Exchange-Induced Autoionization in Eu-Rich EuO†

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Below the Curie temperature, with increasing magnetic order, Eu-rich EuO shows both a change of 0.15 mm/sec in the Eu^{151} isomer shift and an insulator-metal transition with a resistivity change of more than 13 orders of magnitude. These effects are interpreted on the basis of an exchange-induced configurational change (autoionization) of two electrons trapped at an oxygen vacancy.

The Eu chalcogenides show unusually large anomalies in electrical resistivity associated with their magnetic ordering.[1] If these resistivity anomalies result from a change in electronic configuration and carrier concentration, rather than a change in mobility, it is reasonable to expect an effect on the Mössbauer isomer shift (IS) which measures the s-electron density at the nucleus. In this Letter we correlate the Mössbauer spectra and Hall effect with an extremely large change in resistivity at an insulator-metal transition in Eu-rich EuO. We interpret the observations in terms of an exchange-induced electronic delocalization. Consistent with this model we have not observed the increase in T_c usually associated with impure Eu chalcogenides.[1] The model suggests why previous Mössbauer measurements of Eu^{151} in pure EuO,[2] EuSe,[3] and EuS[4] do not exhibit any difference in IS below and above T_c.

Pure EuO samples are insulators.[5] Fig. 1(a) depicts the variation of resistivity of a Eu-rich EuO single crystal with the variation of magnetic exchange energy as measured by the Eu^{151} hyperfine field. The figure exhibits the metal-insulator transition near 50°K previously reported by Oliver, Dimmock, and Reed.[6] For our material the resistivity rises more than 13 orders of magnitude near the Curie temperature T_c to values greater than 10^{10} Ω cm. Near room temperature the resistivity and Hall constant ($R_0 = 6.6\times 10^{-4}$ Ω cm/Oe ± 20%) are thermally activated, as for a normal extrinsic semiconductor, with an activation energy of 0.3 eV, whereas below about 50°K the resistivity decreases only slightly, and the normal Hall constant does not change ($R_0 = 2.6 \times 10^{-9}$ Ω cm/Oe ± 20%). On the assumption that a single parabolic-band model can be used, R_0 yields an effective number of free carriers of 2.4×10^{19} cm^{-3} below 50°K and about 10^{14} cm^{-3} at 300°K. This implies an excess Eu concentration greater than about 10^{19} cm^{-3}. The IS as a function of T/T_c and exchange energy is shown in Fig. 1(b). Above $T_c = 69.3$°K the isomer shift assumes the constant value of -12.25 ± 0.03 mm/sec[7] and below $T \approx 50$°K IS is -12.10 ± 0.03 mm/sec. This change in isomer shift $\Delta IS = 0.15$ mm/sec for Eu-rich EuO is in contrast with the values of -12.207 ± 0.010 mm/sec (67.19°K) and -12.212 ± 0.010 mm/sec (70.13°K) for the IS of pure EuO below and above T_c as reported by Groll.[2]

The Eu^{2+} ions in the cubic Eu chalcogenides have a $4f^7\ {}^8S_{7/2}$ configuration. If the material is insulating, the effective magnetic field at the nucleus arises primarily from core polarization by the half-filled $4f$ shell. The intra-atomic hyperfine coupling constant A_{ii} is then practically temperature independent, as can be seen from the NMR measurements of Eu in EuS.[8] In our present study the EuO sample becomes a metallic conductor at low temperatures, and a small tem-

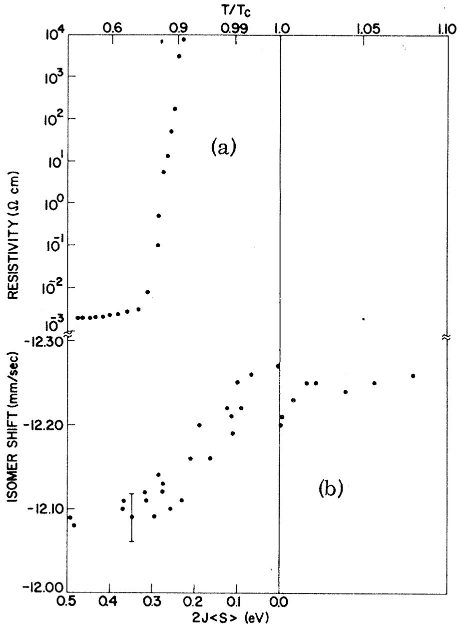

FIG. 1. (a) Resistivity and (b) isomer shift of Eu-rich EuO as a function of T/T_c and exchange interaction (see text).

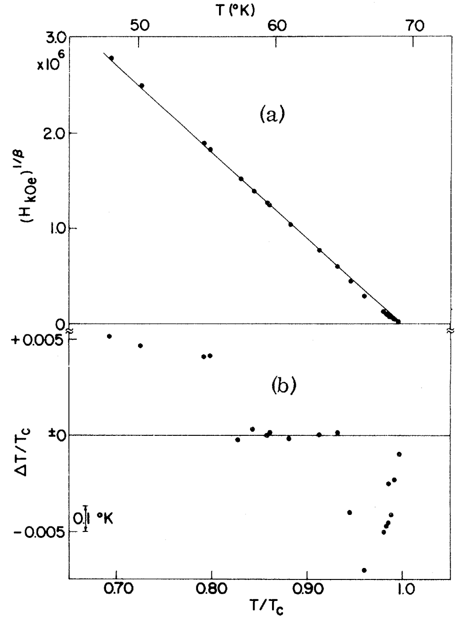

FIG. 2. (a) Temperature dependence of the $1/\beta$ power of the Eu^{151} hyperfine field in Eu-rich EuO. The straight line represents Eq. (1). (b) Deviation of hyperfine field from Eq. (1) in temperature units.

perature-dependent core polarization by the conduction electrons is to be expected. Figure 2(a) shows that the hyperfine field H follows approximately a critical behavior of the form

$$H(T)/H(0) = D(1-T/T_c)^{\beta}. \qquad (1)$$

Using the measured value of $H(1.4°\mathrm{K}) = 296 \pm 4$ kOe, Eq. (1) is satisfied with

$$T_c = 69.29 \pm 0.10°\mathrm{K}, \quad \beta = 0.36 \pm 0.03,$$

and

$$D = 1.13 \pm 0.06$$

in the range $0.82 < T/T_c < 0.94$. This result is in good agreement with the values for pure EuO[2] ($T_c = 69.2$, $\beta = 0.34 \pm 0.02$, $D = 1.14 \pm 0.04$, $H(0) = 298 \pm 4$ kOe) and pure EuS[8] ($\beta = 0.33 \pm 0.015$, $D = 1.145 \pm 0.02$). It is remarkable that $H(0)$ is unchanged for conducting EuO, indicating the small effect that the conduction electrons have on the core polarization. Figure 2(a) shows a small deviation of the hyperfine field $H(T)$ from the behavior of Eq. (1). This deviation may be represented by $\Delta T = T(\mathrm{measured}) - T(H)$. $T(H)$ is the solution of Eq. (1) given the experimental $H(T)$ and T_c, β, and D as above. There are three distinct ranges for ΔT as shown in Fig. 2(b).

An interpretation of the anomalies in $H(T)$, the change in IS, and the resistivity data can be found in a model first suggested by Kasuya.[9] He proposed that the transport properties in Eu-rich EuO will be dominated by oxygen vacancies. These defects may trap two electrons with opposite spins and form a He-like singlet ground state with configuration $^1S(1s\uparrow 1s\downarrow)$. Below T_c the average Eu spin $\langle S\rangle$ produces an effective field $2J\langle S\rangle$ acting on trapped or conducting electrons. For a sufficiently large effective field the triplet state $^3S(1s\uparrow 2s\uparrow)$ with parallel spins will be lowest in energy. The condition is $2J\langle S\rangle > \Delta E(^1S\text{-}^3S)$. With a large number of oxygen vacancies, distributed randomly, the ^3S states will be distributed in energy and conduction-band states will appear in the bandgap degenerate with the highest ^3S states. The result is that the lower states formed from ^3S and the conduction band are bound states while the higher states are conducting. Therefore, with increasing magnetic order, a configurational change ^1S to ^3S (bound electrons) is induced initially. Finally the hybrid ^2S–conduction-band states with energy E_c above the ^1S state are populated by this autoionization process.

The exchange-induced insulator-metal transition at 55°K may be used to estimate J from $2J\langle S\rangle_c = E_c$. The value of $\langle S\rangle$ at the insulator-metal transition temperature $\langle S\rangle_c$, as measured by the hyperfine field, is $0.64 \times \frac{7}{2}$. Assuming that for $T \gg T_c$ the observed conduction activation energy of 0.3 eV is a lower limit for the separation of the ^1S state from the conduction band, we may use 0.3 eV as an estimate for E_c. This estimate yields the value $J \approx 0.065$ eV, used in Fig. 1, as an approximate lower limit in reasonable agreement with a previous estimate[10] of 0.05 eV.

On the basis of this model, ΔIS is produced by the transition of a vacancy electron out of the localized ^1S state with increasing magnetic exchange. For Eu^{151} a less negative IS corresponds to an increased electron density at the nucleus. Since IS does not seem to change for $2J\langle S\rangle \lesssim 0.1$ eV, a minimum separation of the ^1S-^3S density of states of about 0.1 eV is estimated. Only when the states at the crossing of the ^3S density of states with the conduction band are filled, will the complete delocalization and increased mobility of the vacancy electron give rise to metallic conduction. No drastic change in IS can be seen at this temperature since the wave functions of the bound ^3S electrons are already highly extended. The increased exchange interaction due to the conduction electrons generates a small change in hyperfine coupling constant A_{ij} of an Eu^{2+} ion i with its neighbors j as seen in Fig. 2(b). This positive $\Delta T/T_c$ at low temperatures means that T_c would be increased by 0.5% if the conduction electrons were present at the ordering temperature. A similar change in A_{ij} is observed in the process of the ^1S-^3S ionization with its accompanying spin flip, but here the situation is obscured by the critical slowing down of the spin fluctuations close to T_c.[2]

It is necessary to discuss other possible mechanisms for a temperature dependence of the IS.

Thermal red shift: The temperature of the Sm_2O_3 source was always held to within 0.5°K of the absorber temperature. This essentially eliminates the second-order relativistic Doppler effect that would cause a thermal shift of the absorption spectrum (the Debye temperatures of Sm_2O_3 and EuO are expected to be of about the same magnitude). This is supported by the fact that between 77°K and room temperature no change in IS is observed within the errors of the measurement.

Exchange-induced change of phonon spectrum: Bashkirov and Selyutin[11] calculated for a second-order magnetic phase transition the change in IS that is caused by a change in the vibrational spectrum of the crystal due to the exchange interaction. Using this result the effective Debye temperature Θ' of EuO would have to increase by about a factor of 2 between 70°K and 50°K to account for our observed ΔIS of ~0.15 mm/sec in this temperature interval. Specific heat[12] data on EuO yield $\Theta_{70^\circ}' = 272^\circ\mathrm{K}$ and $\Theta_{50^\circ}' = 287^\circ\mathrm{K}$ leading to an expected ΔIS of only a few times 10^{-3} mm/sec. Thus our shift data cannot simply be explained by an exchange-induced stiffening of the crystal lattice.

Magnetostrictive effects: Another temperature-dependent contribution to the IS would arise from the magnetostriction of the material. This effect can be excluded since the lattice contraction as a function of T/T_c does roughly scale for EuS and EuO.[13] Since our sample shows only minimal deviations from pure EuO[2] in its magnetic characteristics, the same ΔIS would be expected for EuS. Ore measurements do not show, within the error limits, any ΔIS for EuS in going through T_c.[4]

The model of two electrons being trapped at a chalcogen vacancy readily explains why no ΔIS could be observed in pure or Eu-rich EuS. Though a dielectric-constant approximation should not be taken as a valid calculation for the binding energies of the vacancy electrons, we expect the bindings energies in EuS and EuSe to be larger than in EuO, since the dielectric constants of EuS and EuSe are considerably smaller than for EuO.[14] For EuS at all temperatures, the energy gain, by exchange-induced autoionization from the ^1S to the ^3S state and band states, is smaller than the necessary energy difference $\Delta E(^1S$-$^3S)$. This situation is consistent with the fact that we have observed no insulator-metal transition in Eu-rich EuS. Furthermore, it is interesting to note that within the framework of this model, in agreement with our data and Ref. 6, no effect of the vacancies on T_c is expected, since with the ^1S ground state and zero net spin, no magnetic clusters can be formed. This result is in sharp contrast to our findings for Eu chalcogenides doped with trivalent rare earths (hydrogen-like defects) where giant magnetic clusters greatly increase T_c, but no autoionization or insulator-metal transition occurs.[9]

In conclusion, we have seen that for Eu-rich EuO, changes in resistivity, isomer shift, and deviations of the hyperfine field from critical behavior can be related to changes in electronic configuration induced by magnetic order.

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[7] The conventional transmission type experiment employed the 21.7-keV Mössbauer transition of Eu^{151}. The source was $Sm_2{}^{151}O_3$. A double-exchange gas system provided homogenous temperatures over the powdered sample with a constancy of better than 0.01°K. Within the error limits the data were reproducible. The constant-acceleration velocity signal for the electromechanical drive was generated by the address bistables of the multichannel analyzer for optimum synchronization. All spectra below and above T_c were taken at the same velocities to keep the relative error in velocity calibration below 0.2%. Absolute calibration was achieved by simultaneously measuring the α-Fe_2O_3 Mössbauer

absorption at the room temperature end of the transducer. The least-square fits to the Eu^{2+} spectra showed one single phase at all T and were successful even very close to T_c, in contrast to our findings for either EuS or EuSe. No Eu metal could be detected and trivalent Eu impurities were less than 1%. The narrow linewidths indicate an electronic spin relaxation time that is sufficiently short to produce a true time-averaged field at the nucleus. Only close to T_c the lines broaden as a result of short-range-order spin fluctuations.

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Stimulated Emission from the Excitonic Molecules in CuCl

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We report observation of efficient stimulated emission (gain ~10^4 cm^{-1}) from recombination of excitonic molecules. This emission is obtained near 3.16 eV (3920 Å) in optically excited CuCl crystals and shown to be stimulated by use of a recently described technique employing a variable excitation length. These results in CuCl point out the importance of excitonic molecules in intrinsic stimulated-emission processes in semiconductors.

We report the observation of efficient stimulated emission from recombination of excitonic molecules. These molecules represent the lowest intrinsic energy state in many crystals at high excitation levels, and it might be expected that excitonic molecule recombination (EMR) will play an important role in stimulated emission processes. It has previously been speculated,[1] but then discounted,[2] that EMR could be a fundamental recombination route for intrinsic stimulated emission in many semiconductors.[3] The observations described here were made on optically excited CuCl crystals and represent the first demonstration of *stimulated* excitonic molecule recombination. Spontaneous emission due to EMR in CuCl near $\lambda = 3920$ Å had been previously established[4,5] with the reported molecular binding energy being ≃44 meV.[5] CuCl is an ideal crystal in which to investigate stimulated emission from excitonic molecule recombination. It is a zinc-blende semiconductor with a band gap in the uv, the lowest exciton absorption peak occurrring at 3.207 eV at 4.2°K.[6] Three sharp absorption lines of the exciton series have been observed and found to be not hydrogenically spaced. This results because the exciton is deeply bound (binding energy 190 meV and Bohr radius 7 Å) and the usual effective-mass theory breaks down. Low-intensity photoluminescence spectra[7] show the usual bound-exciton lines common to wide-band-gap semiconductors. At very high exciting intensities, a new peak appears[4,5] at 3.164 eV, about 44 meV below the free-exciton energy, and it has been identified as exciton-molecule recombination radiation. In this paper, we discuss new studies of this radiation.

The EMR mechanism is an Auger process whereby one of the excitons is scattered into either the $n = 1$ or higher state of the free exciton while the other is simultaneously scattered down on the polariton curve. A schematic diagram of the EMR process is shown in Fig. 1. The photon is shifted down in energy from the absorption peak of the $n = 1$ exciton by the binding energy of the molecule ($R_m = 44$ meV in CuCl)[5] if the terminal state of the surviving free exciton is $n = 1$. This photon energy represents the high-energy threshold for the EMR radiation. For recombining molecules with large crystal momenta K, the radiation will appear with energies at and below this threshold because of the difference in the dispersion of the molecule and the free exciton, as seen in Fig. 1. The momentum-conserving properties of the Auger process allow radiation to arise even from molecules with large crystal momenta so that the number of initial states that may participate is much larger than for ordinary exciton recombination. Thus there is good rea-