Å. The Weiss constant is positive, $\Theta_c = +5$ K, yet 3-D antiferromagnetic order sets in below 6 K. A metamagnetic transition is observed with a critical field of 0.24 T at low temperatures. Exchange constants derived from such data are $J_1/k = +0.3$ K and $J_2/k = -0.02$ K for the intra- and interchain interactions, respectively. The ratio $|J_2/J_1| \approx 0.1$ is too large to permit realization of ideal 1-D behavior.

Bärnighausen[5] has reported on the structure of the α and the β modifications of Li$_2$Eu$_5$O$_8$ (Li$_2$Eu^{II}Eu$^{III}{}_4$O$_8$), which have structural features similar to Eu$_3$O$_4$. Because ref 5 is not widely circulated, we list the essential structural details for α-Li$_2$Eu$_5$O$_3$ and β-Li$_2$Eu$_5$O$_8$ in Table I. In both phases Eu^{II} ions are found in linear chains with short intrachain distances, 3.539 Å (α-Li$_2$Eu$_5$O$_8$) and 3.545 Å (β-Li$_2$Eu$_5$O$_8$), and interchain distances of 7.72 and 8.57 Å, respectively. These intrachain distances are comparable to those of Eu$_3$O$_4$, and the interchain distances are greater, suggesting that α- and β-Li$_2$Eu$_5$O$_8$ might show more ideal 1-D ferromagnetic behavior.

Experimental Section

Preparation of Compounds. Following Bärnighausen,[5] EuOCl and LiH were mixed in the molar ratio 1.5:1, pelletized, sealed into molybdenum crucibles, and fired for 24 h at 850 °C for α-Li$_2$Eu$_5$O$_8$ and 14 h at 650 °C for β-Li$_2$Eu$_5$O$_8$, followed by rapid quenching to room temperature. Best results were obtained with a 10% molar excess of LiH. Handling of the LiH was done in a glovebox. α-Li$_2$Eu$_5$O$_8$ formed as yellow-orange crystals and β-Li$_2$Eu$_5$O$_8$ as red crystals. The X-ray powder patterns agreed with those calculated from the published cell constants.[5] X-ray and microscopic examination disclosed the presence of varying amounts of Eu$_2$O$_3$ in all preparations. It was impossible to separate this phase so magnetic measurements were performed on the mixtures. The amount of the appropriate Li$_2$Eu$_5$O$_8$ phase in the samples used for magnetic measurements was determined by thermal gravimetric oxidation.

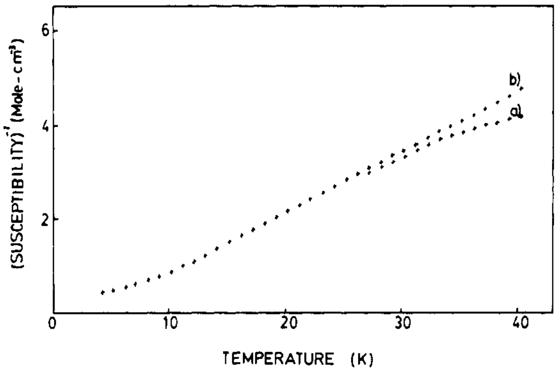

Figure 1. Inverse susceptibility vs. temperature for α-Li$_2$Eu$_5$O$_8$: (a) raw data; (b) data corrected for χ_{TIP} due to Eu^{III}. $\chi_{TIP} = 1.02 \times 10^{-2}$ cm^3 mol^{-1}; $C = 7.70 \pm 0.41$; $\Theta_c = +3.8 \pm 0.2$ K.

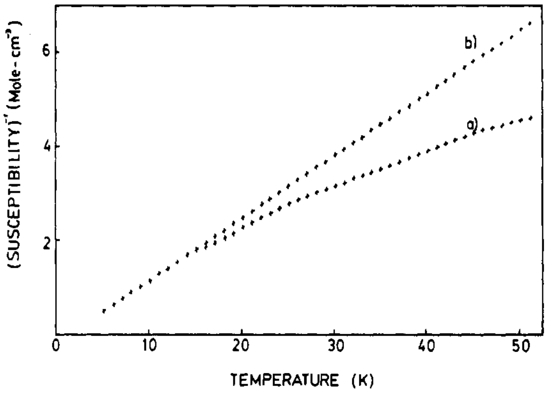

Figure 2. Inverse susceptibility vs. temperature for β-Li$_2$Eu$_5$O$_8$: (a) raw data; (b) data corrected for χ_{TIP} due to Eu^{III}. $\chi_{TIP} = 5.6 \times 10^{-2}$ cm^3 mol^{-1}; $C = 7.67 \pm 0.20$; $\Theta_c = +1.5 \pm 0.2$ K.

Magnetic Measurements. Magnetic susceptibility and magnetization measurements were performed on powdered samples between 1.2 and 50 K with a variety of applied fields with use of a PAR vibrating-sample magnetometer. Samples were in the form of pellets attached to a quartz rod with GE 7031 low-temperature varnish. Temperatures were monitored with a gold–iron vs. chromel thermocouple mounted near the sample.

Diffuse Reflectance. These spectra were obtained by using a Cary Model 1411 diffuse-reflectance accessory (integrating sphere) attached to a Cary 14 spectrophotometer in the wavelength range 3500–7000 Å. MgCO$_3$ was the standard.

Results and Discussion

The susceptibility data for both α- and β-Li$_2$Eu$_5$O$_8$ are shown in Figures 1 and 2. As mentioned earlier the samples used for susceptibility measurements contained known amounts of Eu$_2$O$_3$. Fortunately, the susceptibility of Eu$_2$O$_3$ is well-known[6] in this temperature range and is temperature independent. Eu^{III}, ^{6}F$_0$, has a nonmagnetic ($J = 0$) ground state and at low temperatures contributes only a Van Vleck paramagnetism due to interaction with excited states. The data shown in Figures 1 and 2 have been corrected for Eu$_2$O$_3$. The corrected susceptibility data can be fitted to a function of the type $\chi = C/(T - \Theta) + \chi_{TIP}$. The Curie–Weiss term is due

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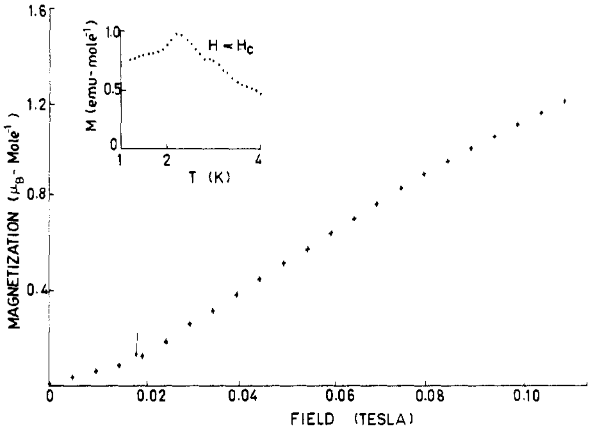

Figure 3. Magnetic moment vs. applied field at 1.2 K for α-$Li_2Eu_5O_8$. A metamagnetic transition occurs at a critical field of 0.019 ± 0.001 T. Inset shows magnetic moment vs. temperature for a field less than H_c. T_N = 2.2 K.

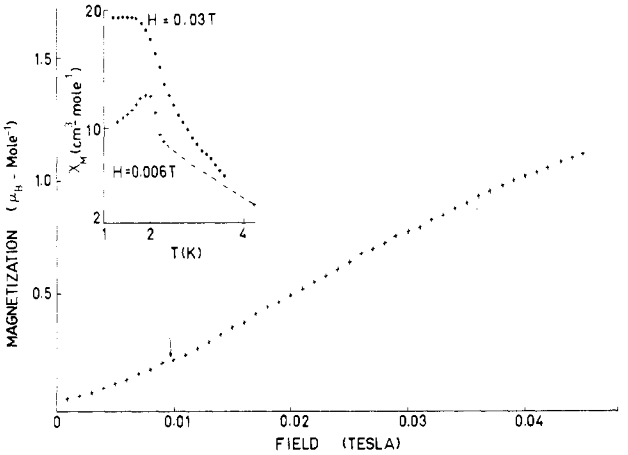

Figure 4. Magnetic moment vs. applied field at 1.2 K for β-$Li_2Eu_5O_8$. A metamagnetic transition occurs at a critical field of 0.010 ± 0.001 T. Inset shows susceptibility vs. temperature for fields above and below H_c.

Table II. Calculated Dipole Fields and Derived Exchange Parameters for α-$Li_2Eu_5O_8$ and β-$Li_2Eu_5O_8$

	α-$Li_2Eu_5O_8$	β-$Li_2Eu_5O_8$
Δh^{dip}, T	0.1363	0.1364
$^4/_3\pi N\mu_s$, T	0.1366	0.1361
Δh^{ex}, T	0.0382	0.0197
J_1/k, K	+0.2	+0.1
J_2/k, K	−0.002	−0.001

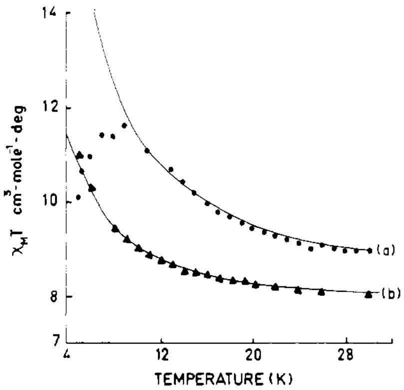

Figure 5. Low-temperature susceptibility data for (a) α-$Li_2Eu_5O_8$ and (b) β-$Li_2Eu_5O_8$ plotted as χT vs. T. Solid lines are theoretical curves calculated for the Fisher model[7,8] with (a) J/k = 0.20 K and (b) J/k = 0.08 K.

to Eu^{II} while the temperature-independent term is contributed by Eu^{III} from $Li_2Eu^{II}Eu^{III}{}_4O_8$. For α-$Li_2Eu_5O_8$ the TIP term can be measured independently from data on α-$Li_2SrEu_4O_8$. Our measurements of this compound give χ_{TIP} = 0.0102 cm^3/mol^{-1}, which has been subtracted from the raw data to give the Curie–Weiss plot of Figure 1. No independent measure of χ_{TIP} for β-$Li_2Eu_5O_8$ was available as all attempts to prepare β-$Li_2SrEu_4O_8$ failed. χ_{TIP} for β-$Li_2Eu_5O_8$ was determined to be 0.0564 cm^3 mol^{-1} from a least-squares fit. The Curie–Weiss parameters for both materials were C = 7.70 ± 0.14 and Θ = +3.8 ± 0.2 K for the α phase and C = 7.67 ± 0.20 and Θ = +1.5 ± 0.2 K for the β phase. The free-ion value of C for Eu^{2+} is 7.87.

As shown in Figures 3 and 4, 3-D antiferromagnetic (AF) order sets in with T_N = 2.2 and 1.9 K for the α and β phases, respectively. Due to the structural similarity with Eu_3O_4, one anticipates a metamagnetic transition for these compounds as well. Since only polycrystalline samples are available, the metamagnetic transition will be manifested as a relatively subtle change in slope of the isothermal M vs. H curve.[4] The field at which the slope change occurs gives a reasonable approximation to the critical field, H_c, at that temperature.[4] On this basis evidence is found for metamagnetic transitions at 1.5 K for both α- and β-$Li_2Eu_5O_8$ with critical fields of 0.019 and 0.010 T, respectively. Futher evidence for metamagnetic behavior is shown in the inset of Figure 4. At 0.006 T the χ vs. T curve is characteristic of an AF state while the data at 0.030 T indicate ferromagnetism. Clearly, at some field between these extremes a transition from an AF to a saturated paramagnetic state, i.e., a metamagnetic transition, must take place.

Following Holmes and Schieber,[4] the intra- and interchain exchange constants can be derived from values for Θ_c and H_c. For a system of identical spins, S

$$\Theta_c = \tfrac{2}{3}S(S+1)\sum_m Z_m(J_m/K) \qquad (1)$$

where Z_m is the number of nth neighbors and J_m is the exchange constant with the nth neighbor. For α- and β-$Li_2Eu_5O_8$, $\Theta_c = {}^2/_3S(S+1)[2J_1 + 4J_2]$. With the assumption that the AF ground state consists of ferromagnetic chains oriented antiparallel to neighboring chains, the change in effective exchange field, Δh^{ex}, in going from the AF state to the final state in the metamagnetic transition is given by

$$\Delta h^{ex} = -14J_2/\mu_B \qquad (2)$$

The critical field is related to Δh^{ex} by

$$H_c = \tfrac{1}{2}[\Delta h^{dip} - \tfrac{4}{3}\pi N\mu_s + \Delta h^{ex}] \qquad (3)$$

where $\Delta h^{dip} - {}^4/_3\pi N\mu_s$ is the decrease in magnetic dipolar field on a given spin in going from the AF to the final state. Δh^{dip} was calculated by lattice summation out to 70 Å for both compounds with a computer program written by E. R. Cowley.

The values obtained for both compounds and the derived exchange constants are shown in Table II.

Due to the many assumptions involved in their derivation, only one significant figure is reported for the exchange parameters. Note that $J_2/J_1 \cong 10^{-2}$ for both compounds. This is an order of magnitude smaller than the value for Eu_3O_4.

Figure 5 shows susceptibility data for both α- and β-$Li_2Eu_5O_8$ plotted as χT vs. T. The solid curves are calculated from the scaled ($S = {}^7/_2$) Fisher model[7,8] for the linear-chain ferromagnet with J/k = 0.20 K for α-$Li_2Eu_5O_8$ and J/k =

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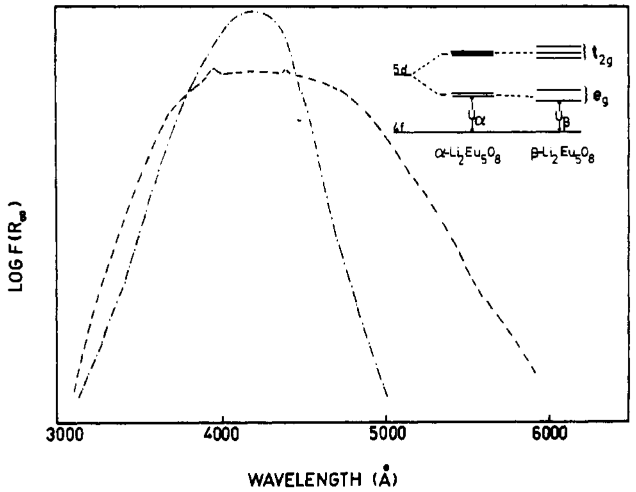

Figure 6. Diffuse-reflectance spectra for α-$Li_2Eu_5O_8$ (–·–) and β-$Li_2Eu_5O_8$ (– – –).

0.08 K for β-$Li_2Eu_5O_8$. In Fisher's model the susceptibility behaves as

$$\chi T = \frac{Ng^2\mu_B{}^2S(S+1)(1+\mu)}{3k(1-\mu)} \tag{4}$$

where

$$\mu = \coth\,[2JS(S+1)/kT] - kT/[2JS(S+1)]$$

Note that the susceptibility of both compounds follows the Fisher model over a fairly wide temperature range with values of J/k essentially identical with those derived previously from different considerations. Note also the downturn in χT below 10 K for α-$Li_2Eu_5O_8$ showing the influence of the negative interchain interaction for this material. Data for β-$Li_2Eu_5O_8$ fit the Fischer model down to 5 K although 3-D order sets in at 1.9 K as noted previously. This suggests that $|J_2/J_1|$ is smaller for the β phase than for the α phase. This is reasonable as the interchain distance is greater for the β phase.

It is clear that J_1 for the α phase is greater than J_1 for the β phase. This may be related to subtle differences in Eu^{II} geometry for the two materials. Ferromagnetic exchange interactions in Eu^{II} compounds are generally ascribed to a 4f–5d transfer effect such as that proposed by Goodenough[9] and Kasuya.[10] The exchange parameters, J_1, are given by

$$J_1 \approx \frac{b^2 J_{\mathrm{INTRA}}}{U^2} \tag{5}$$

where b is the transfer integral, which depends on the Eu^{II}–Eu^{II} distance, J_{INTRA} is the intraatomic exchange constant between 4f and 5d wave functions, and U is the excitation energy from the 4f levels to the 5d levels. In Eu^{II} compounds U can be obtained from the optical absorption spectrum. This 4f–5d transition is strongly allowed, giving a very intense band the position and shape of which are strongly influenced by crystal field effects on the 5d excited state. For α-$Li_2Eu_5O_8$ the Eu^{II}–O nn geometry is nearly cubic (8-fold) while in β-$Li_2Eu_5O_8$ this site is strongly distorted from cubic. Qualitative energy-level diagrams and diffuse-reflectance spectra for the α and β phases are shown in Figure 6. The 4f → $5d_{e_g}$ band for the α phase is more narrow and slightly shifted to higher energies than the band for the β phase.

This indicates that $U_\alpha > U_\beta$. The Eu^{II}–Eu^{II} nn distance is 0.006 Å shorter in the α phase, but this is just barely significant in the crystallographic sense and amounts to a difference of only 0.2%. It is reasonable to consider these distances as essentially the same and thus $b_\alpha \approx b_\beta$. On this basis we expect $J_\beta > J_\alpha$, which is not observed. Thus, it is difficult to understand the differences in J_1 for the α and β phases in terms of the Goodenough–Kasuya mechanism alone. Other effects such as superexchange through Eu^{II}–O–Eu^{II} linkages may play an important role in these materials.

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