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Unusual Hysteresis in the Magnetic Susceptibility of Cubic Hexaboride KB_6

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Electrical resistivity, magnetic susceptibility, and electron paramagnetic resonance measurements were carried out for cubic hexaboride KB_6, which is one electron short of completely filling its conduction band. It is found that KB_6 is not metallic and has localized spins. KB_6 exhibits a highly unusual hysteresis in the magnetic susceptibility below 100 K, which suggests that it undergoes a slow relaxation process.

The cubic hexaboride KB_6[1] is isostructural with the cubic hexaborides of alkaline-earth and rare-earth elements. These borides have a three-dimensional boron network in which each B_6 octahedron is linked to the surrounding six B_6 octahedra by its vertices to form six B−B bonds. Despite the simplicity of their crystal structures, rare-earth hexaborides show a variety of interesting physical properties.[2−6] Lanthanum doped calcium hexaboride $Ca_{1-x}La_xB_6$ has attracted a lot of attention recently due to the report of its high-temperature weak ferromagnetism.[7] However, this phenomenon is due probably to iron impurities.[8] With 20 valence electrons per formula unit (FU), alkaline-earth hexaborides are predicted to be either semiconductors[9] or semimetals.[10] With 19 valence electrons per FU, the valence bands of the alkali hexaboride KB_6 become partially empty, so one might expect either a metallic or a magnetic insulating character for KB_6.[11,12] We carried out electrical resistivity, magnetic susceptibility, electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR) measurements using powder samples of KB_6 that are free of transition metal elements. Our work shows that KB_6 has localized spins and exhibits a striking hysteresis in magnetic susceptibility.

Powder samples of KB_6 were prepared by direct synthesis of the element with potassium excess[1] in a sealed molybdenum crucible at 800−1100 °C for 2 days. We determined by inductive coupled plasma spectroscopy that these KB_6 samples show a slight potassium deficiency and are free of transition metal elements. In this work, we present experimental results for almost stoichiometric samples $K_{0.97}B_6$. The electrical resistivity is temperature independent below 170 K, with no evidence for variable range hopping, and shows a slight decrease with raising temperature above 170 K. Thus, our resistance measurements suggest that KB_6 is not a metal. Figure 1 shows the magnetic susceptibility of $K_{0.97}B_6$ measured while field-cooling the sample from room temperature down to 4.2 K (the first cooling) and subsequently field-heating from 4.2 K to room temperature (the first heating) under $\mu_0 H = 1$ T with cooling/heating rate $v = 10$ K/min. $K_{0.97}B_6$ appears practically diamagnetic above 100 K. The first field-heating curve shows a susceptibility peak around 57 K, which is absent in the first field-cooling curve. A small kink at 53−58 K in the first field-cooling curve is highly reproducible. To examine the nature of this unusual hysteresis, the susceptibility was further investigated. At the

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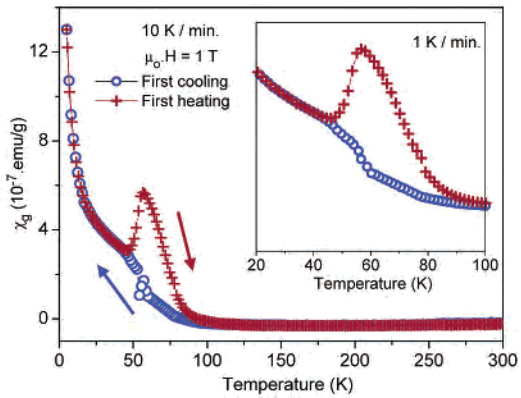

Figure 1. Thermal variation of the magnetic susceptibility of $K_{0.97}B_6$ under $\mu_0H = 1$ T for the first field-cooling and the first field-heating cycle with cooling/heating rate of 10 K/min for the 4.2−300 K region. The inset shows the corresponding result determined with a slow cooling/heating rate for the 4.2−100 K region (i.e., 1 K/min for the 4.2−100 K region and 10 K/min for the 100−300 K region).

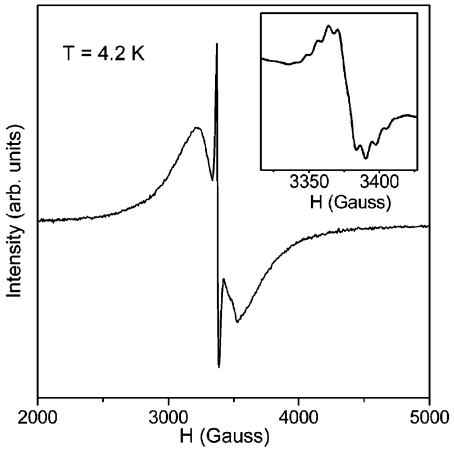

Figure 2. EPR spectrum of $K_{0.97}B_6$ recorded at 4.2 K. The hyperfine structure of the narrow EPR signal observed at 4.2 K after 40 scans is shown in the inset.

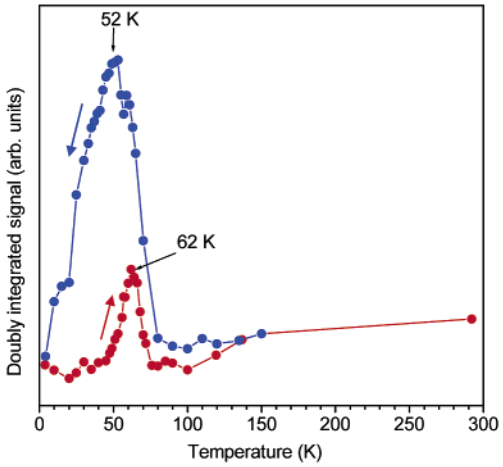

Figure 3. Thermal variation of the intensity of the broad EPR signal of $K_{0.97}B_6$ derived from the first heating/cooling cycle (see text).

end of the first field-heating at room temperature, we quickly field-cooled the sample down to 57 K under $\mu_0H = 1$ T. While staying at 57 K under μ_0H = 1 T, the susceptibility was measured as a function of time. The susceptibility increases gradually with time nearly reaching the value of the susceptibility peak in 50 min. The dependence of the susceptibility on cooling/heating cycles was examined further between 40 and 100 K. The second field-cooling and the second field-heating cycles reproduce the susceptibility hysteresis found in the first field-cooling and the first field-heating cycles ($\mu_0H = 1$ T and $v = 10$ K/min). These observations show that $K_{0.97}B_6$ undergoes some kind of slow relaxation process below 100 K.

To see if KB_6 has unpaired spins and to further characterize a slow relaxation process in KB_6, we carried out EPR measurements for $K_{0.97}B_6$. The sample was first zero-field-cooled to 4.2 K. Subsequently, EPR measurements were performed while heating the sample (frequency = 9.465 GHz, power = 0.2 mW, center field = 3500 G, sweep field = 0−7000 G for each point, sweep time = 167 s, resolution = 1024 points) to room temperature and then cooling the sample back to 4.2 K. The effective heating/cooling rate for the EPR measurements was slower than the corresponding rate for the magnetic susceptibility measurements by a factor slightly greater than 10. At 4.2 K, a narrow signal ($\Delta H \approx$ 26.4 G) is superimposed on a broad signal ($\Delta H \approx$ 315 G) (Figure 2). The narrow signal is hidden under the broad signal at 300 K and becomes clearly visible below 100 K. The peak-to-peak width ΔH of the broad signal is practically temperature independent. The intensity of the broad signal, obtained by double integration of the EPR signal, is proportional to the magnetic susceptibility. The EPR susceptibility curves for the heating and cooling cycles show a strong hysteresis below 100 K. The EPR susceptibility for the heating cycle exhibits a sharp peak at around 62 K and is nearly independent of temperature above 100 K (Figure 3), in agreement with the corresponding features of the magnetic susceptibility curve for the first field-heating cycle (Figure 1). However, the EPR susceptibility for the cooling cycle differs from the magnetic susceptibility of the first field-cooling cycle (Figure 1) in that the former exhibits a prominent susceptibility peak around 52 K whereas the latter shows a small kink at 53−58 K. Thus, the magnetic properties of $K_{0.97}B_6$ samples depend on their thermal history as well as on their magnetic history. Our EPR study shows that $K_{0.97}B_6$ has unpaired spins above and below 100 K, and that there exist two kinds of environments for unpaired spins (one for the broad EPR signal and the other for the narrow one).

To understand the probable origin for the narrow and broad EPR peaks, it is crucial to estimate how many spins per FU are responsible for the narrow and broad EPR peaks (f_N and f_B, respectively). The comparison of the areas of the narrow and broad EPR peaks shows that f_N is a very small fraction of f_B (i.e., $f_N/f_B = 10^{-3}-10^{-4}$). A careful examination of the narrow EPR signal (sweep field = 130 G) clearly shows evidence of a hyperfine structure (of at least 10 lines) centered at $g = 2.0025$ (inset of Figure 2). Our NMR experiment rules out any spin density on the potassium nucleus, so this structure can only be explained by a hyperfine coupling between an electron spin and one or more boron nuclei. Boron has two natural isotopes: ^{11}B ($I = {}^3/_2$, abundance 80%) and ^{10}B ($I = 3$, abundance 20%) leading

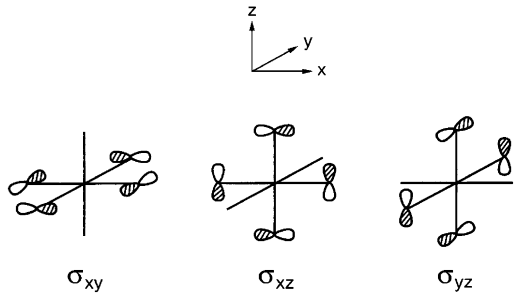

Figure 4. Three degenerate tangential σ-bonding orbitals (i.e., σ_{xy}, σ_{xz}, and σ_{yz}) of a B_6 octahedron leading to the valence bands of KB_6.

to 11 lines when the electron is coupled to one boron nucleus. A good fit is obtained assuming one electron spin coupled with two boron nuclei (coupling constant $a = 9.4$ G, line width $\Delta B = 5$ G). However, the observed number of hyperfine lines should be considered as the lower limit because the intensities of the hyperfine lines decrease rapidly as the distance from the center of the spectrum increases so that some low intensity lines can be masked into the broad EPR signal. We estimate the f_B value for the broad EPR peak by comparing the area of the broad peak of $K_{0.97}B_6$ with that of the EPR peak of $CuSO_4 \cdot 5H_2O$ that has one unpaired spin per FU. The EPR peak area, A, depends on the number of spins per FU, f, the relaxation rate, r, and the microwave power, P, as $A \propto fr\sqrt{P}$. To remove the effect of the relaxation rate on the peak area, we determined the relative relaxation rates of $K_{0.97}B_6$ and $CuSO_4 \cdot 5H_2O$ at a given temperature by measuring each EPR peak area at two different powers (i.e., $P = 0.200$ and 0.795 mW). Thus, by calibrating the peak area ratios with the relative relaxation rates, the f_B values are found to be in the range of $10^{-4}-10^{-2}$ spin/FU.

Analysis of the electronic band structures of KB_6 calculated by both first-principles and tight-binding methods shows that the primary orbital components of the valence bands are the triply degenerate group orbitals of each B_6 octahedron shown in Figure 4 (i.e., σ_{xy}, σ_{xz}, and σ_{yz}), and there are five electrons to fill these group orbitals.[13] Thus, each B_6 octahedron of KB_6 can assume the electron configuration $(\sigma_{xy})^1(\sigma_{xz})^2(\sigma_{yz})^2$, $(\sigma_{xy})^2(\sigma_{xz})^1(\sigma_{yz})^2$, or $(\sigma_{xy})^2(\sigma_{xz})^2(\sigma_{yz})^1$, so that each B_6 octahedron can have one unpaired spin and is subject to Jahn−Teller (JT) instability. If a spin resides in one of the σ_{xy}, σ_{xz}, and σ_{yz} orbitals, the spin density is equally shared among four boron atoms in each B_6 octahedron (Figure 4). This reasoning is consistent with the hyperfine structure of the narrow EPR signal at 4.2 K ($g \approx 2.0025$) (inset of Figure 3). In addition, our analysis shows that, as a function of temperature, the area of the narrow EPR peak below 60 K follows the Curie law. Thus, the narrow EPR signal can be assigned to a spin localized in one B_6 octahedron. Then, the broad EPR signal could be associated with spins delocalized in several B_6 octahedra, which in turn implies that the spins of most B_6 octahedra are paired up to result in the small f_B values observed (i.e., $10^{-4}-10^{-2}$ spin/FU). The average size of a "domain" giving rise to the broad EPR signal (hereafter referred to as a spin bag) would be of the order of 10^4-10^2 B_6 octahedra. If we approximate such a spin bag by a cubic particle of KB_6 with side length $L = Na$, where a is the unit cell parameter (i.e., 0.42 nm) and N is the number of B_6 octahedra forming the side of the cube, then $N \approx 5-22$ so that $L = 2.1-9.2$ nm. Our scanning electron microscopy measurements of powder $K_{0.97}B_6$ samples show cubic single crystals with side length smaller than 700 nm. The average side length is around 400 nm, and such a particle would consist of a very large number of spin bags (i.e., 8×10^4 to 7×10^6). Therefore, a bulk phenomenon is responsible for the broad EPR signal and hence for the unusual hysteresis of KB_6.

In principle, each B_6 octahedron of KB_6 can have one unpaired spin, but f_B is much smaller than 1. Thus, it is important to discuss a probable mechanism for spin pairing and its implications. The spins of two adjacent B_6 octahedra can be antiferromagnetically coupled to form a singlet spin pair if their magnetic orbitals are identical in symmetry and hence overlap substantially. Such singlet spin pairs may be represented by $(\sigma_{xy}-\sigma_{xy})$, $(\sigma_{xz}-\sigma_{xz})$, and $(\sigma_{yz}-\sigma_{yz})$. Larger spin singlet units involving even numbers of B_6 octahedra would be possible. This kind of spin pairing mechanism must cooperate with JT distortion, which introduces strain to the lattice, and should occur in all three directions of a crystal particle without any long range order favorable to distribute the strain evenly in three directions hence limiting the size of a spin-paired structure. This kind of spin pairing will eventually lead not only to a structural unit made up of odd numbers of B_6 octahedra, e.g., $(\sigma_{xy}-\sigma_{xy}-\sigma_{xy})$, $(\sigma_{xz}-\sigma_{xz}-\sigma_{xz})$, and $(\sigma_{yz}-\sigma_{yz}-\sigma_{yz})$, which might be responsible for the broad EPR peak, but also to an "isolated" B_6 octahedron whose magnetic orbital does not match in symmetry with those of the surrounding B_6 octahedra. The slow relaxation process below 100 K might be related to the formation and destruction of spin paired units. The hysteresis in the magnetic susceptibility below 100 K might be associated with how the distributions of the spin paired units depend on the thermal and magnetic histories of the sample.

In summary, $K_{0.97}B_6$ samples have localized spins in two different environments and exhibit a highly unusual hysteresis in the magnetic susceptibility below 100 K suggestive of a slow relaxation process. Though not shown, more nonstoichiometric samples (e.g., $K_{0.84}B_6$) exhibit the same features. Thus, a bulk phenomenon is responsible for these observations.

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