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Intermultiplet transitions in optically opaque $EuBa_2Cu_3O_7$: An Inelastic Neutron Scattering Study.

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Abstract:

We report the results of inelastic neutron scattering (INS) studies of the J=0 to J=1 magnetic transitions in $EuBa_2Cu_3O_7$. The low J values of these multiplets restrict our crystal field analysis to the second order crystalline electric field (CEF) parameters B_0^2 and B_2^2 obtained by fitting the splitting of the J=1 multiplet, and the spin-orbit coupling parameter, which is used to fit the energy of the J=0 to J=1 multiplet splitting. We compare our results to those derived from other INS studies on different rare earths, as well as with B_0^2 and B_2^2 derived from Mössbauer studies. The J=0 to J=1 splitting observed here is smaller than previously seen by optical spectroscopic studies on a variety of transparent, ionic compounds, necessitating the inclusion of a free-ion parameter in the fitting procedure. This work represents the first time that a complete excited multiplet has been seen for R in $RBa_2Cu_3O_7$. These results are particularly germane to crystal field analyses of the light rare earth ions in optically opaque materials, where assumptions about free-ion parameters are essential for a meaningful analysis.

- inelastic neutron scattering, high-T_c superconductor, crystal-field, spin orbit coupling

Introduction

Until recently, systematic investigations of rare-earth (R) energy-level splittings have been largely restricted to optical studies on non metallic systems such as R:LaF_3 [1], RCl_3, RPO_4, and garnets [2]. Optical studies on metallic systems are not possible because they are opaque to electromagnetic radiation. Recently there has been considerable work done to determine systematically the crystal-field splittings of R^{3+} ions in $RBa_2Cu_3O_7$ [3], [4], [5] using inelastic neutron scattering (INS). The results have been used to develop models involving charge transfer [3], [4] percolative superconductivity [6] and coupling of the magnetic response to the CuO_2 states [7]. With two exception [8], [9], the studies published to date have been restricted to splittings within the ground multiplet because of technical restrictions imposed by neutron scattering. In interpreting some of the data, particularly for the lighter rare earths, it has been necessary to include information about the effect of the free-ion parameters, where the intermultiplet splittings are not large with respect to the overall crystal field splitting within a multiplet. The free-ion parameters are generally taken directly from those available for the complete series R:LaF_3 [1].

There is a general interest in expanding crystal field (CEF) studies of these superconducting systems into higher multiplets to obtain information about the free ion Hamiltonian. We report here for the first time the direct determination of a resolved intermultiplet splitting. The results of this study on $EuBa_2Cu_3O_7$ are compared directly with those observed for model systems. We chose $EuBa_2Cu_3O_7$ because the Eu^{3+} spectrum exhibits several low lying J-multiplets with a non magnetic (J=0; $^7F_0$) ground-state and a first excited state (J=1; $^7F_1$) at about 45 meV. The CEF gives rise to a complete decomposition of the $^7F_1$ multiplet into 3 singlets, Γ_1, Γ_2 and Γ_4. The energy expected for these states is within the conventional energy/angular range for inelastic neutron scattering experiments. The difficulty

with this experiment is the necessity of preparing an isotope-enriched ^{153}Eu sample, because natural Eu is a prohibitively strong neutron absorber.

Experiments

A 10 gram isotope enriched $^{153}EuBa_2Cu_3O_7$ sample was prepared by standard ceramic technology. Neutron diffraction confirmed the single-phase character of the sample. The structural results show no significant difference compared to the other rare earths in $RBa_2Cu_3O_7$ except for a small reduction in the expected orthorhombicity for the sample as measured. The rare earth site symmetry is mmm (D_{2h}). The inelastic neutron scattering (INS) experiments were performed using the Low Resolution Medium Energy Chopper Spectrometer (LRMECS) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The incident neutron energy was chosen to be either 80 or 50 meV giving rise to a energy resolution at 40 meV energy transfer of about 3.2 and 2 meV, respectively. The sample was enclosed in a flat aluminum container of 8 cm high and 6 cm wide and then attached to the cold finger of a closed cycle refrigerator to achieve a temperatures of 20 and 300K. The raw data have been corrected for detector efficiency and background by standard procedures. The energy dependent absorption has been measured and was found to be negligible, confirming the high enrichment of the ^{153}Eu isotope.

Results and Discussion

The energy spectra from the low angle detector banks are shown in Figures 1 and 2. Three well resolved peaks are observed at 35.7 ± 0.4 meV, 38.5 ± 0.5 meV, and 44.4 ± 0.4 meV. The magnetic origins of these transitions are established by their decreasing intensity with both increasing Q and temperature, as demonstrated in Figure 3. These peaks are assigned to

transitions from the $^7F_0$ ground state to the crystal-field split $^7F_1$ first excited state, as shown in Figure 4.

The splitting between the J=0 and the center of gravity of the J=1 state (FI in Figure 4) is 39.5 meV. This value is smaller than expected from a comparison with Eu in other oxides, sulfides and chalcogonides, where the splittings are generally in the range of about 44 to 48 meV [2]. Notably, this splitting is 46 meV for Eu:LaF_3, the compound from which the free ion parameters have been extracted for use in tensor operator calculations. This single result suggests that the use of Eu:LaF_3 free ion parameters may overestimate the magnitude of the free-ion splittings in these copper oxides. Nevertheless, it is believed that the inclusion of these free ion parameters in crystal-field calculations involving the lighter rare earths is still a better approximation than disregarding the higher multiplets altogether.

In principle, the experimentally observed energy spacings can be fitted with one spin-orbit parameter to describe the J=0 $\rightarrow$ J=1 intermultiplet splitting, and two crystal-field parameters, B_0^2 and B_2^2 to describe the J=1 intramultiplet splitting. (Whereas the site symmetry necessitates 9 parameters to describe fully the effect of the crystal field, the J=1 multiplet is only affected by the second order parameters to a first approximation.) Unfortunately, the real situation is more complex. We use a tensor-operator method in which all interactions of the free ion and the crystal field are diagonalized simultaneously, as required for an accurate description of the problem. The result is a mixing of states through intermediate coupling and J-mixing that makes the intermultiplet splitting also depend on the electrostatic, radial F_k free-ion parameters [10]. In addition, the values chosen for the fourth and sixth order crystal field parameters influence this splitting, because states with similar symmetry in the J>2 multiplets mix with those of the J=1 multiplet, reducing the center of gravity of the lower energy multiplet.

With the above caveats in mind, we chose to fit our data to a model in which the free ion parameters were fixed at the values found for Eu:LaF_3 [1]. The fourth and sixth order parameters were either extrapolated from other rare-earth ions in the orthorhombic $RBa_2Cu_3O_7$ structure [11], [12] or taken from superposition modeling [13]. Fitting both the energy and intensities of the observed INS transitions resulted in a poor fit because of the small intermultiplet splitting observed here. The B_0^2 determined from this fit overestimates the observed intramultiplet splitting, presumably to partially compensate for the incorrect intermultiplet splitting calculated from the free ion parameters. This result raises concern about the possibility of similar problems in previously published fits of R=Pr or Nd data. If an addition spin-orbit parameter ξ_{SO} is included in the fit, an excellent agreement is obtained when ξ_{SO}=161.5 ± 0.7 meV, B_0^2 = 49.3 ± 1.4 meV and B_2^2 = 4.9 ± 0.7 meV. The calculated spectra based on these results are compared with experiment in Figures 1 and 2.

The spin orbit parameter calculated here is only 3% smaller than that obtained for Eu:LaF_3 [1], whereas the observed multiplet is 13% lower in the oxide, indicating that the splitting between multiplets does not vary in a straightforward manner with ξ_{SO}, but is also influenced by the magnitude of the crystal field. The value of B_0^2 refined from the Eu INS data is within the range of this parameter determined from INS data refined from other rare earths whereas the B_2^2 value is smaller than previously found [3], [11], [12]. The low value for B_2^2 is explained by the smaller orthorhombic distortion seen for the sample under study here when compared with the other $RBa_2Cu_3O_7$. The result determined from this work on Eu is expected to give the most accurate determination of the 2nd order crystal-field parameters, because the J=1 splitting is uninfluenced by the fourth and sixth order parameters to first order, as discussed above. The B_0^2 determined here is smaller than those derived from ^{155}Gd Mossbauer spectroscopy experiments, which range from 32 meV [14] [15] to 43 meV [16]. We do not believe that the B_0^2 determined from INS is significantly overestimated, instead we note that the

derivation of crystal-field parameters from electric-field gradients involves the use of several parameters that are not exactly known [17]. As a result, the Mossbauer values have large errors associated with them.

A good test of our model is to calculate the magnetic susceptibility as a function of temperature . This calculation is done using the transition strengths and energy spacings [12] [18] determined from the fit described above, and plotted together with experiment in Figure 5 [19]. The agreement is found to be very good, even though the large contribution from the temperature independent, vanVleck term renders the curve non-linear.

Conclusions

The energy and splittings of the first excited, J=1 multiplet of Eu in $EuBa_2Cu_3O_7$ have been determined by inelastic neutron scattering. The J=0 to J=1 energy is unusually small, and not well represented by the free-ion parameters determined for Eu:LaF_3. This is an important result that may have implications for other studies involving light R-ions in superconductor-related hosts. The second-order crystal-field parameters are well determined from the J=1 splitting, and found to be similar to those found previously for other rare earths, but larger than those derived from ^{155}Gd Mossbauer. The magnetic susceptibility, calculated as a function of T, agrees very well with experiment.

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Fig. Captions

Fig. 1 Energy spectra of neutrons scattered from $EuBa_2Cu_3O_7$ at T=20K, E_i=80 meV and average angle φ=10°. The solid line corresponds to the fit as explained in the text, the dashed line represents the individual transition that contribute to the observed line and the broken line to the background. Magnetic excitations from the J=0 CEF state within the J=1 multiplet are labeled A-C. The energy splitting scheme corresponding to these labels is shown in Fig.4.

Fig. 2 Energy spectra of neutrons scattered from $EuBa_2Cu_3O_7$ at T=20K, E_i=50 meV and φ=12.5°. The labeling is as in Fig. 1.

Fig. 3 Temperature dependence of the energy spectra of $EuBa_2Cu_3O_7$ with E_i=50 meV and φ=10°.

Fig. 4 Energy level scheme of Eu^{+3} in $EuBa_2Cu_3O_7$ for the two lowest J-multiplets (solid lines). The transition labels refer to the transitions shown in Figs. 1 and 2. The symmetry labels corresponds to those expected for orthorhombic symmetry. H_{FI} represents the free ion Hamiltonian and the dashed lines corresponds to the free ion splitting of the multiplets.

Fig. 5 Paramagnetic susceptibility of $EuBa_2Cu_3O_7$ versus 1000/T [19]. The line corresponds to the calculation as explained in the text.

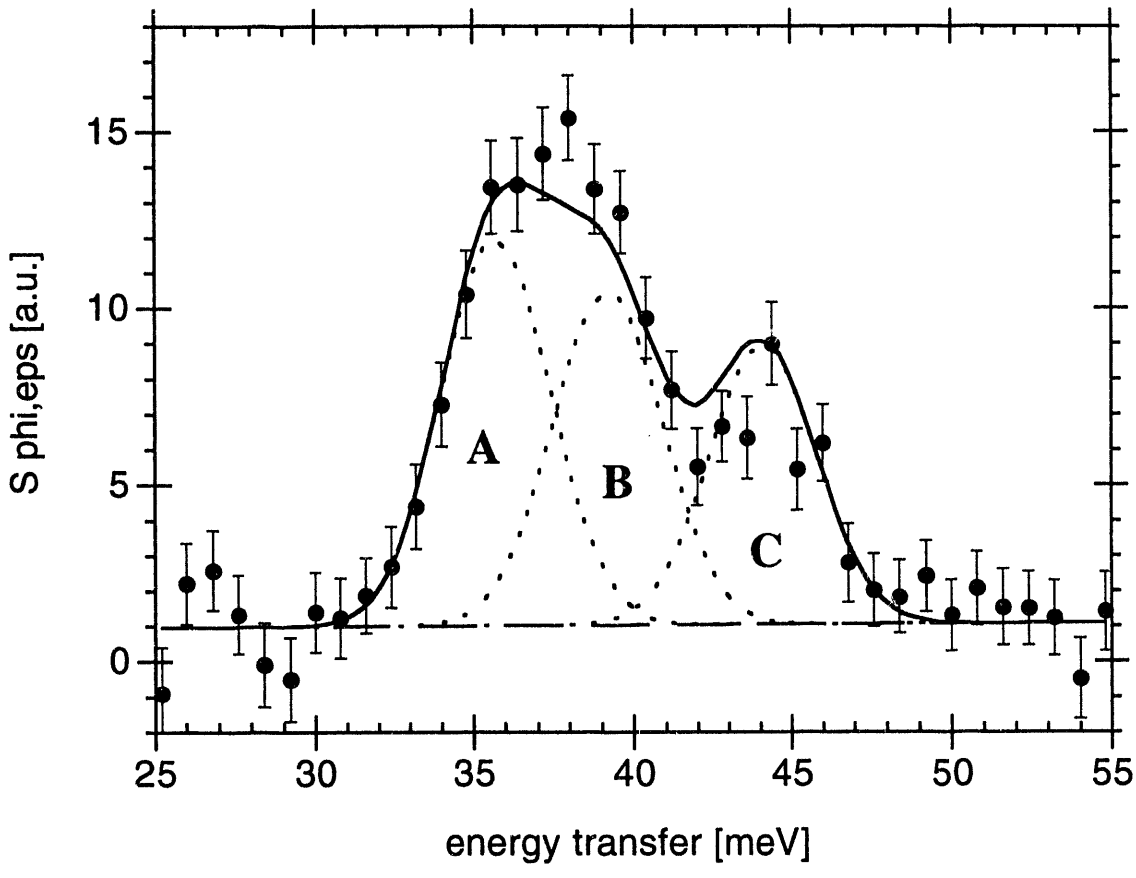

Fig. 1

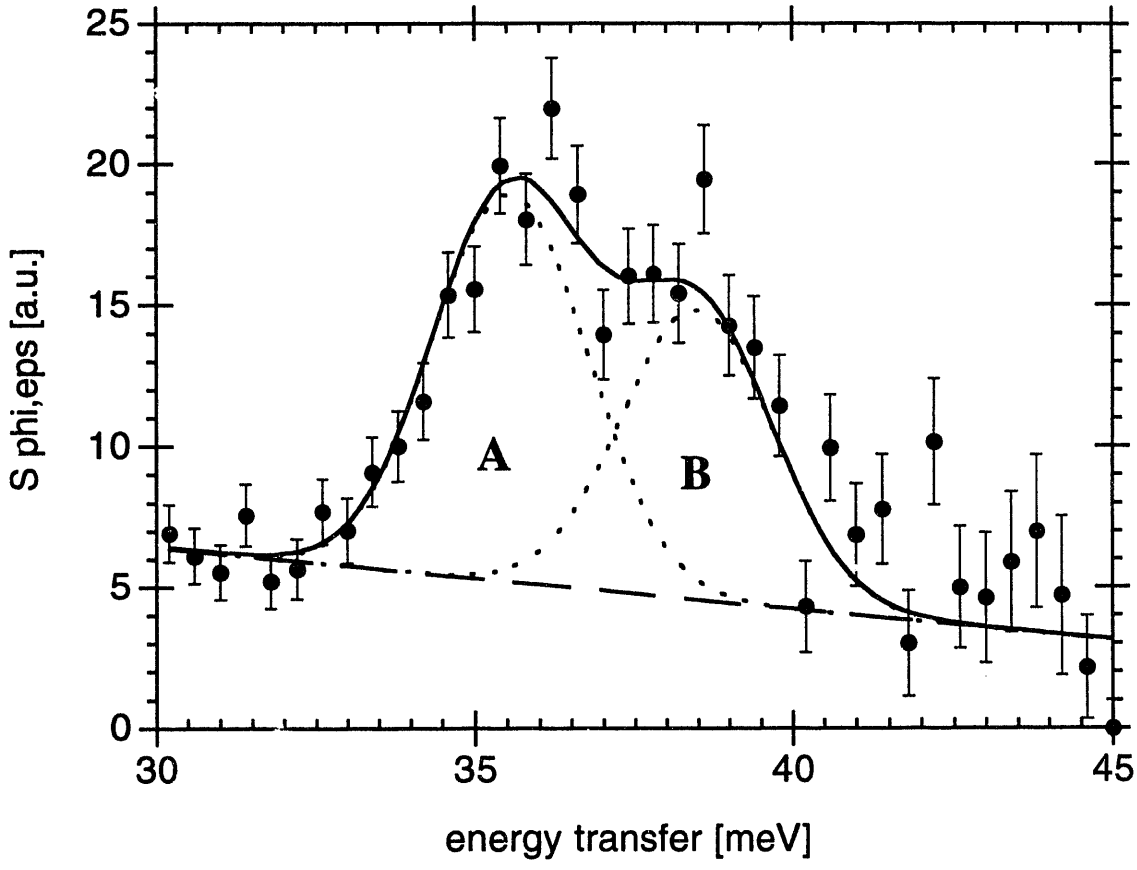

Fig. 2

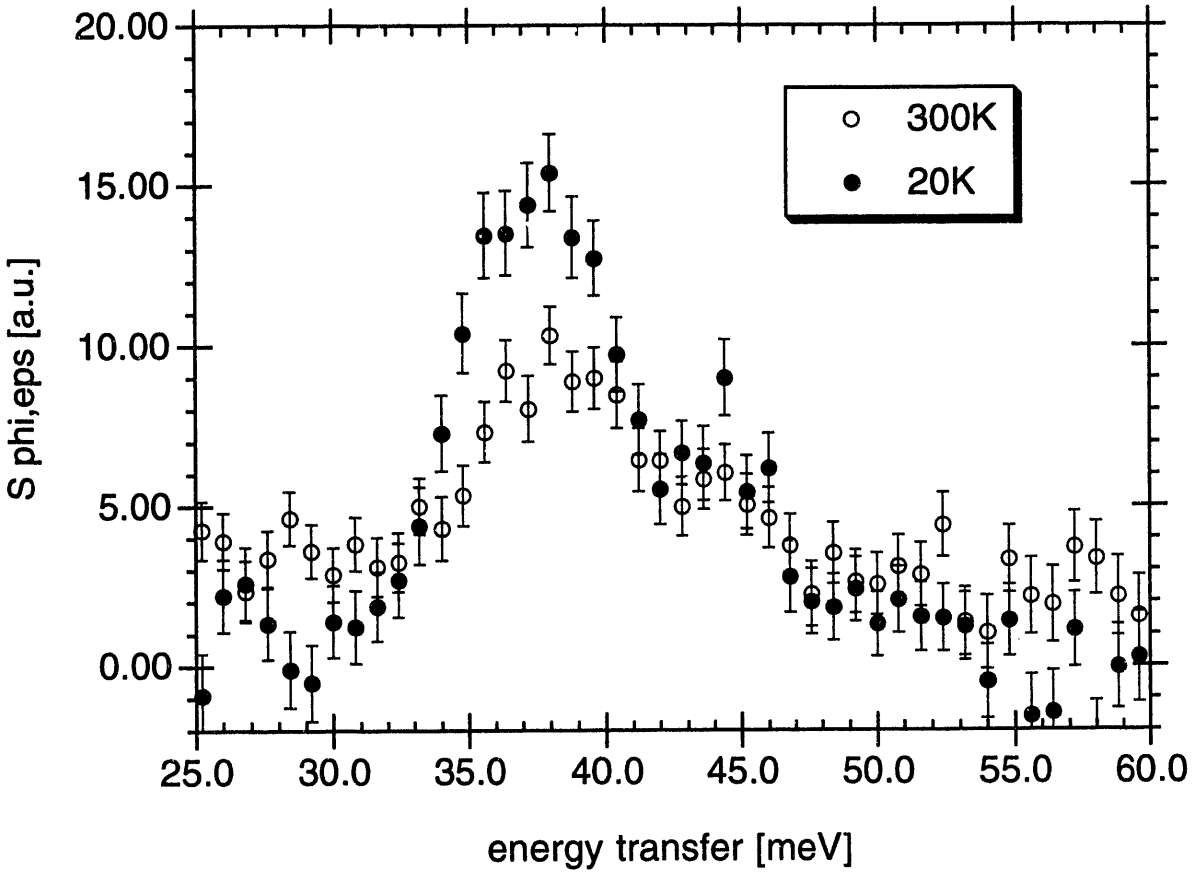
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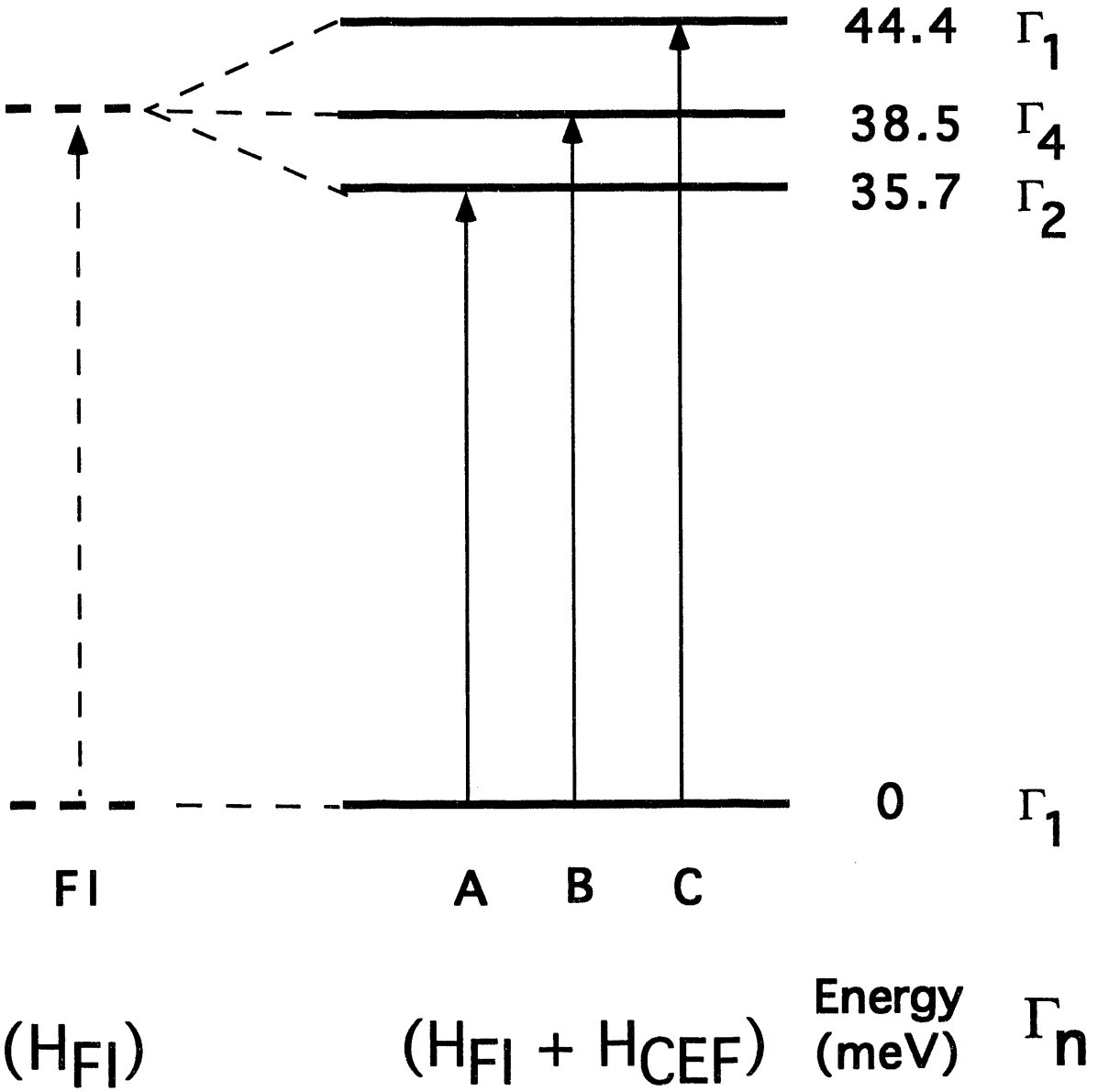
Fig. 3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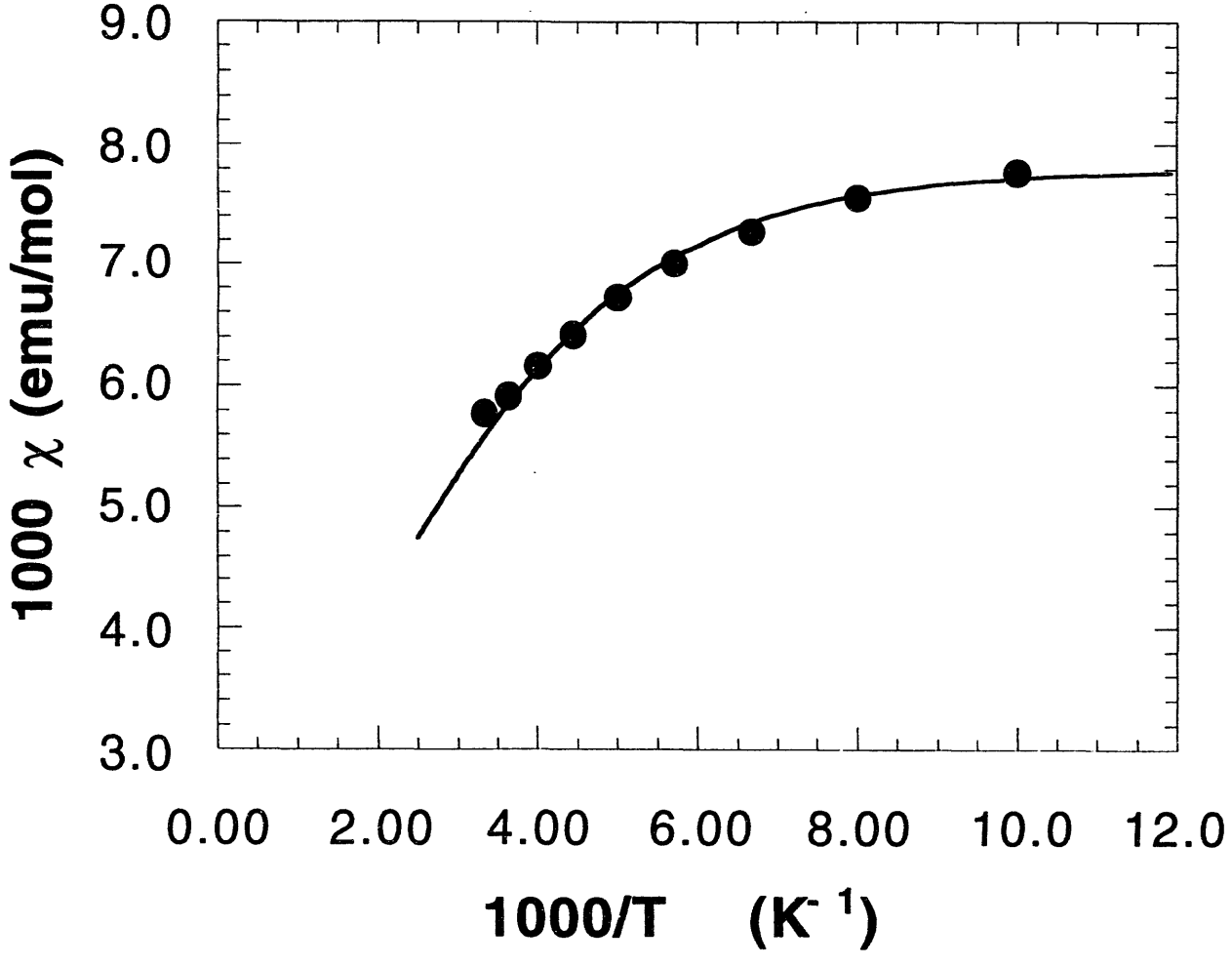
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Fig. 5

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