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Exchange interaction effects in the ESR spectra of Eu^{2+} in LaB_6

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Abstract

The electron spin resonance (ESR) spectra of Eu^{2+} ($4f^7$, $S = \frac{7}{2}$) in LaB_6 single crystal show a single Dysonian resonance for the localized Eu^{2+} magnetic moments. It is shown that the Eu^{2+} ions are covalent exchange coupled to the (B) 2p-like host conduction electrons.

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1. Introduction

The lanthanum hexaboride compound, LaB_6 , is a very stable and hard refractory material characterized by strong covalent bonds [1]. Due to its very low work function, $\sim 2.7\text{ eV}$, it was found to be a very interesting material for electron emitters [2,3]. Besides, LaB_6 was found to be superconductor at $T = 0.45\text{ K}$ [4].

In this work we report on the Electron Spin Resonance (ESR) experiments of diluted Eu^{2+} in LaB_6 . In this cubic metallic compound we found that the Eu^{2+} ($4f^7$; $S = \frac{7}{2}$) ground state, as far as the crystal field effects are concerned, behaves as Gd^{3+} and Eu^{2+} (S-state) ions diluted in any other cubic metallic/semimetallic/isolating hosts [5]. We shall show that the Eu^{2+} and Gd^{3+} ions are probing, via the exchange interaction, different type of host conduction electrons in LaB_6 .

2. Experiment

Single crystals of LaB_6 were grown as described in Ref. [6]. The cubic structure (space group 221, $\text{Pm}\bar{3}\text{m}$, CsCl type) and phase purity were checked by X-ray powder diffraction and the crystals orientation determined by Laue X-ray diffraction. The ESR experiments were done in $\sim 1 \times 1 \times 0.5\text{ mm}^3$ single crystal in a Bruker X, and Q-bands (9.48 and 34.4 GHz) spectrometer using appropriated resonators for low- T measurements coupled to a T -controller using a helium gas flux system for $4.2 \lesssim T \lesssim 300\text{ K}$. The Eu concentration was obtained from a Curie–Weiss fitting of the susceptibility data, assuming $\mu_{\text{eff}} = 7.94\mu_{\text{B}}$ for the Eu ions. Magnetization, $M(T, H)$, measurements for $2 \lesssim T \lesssim 300\text{ K}$ were taken in a Quantum Design Magnetic Properties Measurement System SQUID Dc -magnetometer.

3. Experimental Results

Figs. 1(a) and 1(b) show, respectively, the low- T ESR spectra for 2200 ppm of Eu in LaB_6 at X and Q-bands for

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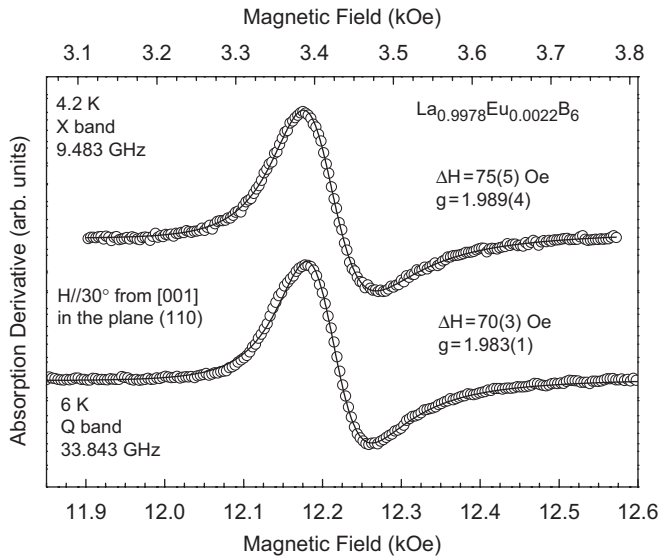


Fig. 1. Low- T X and Q-band ESR spectra of Eu^{2+} in a $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ ($x = 0.0022$) single crystal for $H \parallel 30^\circ$ in the (110) plane.

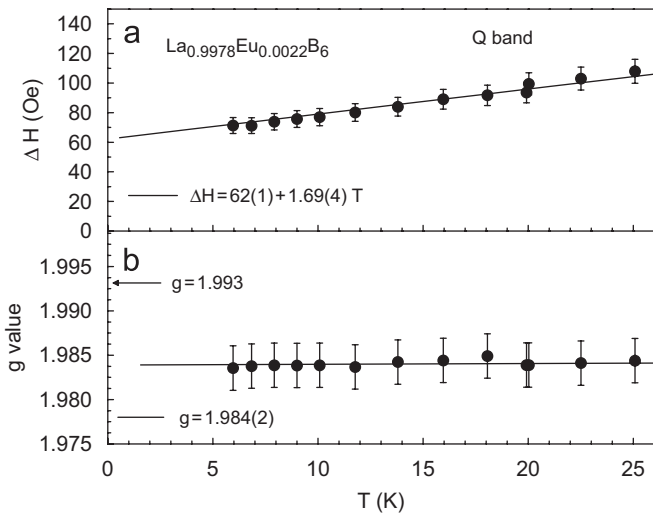


Fig. 2. T -dependence of the Q-band ESR: (a) linewidth, ΔH , and (b) g -value of Eu^{2+} in $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ ($x = 0.0022$) single crystal.

the magnetic field $H \parallel 30^\circ$ from the $[001]$ direction when H is rotated in the (110) plane. No resolved *fine* structure splitting, due to crystal field effects, is expected for this orientation [7]. In all our experiments the ESR spectra showed a single resonance of dysonian (*metallic*) shape [8]. Within the accuracy of the measurements for this orientation the linewidths ($\Delta H \simeq 72(5)$ Oe) are approximately the same at both frequencies, consistent with negligible residual inhomogeneous broadening of the resonance. The measured g -value indicates that there is a negative g -shift ($\Delta g = -0.009(2)$) relative to the g -value found in insulators ($g = 1.993$) [7], in contrast to the positive g -shift found for Gd^{3+} in LaB_6 [9].

Figs. 2(a) and 2(b) display, respectively, the T -dependence of the resonance linewidth, ΔH , and g -value for the

resonance of Fig. 1b. The thermal broadening of the linewidth was fitted to a linear behavior, $\Delta H = a + bT$, with $a = 62(5)$ Oe and $b = 1.70(5)$ Oe/K. For lower concentrations (~ 1000 ppm) the signal to noise/ratio was lower, but the parameters, a and b were found to be independent of concentration, within the accuracy of our measurements. This allows us to assume that the system is in the unbottleneck regime [10]. Similar results were obtained at X-band. Within the studied T -interval and accuracy of the experiments the g -value was found to be T -independent, indicating the absence of dynamic and/or interaction effects between the localized Eu^{2+} magnetic moments [10].

4. Analysis and Discussion

Our results show that the Eu^{2+} resonance in LaB_6 presented a negative g -shift ($\Delta g = -0.009(2)$) in contrast to the positive g -shift ($\Delta g = 0.018(3)$) found for the Gd^{3+} ions in the same host [9]. This change in sign may be understood in terms of a two band model [11] involving the exchange interaction between the Eu^{2+} and Gd^{3+} 4f⁷-localized electrons with: (i) the conduction (R) 5d-like *electrons* and; (ii) the (B) 2p-like *electrons*. The exchange interaction with the (R) 5d-like *electrons* is assumed to be of atomic-type, $J_{\text{at}}^e > 0$, and that with the (B) 2p-like *electrons* of covalent origin, $J_{\text{cv}}^h < 0$. Thus, the g -shift can be written as

$$\Delta g = \Delta g_d + \Delta g_p = J_{\text{at}}^d(0)\eta_F^d + J_{\text{cv}}^p(0)\eta_F^p, \quad (1)$$

where $J_{\text{at}}^d(0)$ and $J_{\text{cv}}^p(0)$ are the $q = 0$ component (zero-momentum transfer between electrons) [12] and, η_F^d and η_F^p the *local* density of d and p *electrons* at the Fermi level per spin direction, respectively. Although Eu^{2+} and Gd^{3+} ions are in a S-ground state with the same electronic configuration ($4f^7$; $S = \frac{7}{2}$), due to their different effective ionic charges the Coulomb interaction with the conduction electrons of LaB_6 will be larger for Eu^{2+} in LaB_6 . Therefore, we argue that in the total g -shift, $\Delta g = \Delta g_d + \Delta g_p$, the $J_{\text{at}}^d(0)\eta_F^d$ term becomes dominant in the case of Gd^{3+} and negligible in the case of Eu^{2+} , leading to $\Delta g \approx \Delta g_d = J_{\text{at}}^d(0)\eta_F^d$ and $\Delta g \approx \Delta g_p = J_{\text{cv}}^p(0)\eta_F^p$ for Gd^{3+} and Eu^{2+} in LaB_6 , respectively.

The linear thermal broadening of the homogeneous part of ΔH shown in Fig. 2a indicates that the spin-lattice relaxation of the Eu^{2+} ions occurs via the exchange coupling between the 4f and the conduction electrons (Korringa mechanism). Therefore, the so-called Korringa rate in the unbottleneck limit, $\Delta H/\Delta T$, [10] should be given by [12]

$$b = (\pi k_B / g \mu_B) [\langle J_{\text{cv}}^p(q) \rangle_F \eta_F^p]^2. \quad (2)$$

In the case that there is a contribution from only one type of conduction electron band and no q -dependence of the exchange interaction, i.e., $J_{\text{cv}}^p(0) = \langle J_{\text{cv}}^p(q) \rangle_F = J_{\text{cv}}^p$, the Korringa rate becomes: $b = (\pi k_B / g \mu_B) [\Delta g_p]^2$. Using the measured g -shift for Eu^{2+} , $\Delta g_p = -0.009(2)$, (see Fig. 2b) we obtain $b \approx 1.9(4)$ Oe/K in excellent agreement with the

value measured experimentally. Hence, we conclude that the Eu^{2+} ions relax to the lattice basically via an exchange interaction with the (B) 2p-like *electrons*. Similar analysis of the data for the case of Gd^{3+} in LaB_6 [9] lead us to conclude that the Gd^{3+} ions relax to the lattice via an exchange interaction with the (R) 5d-like *electrons*. In this case Luft et al. [9], assuming that η_F^d may be approximated by the total density of state obtained from the electronic specific heat corrected by the electron–phonon mass enhancement of LaB_6 , $\eta_F^d \approx 0.50$ states/eV mol spin, have estimated the exchange parameter, $J_{\text{at}}^d \approx 40(1)$ meV. However, band structure calculations suggest that the total density of states at the Fermi level is approximately equally distributed between the (La) 5d and (B) 2p-like *electrons* [13]. Then, assuming that $\eta_F^d = \eta_F^p \approx 0.25$ states/eV mol spin we estimate, from the experimental *g*-shifts and Korringa rates, $J_{\text{at}}^d \approx 80(2)$ meV and $J_{\text{cv}}^p \approx -34(3)$ meV for Gd^{3+} and Eu^{2+} in LaB_6 , respectively. Although we are confident in the analysis our data, in view of the assumptions made, the values for the exchange parameters have to be taken with care.

5. Conclusions

In this work we have shown for the first time, using our data and those from others, [9] that in the same metallic host (LaB_6) two different magnetic ion impurities with the same electronic S-ground state configuration ($4f^7$; $S = \frac{7}{2}$) but with different effective ionic charges (Eu^{2+} and Gd^{3+}), are selectively probing, via an exchange interaction, the presence of different type of conduction electrons at the host Fermi level. We have argued that this unique behavior is a consequence of the Coulomb repulsion potential between the ion effective charges and the host conduction electrons. We observed the simultaneous presence of (R) d and (B) p-like conduction electrons at the Fermi level of LaB_6 by ESR, a result, to the best of our knowledge, not simple to obtain via other experimental techniques. The

angular dependence of the spectra is currently being analyzed at the moment, and will be the subject of a forthcoming publication.

Acknowledgments

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References

- [1] E.L. Muetterties (Ed.), *The Chemistry of Boron and its Compounds*, Wiley, New York, 1967.
- [2] J.M. Lafferty, *J. Appl. Phys.* 22 (1951) 299.
- [3] H. Ahmed, A.N. Broers, *J. Appl. Phys.* 43 (1972) 2185.
- [4] J.M. Vanderberg, B.T. Matthias, E. Corenzwit, H. Borz, *Mater. Res. Bull.* 10 (1975) 889.
- [5] R.R. Urbano, P.G. Pagliuso, C. Rettori, S.B. Oseroff, J.L. Sarrao, P. Schlottmann, Z. Fisk, *Phys. Rev. B* 70 (2004) 140401 (Rapid Communication).
- [6] D.P. Young, D. Hall, M.E. Torelli, Z. Fisk, J.L. Sarrao, J.D. Thompson, H.R. Ott, S.B. Oseroff, R.G. Goodrich, R. Zysler, *Nature* 397 (1999) 412.
- [7] A. Abragam, B. Bleaney, *EPR of Transition Ions*, Clarendon Press, Oxford, 1970.
- [8] G. Feher, A.F. Kip, *Phys. Rev.* 98 (1955) 337; F.J. Dyson, *Phys. Rev.* 98 (1955) 349; G.E. Pake, E.M. Purcell, *Phys. Rev.* 74 (1948) 1184.
- [9] H. Luft, K. Baberschke, K. Winzer, *Z. Phys. B—Condens. Matter* 47 (1982) 195.
- [10] C. Rettori, H.M. Kim, E.P. Chock, D. Davidov, *Phys. Rev.* 10 (1974) 1826.
- [11] P.M. Bisch, A. Troper, A.A. Gomes, *Phys. Rev. B* 13 (1976) 3902; A. Troper, O.L.T. de Menezes, P. Lederer, A.A. Gomes, *Phys. Rev. B* 18 (1978) 3709; G.E. Barberis, D. Davidov, J.P. Donoso, C. Rettori, J.F. Suassuna, H.D. Dokter, *Phys. Rev. B* 19 (1979) 5495; P.G. Pagliuso, C. Rettori, J.L. Sarrao, A. Cornelius, M.F. Hundley, Z. Fisk, S.B. Oseroff, *Phys. Rev. B* 60 (1999) 13515.
- [12] D. Davidov, K. Maki, R. Orbach, C. Rettori, E.P. Chock, *Solid State Commun.* 12 (1973) 621.
- [13] F.M. Hossain, D.P. Riley, G.E. Murch, *Phys. Rev. B* 72 (2005) 235101.