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Eu₂CuO₄: An anisotropic Van Vleck paramagnet

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Magnetic susceptibility measurements have shown anisotropic Van Vleck paramagnetism in Eu₂CuO₄ single crystals. This behavior is associated with the singlet ground state ($^7F_0$) of Eu^{3+} ions, and the measured anisotropy is related to a crystal-field splitting of the excited multiplets (^7F_J). From the experimental data at low temperatures ($T \lesssim 50$ K) a crystal-field parameter $A_2^0 \langle r^2 \rangle = -93(5)$ cm^{-1} and a spin-orbit coupling constant $\zeta = 303(15)$ cm^{-1} have been estimated. The temperature dependence of the magnetic susceptibility is predicted in terms of the Boltzmann population of the excited multiplets, and a comparison with experimental data up to 350 K is made. The possibility of a magnetic contribution arising from the Cu ions is discussed in connection with some discrepancies observed between the experimental and calculated magnetic susceptibilities.

The discovery of high-T_c superconductivity in a series of copper oxides, e.g., (LaSr)₂CuO₄, YBa₂Cu₃O₇, Bi₂(Ca,Sr)₃Cu₂O₉,Tl₂Ca₂Cu₃O₁₀, etc.,[1-4] has led to a large amount of experimental and theoretical work in these and other related compounds. All these materials commonly share layered structures with almost square planar Cu-O arrangement. Some of them are, as mentioned, high-T_c superconductors, while other related compounds have been found to order antiferromagnetically,[5,6] such as La₂CuO₄ and YBa₂Cu₃O₆. Another series of compounds, the (R)₂CuO₄ family with R=Pr, Nd, Sm, Eu, Gd, form also in a layered tetragonal structure[7] related to the orthorhombic structure of La₂CuO₄ but with a somewhat larger lattice spacing in the planes. These materials are not superconducting or even metallic, and for this reason it is important to study in detail their magnetic properties in order to obtain more experimental evidence on the interplay of magnetic ordering and superconductivity in these layered copper oxides.

Single crystals of Eu₂CuO₄ were grown from a PbO-based flux. The crystal structure is tetragonal[8] with lattice constants $a = 3.910(1)$ Å and $c = 11.925(3)$ Å.

The magnetic susceptibility was determined from the magnetization measured in fields up to 5 T, and the results are shown in Fig. 1. The temperature dependence of the magnetic susceptibility corresponds to a Van Vleck paramagnet,[9] as expected for Eu^{3+} ions having a singlet ground state ($4f^6$, $^7F_0$). Our results show a dependence similar to that previously found in polycrystalline material.[7] At the lowest temperatures only the ground state is thermally populated and the susceptibility becomes temperature independent. The magnetic moment observed is induced by the external magnetic field through the admixture of the excited levels into the ground state. The

magnetic susceptibility for such a case is given by

$$X_{vv} = N_A \sum_k \frac{|\langle \Psi_0 | H_Z | \Psi_{1,k} \rangle|^2}{\Delta_{1,k}}, \tag{1}$$

where N_A is Avogadro's number, H_z is the Zeeman Hamiltonian, Ψ_0 and $\Psi_{1,k}$ are the eigenfunctions of the ground state $^7F_0$ and the first excited multiplet $^7F_1$, respectively; and $\Delta_{1,k}$ are the corresponding energies measured from the ground state. A scheme of the energy levels is given in Fig. 2.

In the presence of crystal-field interactions the eigenfunctions are not pure $^7F_0$ states but contain components from other multiplets, thus affecting the matrix elements in Eq. (1). Besides, as a result of crystal-field effects, the
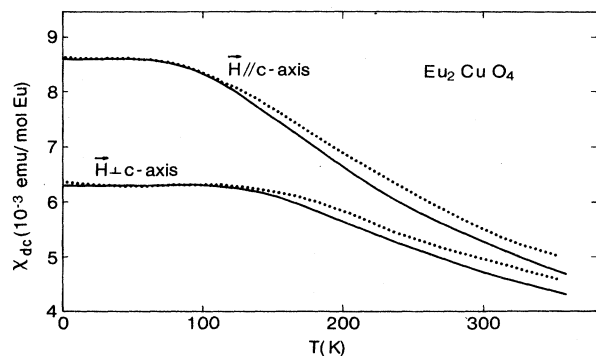

FIG. 1. Magnetic susceptibility vs temperature of Eu₂CuO₄, measured with external magnetic field (0.4 T) parallel and perpendicular to the c-axis. Continuous lines correspond to the calculated Van Vleck susceptibility.
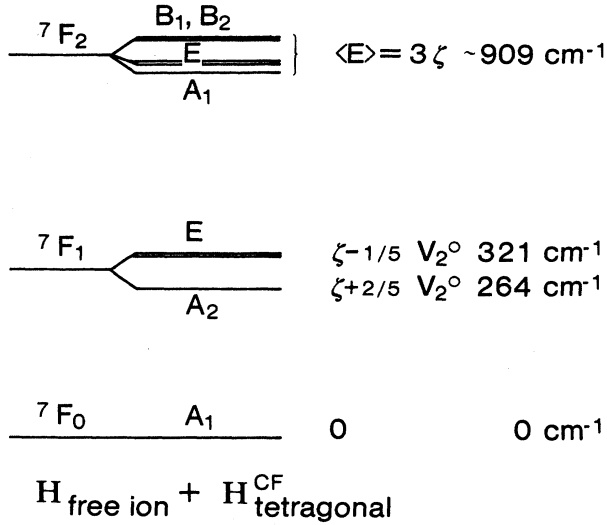
FIG. 2. Energy level scheme for Eu^{3+} ions in tetragonal symmetry. The energy values indicated have been estimated from the measured Van Vleck magnetic susceptibility of $EuCuO_4$.

energy splitting of the $^7F_1$ multiplet changes the relative weight of the terms in Eq. (1), giving rise to an anisotropic Van Vleck susceptibility.

Eu ions occupy sites of tetragonal symmetry (C_{4v}) in the Eu_2CuO_4 lattice,[7] and we have thus considered a crystal-field Hamiltonian with the appropriate symmetry:

$$\mathcal{H} = \mu_B(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{H} + \alpha V_2^0 O_2^0(\mathbf{L}) + \cdots , \quad (2)$$

where the ellipsis represents fourth- and sixth-order terms, $O_2^0(\mathbf{L})$ is a Stevens operator, $V_2^0 \equiv A_2^0 \langle r^2 \rangle$, and $\alpha = 2/45$ is the Stevens multiplicative factor for the ^7F term. This Hamiltonian splits the $^7F_1$ triplet into a singlet (A_1) and a doublet (E). The $^7F_2$ multiplet is split into three singlets $(A_1, B_1, \text{and } B_2)$ and one doublet (E), although two of the singlets $(B_1 \text{ and } B_2)$ are accidentally degenerate when we limit Eq. (2) to second-order operators. The different levels are shown in Fig. 2. Although fourth- and sixth-order operators are symmetry allowed, we have not included them into our calculation because (i) the crystal-field splitting of the $^7F_1$ multiplet is determined in first-order perturbation theory only by the second-order term of Eq (2); and (ii) even though the neglected higher order terms contribute to the splitting of the $^7F_2$ levels, we are only interested in their admixture into the ground state and this can be well approximated by using the average energy separation that results from the spin-orbit interaction. In such a case the expressions for the low-temperature limit of the susceptibility reduce to

$$\chi_\| = 2(2 - \sqrt{3}\gamma)^2\mu_B^2/\Delta_\| , \quad (3)$$

$$\chi_\perp = 2(2 + \sqrt{3}\gamma/2)^2\mu_B^2/\Delta_\perp ,$$

where $\chi_\|$ and $\chi_\perp$ correspond to the magnetic susceptibility measured with the applied field parallel and perpendicular to the c axis, respectively. The parameter $\gamma = (4\sqrt{3}/15)V_2^0/\Delta_2$ takes into account the crystal-field admixture of the $^7F_2$ multiplet into the ground state. $\Delta_\|$, $\Delta_\perp$, and Δ_2 are the appropriate energy differences given by

$$\Delta_\| = \varepsilon(J=1, A_2) - \varepsilon(J=0) ,$$

$$\Delta_\perp = E(J=1, E) - \varepsilon(J=0) ,$$

and

$$\Delta_2 = \langle \varepsilon(J=2) \rangle - \varepsilon(J=0) ,$$

where $\langle \varepsilon(J=2) \rangle$ is the average energy of the $^7F_2$ level.

In order to separate the contribution of Eu ions to the magnetic susceptibility, it is necessary to introduce corrections for core diamagnetism and for the contribution arising from the Cu-O planes. Since we do not know what the magnetic behavior of the Cu planes is in this material, we have used as total a correction, $\chi_0 = 0.06 \times 10^{-3}$ emu/mol Eu, equal to the measured susceptibility[10] for La_2CuO_4, averaged over the temperature range of our measurements. From the measured values at low temperatures, $\chi_\| = 8.6(4) \times 10^{-3}$ emu/mol Eu and $\chi_\perp = 6.3(3) \times 10^{-3}$ emu/mol Eu, we have determined $V_2^0 = -93(5)$ cm^{-1} and $\zeta = 303(15)$ cm^{-1}.

The value obtained for the crystal-field parameter can be compared with the predictions of a simple point charge model. Gd^{3+} ions are surrounded[7] by a distorted cube of oxygen ions whose contribution to the crystal field is estimated to be $A_2^0 \langle r^2 \rangle = +43$ cm^{-1}, assuming a shielding factor[11] $(1 - \sigma_2) = 0.20$. The order of magnitude is correct, but the opposite sign is obtained. Only minor changes are observed if semiempirical parameters[11] are considered for the Eu^{3+}-O^2 interaction. This result is not unexpected, since second-order crystal-field parameters usually have significant contributions from distant ions and also from dipolar or quadrupolar polarization of the ions of the lattice. In fact, we have observed that including neighbors up to a distance of 5 Å reverses the sign of the calculated parameter.

At higher temperatures the excited levels become thermally populated and, in the absence of a crystal field, the susceptibility is given by Van Vleck's formula[8]

$$\chi_{vv} = \frac{\sum_J (2J+1)(\alpha_J + C_J/k_B T)\exp[-\varepsilon(J)/k_B T]}{\sum_J (2J+1)\exp[-\varepsilon(J)/k_B T]} , \quad (4)$$

where α_J and C_J are the Van Vleck and Curie constants for each multiplet ^7F_J. For the free ions $\alpha_0 = 8N_A\mu_B^2/\zeta$ and $\alpha_1 = -\alpha_0/48$. The Curie constants are given by

$$C_J = g_J^2\mu_B^2 J(J+1)/3k_B ,$$

where $g_J = 3/2$ for all the excited multiplets. When there is a crystal-field interaction present, proper eigenvalues and eigenfunctions should be used to evaluate α_J and C_J. Crystal-field effects for α_0 have already been considered in Eq. (3). The values of C_J, when corrected for the pres-

ence of crystal-field effects, result in the following expressions:

$$C_1^{\parallel} = C_1(1 + \tfrac{2}{5}V_2^0/k_B T)$$

and

$$C_1^{\perp} = C_1(1 - \tfrac{1}{5}V_2^0/k_B T)$$

for the first excited multiplet, and similar expressions can be derived for the other excited levels. The Boltzmann factors should also be modified to include the splitting of the multiplets.

The results of this calculation are shown in Fig. 2 as a continuous line. It should be mentioned that this estimate does not significantly depend on the neglected fourth- and sixth-order terms in Eq. (2).

The differences between the experimental and calculated values are of the order of 2×10^{-4} emu/mol Eu at room temperature, and are beyond both the experimental resolution and the estimated uncertainties of the calculated curves. The temperature dependence of the magnetic susceptibility is dominated by the energy differences between the ground state and the excited states of the Eu ions. Unfortunately, there are no optical data available to check our estimates for these energies, derived under the assumption that the contribution from Cu planes are as small as in the metallic compound La₂CuO₄. However, it is interesting to notice that the value estimated for the spin-orbit parameter $\zeta = 303$ cm^{-1} is smaller than the values observed in other compounds,[12] i.e., the measured average low-temperature susceptibility is larger in this material. This fact makes likely the existence of larger magnetic contributions from Cu planes for Eu₂CuO₄. For example, if we arbitrarily assume that their contribution is temperature independent, isotropic, and equivalent

to 3×10^{-4} emu/mol Eu, and subtract it from the measured susceptibilities, then the estimated spin-orbit value would be $\zeta = 315$ cm^{-1} and the crystal-field parameter $V_2^0 \cong -100$ cm^{-1}. These values imply energies for the first excited levels of 275 cm^{-1} and 335 cm^{-1}, respectively. These values are larger than those previously derived and could result in a smaller decrease of the susceptibilities with temperature. In particular these values would make a better fit of the data.

In conclusion, we have found that Eu₂CuO₄ is a Van Vleck paramagnet whose magnetic anisotropy can be related to the crystal-field splitting of the excited multiplets. We have also found indications that the Cu-O planes have a non-negligible contribution to the measured magnetic susceptibility. If that is indeed the case, some kind of magnetic order must be present because no significant paramagnetic Curie-like behavior is observed at low temperatures. This observation is consistent with the Mössbauer results[13] which indicate correlated spin behavior up to temperatures above 400 K, and also with electron spin resonance experiments[14] that show an antiferromagnetic-like low field resonance line below ~ 200 K. The existence of magnetic ordering at these temperatures is not unexpected since the same order of magnitude coupling is seen here[15] between Cu spins as in La₂CuO₄ which orders antiferromagnetically[5] at 220 K.

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